Towards a Quantum Dynamical Study of the H$_2$O$+$H$_2$O Inelastic Collision: Representation of the Potential and Preliminary Results

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Water in the Universe, van der Waal dimer and Quantum Dynamics
Water in the Universe, vdW Dimers and QD
H$_2$O in the gas phase

- Water, also called the molecule of life is the most abundant polyatomic molecule in the galaxy and the 3$^{rd}$ most abundant molecule in the Interstellar Medium (ISM).

- In the ISM, water is one of the main reservoir of oxygen. It is strongly involved in the chemical reactivity of the ISM, but also of our atmosphere. At low pressure (such as in the ISM), water can bond with other molecules into van der Waal (vdW) molecules.

- Van der Waal molecules are weakly bound complexes, held together by intermolecular attractions. It is believed that vdW molecules are the first steps towards the nucleation of several systems: as such their study and characterization is of interest in the spectroscopy and dynamics communities.

- Theoretically, the standard approach to investigate small or medium size molecules and clusters is by solving the Schrödinger equation for the electrons to obtain the PES and subsequently run quantum dynamics calculations to describe the spectroscopy and collisional dynamics.

- While several vdW systems have been studied up to date, the frequent discovery of new molecules (usually "heavy") in the ISM prompts for improved methods to describe the dynamics and thus constitutes a challenge for today’s theoreticians.
The MultiConfiguration Time Dependent Hartree (MCTDH) algorithm is the computational method used to obtain cross-sections from a wave packet propagation. The MCTDH wavefunction ansatz writes

$$\Psi(q_1, \ldots, q_f, t) \equiv \Psi(Q_1, \ldots, Q_p, t),$$

$$= \sum_{m_1}^{n_1} \cdots \sum_{m_p}^{n_p} A_{m_1, \ldots, m_p}(t) \prod_{\kappa=1}^{p} \varphi_{m_{\kappa}}^{(\kappa)}(Q_{\kappa}, t),$$

$$= \sum_{M} A_{M} \Phi_{M},$$ \hspace{1cm} (1)

and is used to solve the time-dependent Schrödinger equation by the following equations of motion

$$i \dot{A}_M = \sum_{L} \langle \Phi_M | H | \Phi_L \rangle A_L,$$ \hspace{1cm} (2)

$$i \dot{\varphi}^{(\kappa)} = \left(1 - P^{(\kappa)}\right) \left(\rho^{(\kappa)}\right)^{-1} \langle H^{(\kappa)} \rangle \varphi^{(\kappa)}.$$ \hspace{1cm} (3)

The MCTDH algorithm is also used to obtain the rovibrational bound and resonant states of the system. The MCTDH Improved Relaxation method where the SPFs of the expansion are obtained by relaxation while the coefficients vectors are obtained by diagonalization is the method of choice for accurate results. The SPF relation thus transforms from Eqn (3) to the following Eqn (4)

$$\varphi_{m}^{(\kappa)} = -(1 - P^{(\kappa)}) \sum_{k, l=1}^{n_{\kappa}} (\rho^{(\kappa)})_{mk}^{-1} \langle H^{(\kappa)} \rangle_{kl} \varphi_{l}^{(\kappa)} = 0.$$ \hspace{1cm} (4)
Outline

1  The $\text{H}_2\text{O}$-$\text{Ar}$ Dimer

2  The $\text{H}_2\text{O}$-$\text{HCN}$ Dimer

3  The $(\text{H}_2\text{O})_2$ Dimer

4  Conclusion – Perspectives
The H$_2$O-Ar Dimer
The weak interaction between a polar molecule ($\text{H}_2\text{O}$) and a rare gas atom (Ar) is a prototype of hydrophobic interaction which plays an important role in biological processes such as protein folding, stability of the micelles and biological membranes.

Recently several new experimental rotational transitions involving excited vibrational states of $\text{H}_2\text{O}$ have been published and required theoretical calculations for their interpretation.

The $\text{H}_2\text{O}$-Ar complex has been extensively studied in the past decades and is considered as a benchmark system for this type of dimer interaction because of the relatively deep well of the intermolecular PES.

It is important to test the MCTDH procedure on this benchmark system where rovibrational results are available and inelastic scattering calculations are still possible with traditional Time Independent methods.
The H$_2$O-Ar Dimer
Electronic Structure and PES

- Cohen et al AW1 and AW2 empirical PESs obtained from a fit of far infrared vibration and rotation spectrum of the complex. Tao and Klemperer at the MP4. Hou et al Full Dimensional PES with the Intermolecular PES (IPS) at the CCSD(T)/aug-cc-pVQZ level with additional set of bond functions.

- Majumder et al CCSD(T*)-F12b/VTZ-F12a (single reference explicitly correlated F12 method with triplet corrections with Peterson’s basis set VTZ-F12 for valence-only electron correlation) were selected after careful assessment for accuracy and cost.

Fig: Contour Plot Cut of H$_2$O–Ar Ground State PES.

<table>
<thead>
<tr>
<th></th>
<th>R (Å)</th>
<th>θ (°)</th>
<th>φ (°)</th>
<th>ΔV (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>V$_{IMLS}$</td>
<td>3.670</td>
<td>103.4</td>
<td>0.0</td>
<td>-142.2</td>
</tr>
<tr>
<td>V$_{MLR}$</td>
<td>3.630</td>
<td>100.5</td>
<td>0.0</td>
<td>-139.5</td>
</tr>
<tr>
<td>V$_{AW2}$</td>
<td>3.518</td>
<td>105.7</td>
<td>0.0</td>
<td>-143.0</td>
</tr>
<tr>
<td>V$_{MP4}$</td>
<td>3.603</td>
<td>105.0</td>
<td>0.0</td>
<td>-130.2</td>
</tr>
<tr>
<td>V$_{CBS}$</td>
<td>3.695</td>
<td>111.0</td>
<td>0.0</td>
<td>-141.2</td>
</tