INVITED ARTICLE

Vibrational conical intersections in the water dimer

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A recent paper by Hamm and Stock [Phys. Rev. Lett. 109, 173201 (2012)] has introduced the concept of vibrational conical intersections as a potential source of ultrafast vibrational relaxation, using the coupling between high-frequency OH modes and low-frequency intramolecular hydrogen bonding modes of malonaldehyde as an example. Here, the question is addressed whether such conical intersections may also appear for intermolecular hydrogen bonds. To that end, the water dimer [(H\textsubscript{2}O\textsubscript{2})] is studied as a minimal model for the hydrogen bonding in liquid water. Although a significant separation of time scales between intramolecular and intermolecular degrees of freedom exists in (H\textsubscript{2}O\textsubscript{2}), a standard normal-mode description is found to lead to a complete breakdown of the adiabatic ansatz. This is due to strong nonlinear couplings between high- and low-frequency normal modes, which in turn give rise to large overall non-adiabatic couplings. A valid adiabatic picture is obtained, on the other hand, when internal coordinates are employed. The resulting adiabatic potential energy surfaces indeed exhibit low-lying conical intersections, whose possible relevance for ultrafast relaxation and energy transfer in water is discussed.

Keywords: water dimer; conical intersection; adiabatic approximation; vibrational relaxation; hydrogen bond

1. Introduction

Conical intersections are true crossings of two Born–Oppenheimer potential energy surfaces (PESs), which may lead to extremely fast and efficient transfer of populations between the two coupled electronic states. Although conical intersections were already predicted more than 80 years ago [1], their ubiquity and utmost importance in ultrafast photochemical and photophysical processes have been recognised only much later (see Refs. [2,3] for a timely overview). In a recent paper [4], we have shown that the concept of a conical intersection may also apply for vibrational adiabatic states. That is, while the Born–Oppenheimer ansatz is based on the adiabatic separation of time scales between the fast motion of the light electrons and the slow motion of the heavy nuclei, a similar situation also arises in the vibrational dynamics of larger molecules, e.g. when a high-frequency mode (such as a OH-stretch vibration) is coupled to a low-frequency mode (such as a hydrogen bond mode) [5]. Adopting an adiabatic perspective, one may solve the Schrödinger equation for the high-frequency mode with the low-frequency coordinate introduced parametrically [6–11]. In direct analogy to the Born–Oppenheimer approximation for electronic states, this leads to PESs for the vibrational states of the high-frequency modes as a function of the low-frequency coordinates.

In Ref. [4], we derived the conditions that vibrational conical intersections occur and presented quantum-dynamical model calculations to show the consequences for the vibrational dynamics and spectra. As a first simple example, we considered malonaldehyde which is a prototype molecule with a medium-strong intramolecular hydrogen bond [10,12–16]. We showed that a conical intersection exists between the first excited states of the OH-stretch and the OH-bend modes, which might provide an explanation for the ultrafast (a few 100 fs) vibrational relaxation and the complex oscillatory features found in infrared time-resolved pump-probe experiments for this type of molecular systems [17–21].

Another paradigm of ultrafast vibrational dynamics is water in its various condensed-phase forms [22–29]. In isotope diluted water, where the OH (or OD) vibration is spectrally and spatially isolated, vibrational relaxation times of the order of 1–2 ps have been observed [30,31], which is still within the ‘normal’ range of vibrational relaxation. In neat water, in contrast, vibrational relaxation appears to be even faster both in the liquid [32,33] state and in the icy [34] state. An extremely fast initial signal of the order of 200 fs is found, which tentatively has been attributed to vibrational energy relaxation. However, in both cases, this assignment to vibrational energy relaxation is no longer clear since the signal does not decay to zero, but into a ‘heated’ state, which dissipates energy from the OH-excited state into intermolecular degrees of freedom. The distinction of what is called the ‘OH-excited state’ and the ‘heated’ state breaks
down as the adiabatic approximation breaks down. When vibrational energy relaxation occurs on a time scale of a few 100 fs, which comprises only a few tens of oscillation periods of an OH-stretch vibration, a perturbative treatment, which works well for most vibrations with somewhat longer relaxation times [29,35–38], does no longer seem to be appropriate.

In the case of neat water, the situation is further complicated by the presence of energy transport along coupled (and approximately resonant) high-frequency OH vibrations. This kind of vibrational energy transfer is conceptually similar to excitation transport via excitonic coupling [23,39–41]. As both processes, vibrational energy relaxation and transport, in an adiabatic perspective are viewed as non-adiabatic transitions between coupled high-frequency vibrational states [42,43], the question arises if vibrational conical intersections may also be responsible for the ultrafast relaxation and energy transfer in water.

As a first step towards this question, in this work, we consider the water dimer [(H$_2$O)$_2$] as a minimal model for the hydrogen bonding in liquid water, whose PES, structure and vibrational spectroscopy have been studied in great detail [9,44–52]. The hydrogen bond in the water dimer in the gas phase is relatively weak, and the infrared spectra do not yet evolve the same complicated structure as stronger intramolecular hydrogen bonds [17–21]. Nevertheless, because of its obvious importance for the understanding of liquid water, whose peculiar properties have their origin in hydrogen bonding, the ‘water dimer serves as a sort of hydrogen atom, or prototype, of hydrogen bonding’ [44].

Employing a recently published water potential of Bowman and co-workers [53–55], we determine the adiabatic PESs pertaining to the first few eigenstates of the standard normal-mode representation of (H$_2$O)$_2$ is found to lead to a complete breakdown of the adiabatic ansatz, we adopt internal coordinates, i.e. we use normal modes of each monomer to describe the intramolecular motion of each water molecule and intermolecular coordinates to describe the relative motion of the two molecules. One- and two-dimensional plots of the resulting adiabatic PESs along selected intermolecular coordinates clearly exhibit energetically low-lying conical intersections. The possible relevance of these intersections in the discussion of ultrafast relaxation and energy transfer in water is discussed.

2. Theory and Methods

2.1. Adiabatic ansatz

The adiabatic description of vibrational dynamics follows in direct analogy the standard Born–Oppenheimer approach to separate electronic and nuclear degrees of freedom. In order to introduce a separation between fast and slow degrees of freedom, we partition the vibrations into $M$ high-frequency modes $q = \{q_n\}$ and $N$ low-frequency modes $Q = \{Q_i\}$, and write the Hamiltonian as

$$\begin{align*}
H &= T_q + T_Q + V(q, Q).
\end{align*}$$

Here $T_q$ and $T_Q$ denote the kinetic energy of the high- and low-frequency modes, respectively, and $V(q, Q)$ represents the electronic ground-state PES. By keeping the low-frequency modes $Q_i$ fixed to a constant value, we first solve the Schrödinger equation for the high-frequency modes

$$\begin{align*}
[T_q + V(q, Q) - W_k(Q)]\phi_k &= 0,
\end{align*}$$

which yields the vibrational adiabatic PESs $W_k(Q)$ and the corresponding adiabatic vibrational states $|\phi_k\rangle$. We now expand the total vibrational wavefunction as

$$\begin{align*}
|\Phi(Q)\rangle &= \sum_k \Psi_k(Q)|\phi_k\rangle,
\end{align*}$$

where the dynamics of the low-frequency modes are represented by the wavefunctions $\Psi_k(Q)$. Insertion into the Schrödinger equation for the total system (1) yields the coupled-channel equations

$$\begin{align*}
[T_Q + W_k(Q) - E] \Psi_k(Q) &= \sum_{k'} \Lambda_{kk'} \Psi_{k'}(Q),
\end{align*}$$

where the operator $\Lambda_{kk'} = \langle \phi_k|T_Q|\phi_{k'}\rangle$ accounts for the non-adiabatic coupling between the adiabatic vibrational states $|\phi_k\rangle$ and $|\phi_{k'}\rangle$. In the Born–Oppenheimer approximation, one assumes that $\Lambda_{kk'} = 0$, which leads to independent low-frequency vibrational dynamics on the adiabatic PESs $W_k(Q)$.

2.2. Normal-mode model

To discuss the main features of the non-adiabatic dynamics exhibited by Equation (4) and to introduce the concept of a vibrational conical intersection, it is instructive to employ a simple model for the vibrational system. To this end, we assume that the high-frequency and low-frequency modes are well described by dimensionless normal-mode coordinates (again denoted by $\{q_n\}$ and $\{Q_i\}$). For the example of the water dimer, the normal modes are comprised in Figure 1. We perform a Taylor expansion of the potential energy, which allows us to rewrite the Hamiltonian (1) as ($\hbar = 1$)

$$\begin{align*}
H &= H_0 + H_{\text{anh}},
\end{align*}$$

$$\begin{align*}
H_0 &= \sum_n \frac{\omega_n}{2} (p_n^2 + q_n^2) + \sum_j \frac{\Omega_j}{2} (P_j^2 + Q_j^2),
\end{align*}$$

where $\omega_n$ and $\Omega_j$ are the high-frequency and low-frequency vibrational frequencies, respectively.
where \( H_0 \) contains the harmonic part and \( H_{\text{anh}} \) all anharmonic couplings. For interpretational purposes, it is furthermore advantageous to expand the total vibrational wavefunction \( |\Phi(k)\rangle = \sum_k |\Psi_k(k)\rangle |k\rangle \) in terms of the zero-order harmonic basis states \( |k\rangle \), with \( k = (k_1, \ldots, k_M) \) comprising the quantum numbers of the \( M \) high-frequency modes. Representation of the Hamiltonian (5) in this basis yields

\[
\mathcal{H} = h_0 1 + \sum_{k,k'} |k\rangle h_{kk'}\langle k'|,
\]

\[
h_0 = \langle k|H_0|k'\rangle = \delta_{kk'}\varepsilon_k + \delta_{kk'}\sum_j \frac{\Omega_j}{2}(P_j^2 + Q_j^2),
\]

\[
h_{kk'} = \langle k|H_{\text{anh}}|k'\rangle,
\]

where 1 is the unit matrix and \( \varepsilon_k = \sum_n (k_n + 1/2)\omega_n \) \( (k_n = 0, 1, 2, \ldots) \) denotes the harmonic energy of the high-frequency modes. Containing a diagonal kinetic energy and a non-diagonal potential energy matrix \( h_{kk'}(Q) \), the Hamiltonian (7) can be regarded as a diabatic representation of the vibrational problem.

To characterise the matrix elements of the Hamiltonian (7) and to explain how they give rise to vibrational conical intersections, it is helpful to restrict ourselves to the couplings

\[
H_{\text{anh}} = \sum_{n,m,j} f_{nm,j} q_n q_m Q_j + \sum_{n,j} g_{nn,jj} q_n^2 Q_j^2,
\]

where \( f_{nm,j} = 1/3! \partial^3 V/\partial q_n \partial q_m \partial Q_j \) and \( g_{nn,jj} = 1/4! \partial^4 V/\partial q_n \partial q_n \partial Q_j \partial Q_j \) are the cubic and quartic coefficients of the Taylor expansion, respectively. Insertion into Equation (7) yields

\[
h_{kk'} = \sum_j \kappa_{k,j} Q_j + \frac{\delta\omega_{k',j}}{2} Q_j^2,
\]

\[
h_{kk'} = \sum_j \lambda_{kk',j} Q_j (k \neq k'),
\]

where non-resonant terms were neglected. The coupling constants are given by

\[
\delta\omega_{k,j} = \sum_{n,m} 6g_{nn,jj} |k| q_n^2 |k|, \quad k_{k,j} = \sum_n 3f_{nn,jj} |k| q_n^2 |k|, \quad \lambda_{kk',j} = \sum_{n,m} 6f_{nm,j} |k| q_n q_m |k'| = \lambda_{k,k'},
\]

where the prefactors account for the fact that there are three and six possibilities to permute the order of the different vibrational modes in the Taylor expansion, respectively.

The first term (Equation 11) simply describes the frequency shift \( \delta\omega_{k,j} \) of the low-frequency mode \( Q_j \) in the high-frequency state \( |k\rangle \), which is caused by quartic coupling. The other two couplings are only non-zero, if the corresponding matrix elements \( \langle \Psi_k|Q_j|\Psi_k\rangle \) and \( \langle \Psi_k|Q_j|\Psi_k\rangle \) do not vanish by symmetry. This means that the low-frequency mode \( Q_j \) needs to be totally symmetric to obtain non-zero diagonal couplings \( \kappa_{k,j} \). According to Equation (9), these modes modulate the vibrational excitation energy of the high-frequency modes and are therefore referred to as ‘tuning coordinates’. Non-zero off-diagonal couplings \( \lambda_{kk',j} \), on the other hand, require that the direct product of the symmetry representations pertaining to \( \Psi_k \), \( Q_j \) and \( \Psi_k \) includes the totally symmetric representation \( \Gamma_A \), that is, \( \Gamma_k \times \Gamma_j \times \Gamma_k \supset \Gamma_A \) [56]. These modes couple the high-frequency modes, with the amount of the mixing depending on \( Q_j \) (i.e. the mixing vanishes for \( Q_j = 0 \)). They are therefore referred to as ‘coupling coordinates’. In molecules with low symmetry, vibrations may exist that simultaneously act as tuning and coupling modes. Moreover, higher order couplings (e.g. \( \propto q_n q_m Q_j^2 \)) of various symmetries may exist.

The model defined by Equations (7)–(13) has several interesting features. First, we notice that due to the harmonic ansatz the matrix elements of the Hamiltonian (7) are readily obtained in analytic form, which facilitates the interpretation of the vibrational interactions, e.g. in terms of tuning and coupling modes. Most interestingly, we note that the above model of vibrational coupling between high- and low-frequency modes is formally entirely equivalent to the standard linear vibronic-coupling Hamiltonian [56], which accounts for excited electronic states that interact via vibrational tuning and coupling coordinates. That is, the model may give rise to a conical intersection of the adiabatic PESs \( W_k(Q) \), which are obtained through diagonalisation of the diabatic potential energy matrix \( h_{kk'} \). As a simple
illustration, we consider the case of two coupled high-frequency vibrations with the excited states $|k\rangle = |10\rangle$ and $|01\rangle$. The corresponding two adiabatic PESs are given by

$$W_{\pm}(Q) = \tilde{V}(Q) \pm \sqrt{\Delta V^2(Q) + V_C^2(Q)}, \quad (14)$$

where $\tilde{V} = (h_{10,10} + h_{01,01})/2$, $\Delta V = (h_{10,10} - h_{01,01})/2$ and $V_C = h_{10,01} = h_{01,10}$. A conical intersection of these two surfaces arises for $W_- = W_+$, that is, if $\Delta V(Q) = 0$ and $V_C(Q) = 0$. In the simplest case of a single-tuning and a single-coupling coordinate (i.e. $N = 2$), we obtain a crossing point; in general, we have a $(N - 2)$-dimensional intersection surface.

### 2.3. Internal-coordinate representation

Being concerned with the vibrational dynamics of the water dimer, we need to describe the coupled motions of two molecules. Due to the absence of strong through-bond interactions, these molecules may perform large-amplitude motions with respect to each other. Using normal coordinates of the complete system (defined with respect to the overall potential energy minimum), these motions are only poorly described. That is, one typically obtains strong nonlinear potential energy minimum), these motions are only poorly described. That is, one typically obtains strong nonlinear couplings between the normal modes [57], which hamper a simple and correct picture of the vibrational motion.

As an alternative, one may invoke a set of internal coordinates of a multi-molecular system. That is, we use the normal modes of each monomer (i.e. symmetric stretch, asymmetric stretch and bend) to describe the intramolecular motion and the intermolecular coordinates defined in Figure 2 to describe the relative motion of the molecules. This procedure again partitions the vibrations into $M$ high-frequency coordinates $x = \{x_n\}$ and $N$ low-frequency coordinates $X = \{X_i\}$. In the case of the water dimer, it yields $M = 2 \times 3$ modes $(x_1, x_2, x_3)$ and $(x_4, x_5, x_6)$ to describe the intramolecular normal modes of each of the two water molecules, and $N = 6$ low-frequency degrees of freedom to account for the intermolecular motion. The latter are defined by the curvilinear coordinates $X = (X_7, \ldots, X_{12})$ shown in Figure 2, i.e. the O–O distance $R_{O-O}$ and five rotational angles $\alpha_x$, $\alpha_y$, $\beta_x$, $\beta_y$ and $\beta_z$. For a given geometry $X$, the associated modes $x_n$ are defined in a coordinate system that is fixed to the corresponding monomer. As one of the monomers rotates along one of the angles $\alpha_x$, $\alpha_y$, $\beta_x$, $\beta_y$ and $\beta_z$, the three monomer-mode vectors $(x_1, x_2, x_3)$ or $(x_4, x_5, x_6)$ of the corresponding water molecule are rotated as well (see Figure 3c). The monomer modes therefore become a function of the rotational low-frequency degrees of freedom, $x_n = x_n(X)$. The translation of a molecule along the O–O vector $R_{O-O}$, in contrast, has no effect on the monomer mode vectors $x_n$.

In the discussion below, we wish to compare adiabatic PESs that were calculated in the internal-mode representation (using $x, X$) and in the normal-mode representation (using $q, Q$) [58]. To obtain a suitable transformation between the two sets of coordinates, we first calculate the normal modes in the $\{x_n\}$ subspace by diagonalising the corresponding Hessian matrix, which yields the normal modes $\{q_n\}$ as linear combinations of the monomer modes

$$q'_n = \sum_m a_{nm} x_m. \quad (15)$$

Moreover, we introduce low-frequency normal modes $\{Q'_i\}$ defined in terms of the intermolecular coordinates $\{X_i\}$. Since the latter are curvilinear coordinates, we need to invoke nonlinear transformation operators $\tilde{X}_i$, which account for the translation or rotation associated with coordinate $X_i$. For example, for $X_2 = \alpha_y$, $\tilde{X}_2$ is a rotation matrix $D_{\alpha_y}$ around the $y$-axis with angle $\alpha_y$, which acts on the
Cartesian coordinates \( R = \{ R_n \} \) of the hydrogen-bond-donating water molecule. The desired normal-mode coordinates are then given by \( Q_j' = \hat{Q}_j R \) with

\[
\hat{Q}_j = \sum_i A_{ji} \hat{X}_i. \tag{16}
\]

In order to determine the transformation matrix \( A_{ji} \), we first linearised the transformations \( \hat{X}_i \) for small displacements and removed the centre-of-mass motion and the angular momentum from the coordinates. This yields linear vectors \( Q_j' \) that can be compared to \( Q_j \).

Close to the minimum energy configuration, we find \( Q_j' \approx Q_j \) and \( q_n' \approx q_n \). This is no longer the case, when the system is displaced from its minimum energy configuration, where, on the one hand, we have \( \{ q_n \} = \) constant and, on the other hand, we have \( q_n = q_n'(Q) \), i.e. the high-frequency modes \( q_n' \) become a nonlinear function of the low-frequency modes. The low-frequency coordinates \( \{ Q_j \} \) agree with \( \{ Q_j \} \) as long as the former can be approximated by their linearised counterparts.

The effect is illustrated in Figure 3, adopting \( q_3 \) and \( Q_{10} \) as a representative example. Figure 3(a) shows the displacement vector of mode \( q_3 \) for the dimer in its minimum energy configuration, while Figure 3(b) shows the same high-frequency mode for the dimer displaced along \( Q_{10} \). As \( Q_{10} \) includes a rotation of the hydrogen-bond-accepting water molecule, the normal-mode \( q_3 \) no longer displaces the proton parallel to the OH bond, but with an angle \( \theta \) out of the plane of the hydrogen-bond-accepting water. Hence, the normal-mode \( q_3 \) to a certain extent rotates the water molecule back, so the high-frequency modes \( q_3 \) start to include low-frequency degrees of freedom. In contrast, in an internal-coordinate representation (Figure 3(c)), the mixing of low- and high-frequency degrees of freedom is avoided by construction, since we rotate the high-frequency coordinate \( q_3 \) as the water rotates along the low-frequency coordinate \( Q_{10} \).

### 2.4. Calculation of adiabatic PESs

The electronic PES of the water dimer was calculated at two levels of \textit{ab initio} theory. As a state-of-the-art description of the water dimer, we used a parameterised multidimensional water potential derived from aug-cc-pVTZ/CASSCF(T) \textit{ab initio} calculations, which was made available by Bowman and co-workers [53–55]. In this case, the potential \( V(q, Q) \) was used in Schrödinger Equation (2) directly. For a more qualitative discussion, we also used a Taylor expansion which directly gives the coupling terms (cf. Equation 8) of the simple model of non-adiabatic coupling introduced above. Harmonic frequencies and anharmonic terms up to fourth order were calculated with the Gaussian program package [59] on the MP2/6-311++G(2df,2pd) level of theory. The normal modes calculated from both levels of theory were virtually the same (Figure 1).

In the next step, we calculated the vibrational adiabatic PESs associated with the ground and lowest excited states of the high-frequency modes. In the case of the parameterised water potential of Bowman [53–55], we need to numerically solve the Schrödinger Equation (2) for the high-frequency modes \( q_n \) in order to obtain the eigenstates \( \phi_k \) and the eigenenergies (or adiabatic PESs) \( W_k \), which both depend parametrically on the low-frequency coordinates \( Q_j \). The potential energy is given in the corresponding set of coordinates (normal or internal coordinates, respectively). In the case of the internal coordinates, the intramolecular normal modes of the two monomers are used for the kinetic energy operator of the high-frequency modes (which are the only ones needed at this stage). We define a basis \( \{ \psi_k \} \) by the product ansatz

\[
\psi_k = \prod_{n=1,6} \psi_{i,k_n}(q_n), \tag{17}
\]

where \( k = (k_1, \ldots, k_6) \) comprises all quantum numbers. For a given set of fixed coordinates \( \{ Q_j \} \), the single-coordinate function \( \psi_{i,k_n}(q_n) \) is the \( k_n \)th eigenstate of the high-frequency mode \( q_n \) with respect to the one-dimensional Schrödinger equation

\[
\left[ \frac{\omega_n}{2} p_n^2 + V(q_n) \right] \psi_{i,k_n} = \epsilon_{i,k_n} \psi_{i,k_n}, \tag{18}
\]

where \( V(q_n) \) denotes a one-dimensional cut of the potential energy along \( q_n \) with all other coordinates \( q_{\neq n} \) set to zero. To solve the six-dimensional Schrödinger Equation (2), the Hamiltonian \( \hat{H}_q = \hat{T}_q + V(q, Q) \) was represented by the basis functions \( \psi_k \), where the potential energy matrix was calculated by full quadrature and the associated kinetic energy matrix according to Ref. [60]. We included all one-dimensional functions with up to six excitations in total in the OH stretches and/or 12 excitations in the OH bends, thus yielding \( \approx 2300 \) basis functions. The Hamiltonian matrix was diagonalised and the resulting adiabatic states were characterised according to their largest overlap with the zero-order states \( \psi_k \) (which is used for the colouring in Figures 4,5 and 6). Convergence was tested with respect to the number of excitations, as well as the step size and the total size of the six-dimensional grid.

### 3. Results and Discussion

#### 3.1. Normal-mode representation

In what follows, we focus on the seven states in the \( v_1/v_2 \) diad, i.e. all states with either one quantum in the OH-stretch modes or two quanta in the OH-bend modes. For the lowest energy conformation of the water dimer, the energy ordering of the fully anharmonic states remains the
Figure 4. Normal-mode calculation of the adiabatic PESs, represented by one-dimensional cuts along the low-frequency normal modes $Q_7$ to $Q_{12}$. Shown are all states of the water dimer with either one quantum in the OH-stretch modes or two quanta in the OH-bend modes, that is, $|100000\rangle$ (black), $|010000\rangle$ (red), $|001000\rangle$ (green), $|000100\rangle$ (blue), $|000020\rangle$ (magenta), $|000011\rangle$ (yellow) and $|000002\rangle$ (cyan). The curves coloured in grey correspond to lower or higher lying states.

Figure 5. Internal-mode calculation of the adiabatic PESs of the water dimer, using the colour code of the states as in Figure 4. Shown are one-dimensional cuts along the intermolecular coordinates defined in Figure 2.
hydrogen-bond-donating water, $|000002\rangle$ has two quanta of the OH bend of the hydrogen-bond-accepting water, and $|000011\rangle$ is a combination mode with one quantum each of the two OH bends.

To discuss the adiabatic PESs $W_k(Q)$ of these states, we first adopt the normal-mode representation $\{q_n, Q_j\}$ of the parameterised water potential of Bowman [53–55]. Figure 4 shows one-dimensional cuts of the resulting PESs along the low-frequency modes ($Q_7, \ldots, Q_{12}$). The curves along $Q_7$ appear as expected, i.e. (i) they exhibit a minimum at the equilibrium geometry $Q_7 = 0$, (ii) the four states reflecting the OH-stretch excitation are close in energy, and (iii) the three states reflecting double excitations of the OH bends are close. Surprisingly, though, the adiabatic PESs $W_k(Q_i)$ along the other normal modes ($Q_8, \ldots, Q_{12}$) lead mostly ‘downhill’, meaning that $W_k(Q_i)$ is not minimal at the equilibrium geometry as expected. In fact, these curves would predict a redshift of the infrared excitation for increasing values of $Q_i$, thus rendering the breaking of the hydrogen bond energetically favourably. As this is against the common physical intuition, we repeated the calculations using the simple quartic Taylor expansion (Section 2.2) to represent the potential. The results were quite similar and revealed that the negative curvature of the adiabatic PES along the normal modes $Q_6$ to $Q_{15}$ is caused by very large negative anharmonic couplings $\propto q_n^2 Q_j^2$ (cf. Equation 8). For example, the term that couples modes $q_3$ and $Q_{10}$ amounts to $6g_{53,1010} = -378$ cm$^{-1}$. Together with the also negative zero-point energy contributions of all other high-frequency modes, it accounts for the negative curvature of the state $|001000\rangle$ as a function of $Q_{10}$ (green line in Figure 4) according to Equation (9). The spurious behaviour of the adiabatic PESs shown in Figure 4 is not an artefact of the electron-structure theory (because we compare the aug-cc-pVTZ/CCSD(T) calculation by Bowman [53–55] with a MP2/6-311++G(2df,2pd) calculation for the Taylor expansion) or a low-order Taylor expansion (because the calculation based on Bowman’s potential implicitly includes all terms).

### 3.2. Internal-mode representation

Alternatively, we may employ internal modes (Section 2.3) which treat the high-frequency modes in normal-mode coordinates that are defined in the frame of the individual water monomers, and thus rotate as the water molecules rotate along the low-frequency degrees of freedom (Figure 2). Proceeding this way, the resulting adiabatic PESs shown in Figure 5 appear to be quite reasonable, i.e. they exhibit minima very close to the equilibrium geometry $X_i = 0$.

To facilitate the comparison of the adiabatic PESs calculated in normal modes (Figure 4) versus those calculated in internal coordinates (Figure 5), we expand the intermolecular coordinates $\{X_i\}$ in terms of the low-frequency normal modes $\{Q_j\}$ (cf. Equation 16). This allows us to represent the internal-coordinate PESs in terms of the normal modes.
{Q_j'}}, which is shown in Figure 6. Again, these adiabatic PESs look very reasonable and clearly confirm the misconception of the PESs calculated directly from normal modes in Figure 4.

### 3.3. Non-adiabatic couplings

The comparison of Figures 4 and 6 poses the question of what goes wrong in the normal-mode representation. After all, normal modes represent a complete set of coordinates of the system; hence – at least in principle – the problem should be describable also in normal modes. However, one needs to recall that the concept of independent adiabatic PESs rests on the adiabatic approximation, which assumes that (at least for the most part) the non-adiabatic couplings given in Equation (4) can be neglected. These couplings are given by $\Lambda_{kk'} = F_{kk'} + G_{kk'}$ with

$$F_{kk'} = - \sum_j \frac{\Omega_j}{2} \left( \phi_k | \frac{\partial}{\partial Q_j} \phi_k \right) P_j,$$

$$G_{kk'} = - \sum_j \frac{\Omega_j}{2} \left( \phi_k | \frac{\partial^2}{\partial Q_j^2} \phi_k \right),$$

and arise from the partitioning in high- and low-frequency modes $\{q_n\}$ and $\{Q_j\}$. Off-diagonal couplings lead to transfer of populations between adiabatic states (see Equation 4), while diagonal terms may shift the energy of the states and therefore change the appearance of the PESs in Figures 4 and 6. The diagonal contribution of the first derivative coupling vanishes, $F_{kk'} = 0$, but the diagonal second derivative coupling is in general non-zero. It can be expressed as [61]

$$G_{kk} = \sum_j \sum_{k \neq k'} \frac{\Omega_j}{2} \left( \phi_k | \frac{\partial H}{\partial Q_j} | \phi_k \right)^2 \left( W_{k'} - W_k \right)^2,$$

which is easier to evaluate numerically, and also shows that the diagonal non-adiabatic coupling is always positive. Hence, it increases the energies of the corresponding adiabatic states, which may explain the qualitative difference between Figures 4 and 6.

The effect can be illustrated most easily for the vibrational ground state, which is energetically isolated and therefore does not show any curve crossings. Adopting the low-frequency mode $Q_{10}$ as a representative example, Figure 7 compares the PES (top panels) and the

![Figure 7](image-url)
non-adiabatic coupling (bottom panels) as computed in the normal-mode representation (left-hand panels) and the internal-mode representation (right-hand panels). The latter shows the familiar adiabatic picture, that is, the PES accounts for the variation of the potential energy along this mode (Figure 7 b), while the non-adiabatic coupling is very small (Figure 7 d). The additional kinetic couplings originating from the curvilinear intermolecular coordinates, not yet included in the derivative couplings Equations (19) and (20), are expected to be of the same order of magnitude. In the normal-mode representation, on the other hand, we find a very different situation. Here the diagonal non-adiabatic coupling varies even more strongly with $Q$. For higher lying states, the picture is similar but in detail more complicated, since curve crossings occur that lead to discontinuities due to the denominator in Equation (21) and also render off-diagonal couplings more important.

To illustrate the above findings, it is instructive to revisit Figure 3 which demonstrates the coupling of the high-frequency mode $q_3$ to the low-frequency mode $Q_{10}$ in the normal-mode representation. In particular, it reveals that for the displaced mode $Q_{10}$, the OH stretch mode $q_3$ no longer displaces the hydrogens parallel to the OH bonds, but with an angle $\theta$ out of the plane of the hydrogen-bond-accepting water. A simple analysis suggests that a term $\cos \theta$ describes the observed negative curvature of the PES as a function of $Q_{10}$. This is because $\cos \theta$ accounts for the projection of $q_3$ onto the OH bond, which corresponds to an intramolecular displacement. In contrast, the component perpendicular to the OH bond ($\sin \theta$) is of intermolecular character and has a much weaker contribution to the potential energy. This mixing of low- and high-frequency degrees of freedom is particularly problematic when we wish to achieve an adiabatic separation, because that separation is no longer well defined when the dimer is not in its lowest energy configuration.

3.4. Curve crossings

Because of the small non-adiabatic couplings, the internal-coordinate PESs (Figure 6) constitute a physically useful adiabatic picture, and we will focus on them in what follows. It is seen in Figure 6 that many of the curves are quite close to each other. When we zoom in, we find several crossings of the PESs within the four OH-stretch modes and the three OH-bend modes, respectively, some of which are encircled. While many of these curve crossings are avoided in one dimension (the splittings are sometimes hardly visible in Figure 6), they may lead to four-dimensional seams of conical intersections in full six-dimensional space. Symmetry helps to find such conical intersections in lower dimensional cuts. For example, a true crossing occurs if an $A''$ high-frequency state crosses an $A'$ state along an $A'$ low-frequency tuning mode. Moreover, when we add an additional $A''$ coupling mode to that situation in a two-dimensional cut, this crossing will necessarily become a point-like conical intersection, because the $A''$ mode couples both states so the crossing is avoided.

As a representative example, Figure 6 shows a curve crossing (encircled in red in Figure 6) of the states $|100000\rangle (A'')$ and $|010000\rangle (A')$ as a function of the normal-mode $Q_{10} (A')$. It represents a true crossing because both states are of different symmetry ($A''$ versus $A'$). Upon coupling to another $A''$ low-frequency mode, such as, e.g. $Q_{12}$, we obtain a conical intersection as shown in Figure 8.

In contrast to malonaldehyde discussed in Ref. [4], where the hydrogen bond and hence the anharmonic couplings are much stronger, the energy of the conical intersection is not below the Franck–Condon region, such that the crossing may not necessarily play a dominant role in the fast dynamics. Nevertheless, the conical intersection occurs at $Q_{10} \approx -1$, which corresponds to the classical turning point at the zero-point energy; hence, the intersection will be seen by any excited wave packet. Accounting for the interaction of the asymmetric OH-stretch vibration of the hydrogen-bond-accepting water and the dangling...
OH-stretch vibration of the hydrogen-bond-donating water, this intersection leads to intermolecular vibrational energy transport between the two water molecules.

4. Conclusions

Vibrational conical intersections might provide an efficient mechanism to facilitate the ultrafast vibrational dynamics experimentally found for various forms of water. In a very first step towards this question, we have adopted an adiabatic approach to the vibrational structure of the water dimer, which for long has served as a minimal model for the hydrogen bonding in liquid water. Based on a state-of-the-art potential of (H₂O)₂ and subsequent vibrational-structure calculations, we have calculated the adiabatic PESs for the lowest states of the intramolecular high-frequency modes along the intermolecular low-frequency modes. Although a significant separation of time scales exists between both sets of coordinates, we have found that a standard normal-mode description of the adiabatic PESs leads to a qualitatively wrong picture. This complete breakdown of the adiabatic ansatz is caused by strong nonlinear couplings between high- and low-frequency normal modes, which in turn give rise to large overall non-adiabatic couplings. On the other hand, a valid adiabatic picture is obtained, when internal coordinates are employed. Here we have used normal modes to describe the intramolecular motion of each water molecule and intermolecular coordinates to describe the relative motion of the molecules. The chosen coordinates were found to largely decouple the high- and low-frequency degrees of freedom. Of course, the price one has to pay in an internal-coordinate representation with curvilinear intermolecular coordinates is a rather complicated kinetic energy operator of the low-frequency degrees of freedom [9] and additional non-adiabatic coupling terms due to kinetic couplings. We, however, believe that the greatest value of an adiabatic representation lies in the mixed-quantum classical treatment of a larger system, e.g. in order to study the vibrational dynamics in bulk water. In this case, that kinetic energy is needed only for the classical subsystem and hence not so difficult to deal with.

Considering one- and two-dimensional cuts of the adiabatic PESs of (H₂O)₂ along selected intermolecular coordinates, we have been able to show the existence of low-lying vibrational conical intersections in the water dimer. By coupling the motion of the OH modes, the intersections may mediate the vibrational energy transport between the two water molecules. In a similar vein, recent quantum-classical studies of the vibrational energy transport along the coupled CO vibrations of a peptide chain have indicated the existence of numerous conical intersections along the classical trajectory [43]. This excitonic-like energy transport along coupled high-frequency oscillators corresponds to almost resonant transitions between almost equivalent systems, which means that there is only little excess energy, only little change of the equilibrium geometry, and therefore also only little change of the vibrational dynamics. Although conical intersections have been discussed as a possible mechanism for excitonic energy transport [62], one might expect only minor differences in the effect of true and avoided crossings.

The situation is different if the conical intersection mediates a transition from higher to lower adiabatic PESs, thus resulting in the vibrational energy redistribution between, e.g. OH-stretch and OH-bend modes. Due to the typically shifted equilibrium geometry of the lower state and the large excess energy after the transition, the crossing may thoroughly change the vibrational dynamics of the system. In this scenario, a conical intersection that effectively and rapidly transfers populations to another state certainly makes a difference to an avoided crossing with significantly less efficient population transfer [63]. In the case of the water dimer, however, we have not found this type of conical intersection. When we extend the investigations to larger water clusters or even bulk water, we will have more OH modes and thus a higher level density, and would therefore also expect more conical intersections. Unlike the established role of electronic conical intersections in ultrafast photophysical and photochemical processes, the general importance of vibrational conical intersections to account for ultrafast vibrational dynamics remains yet to be shown.

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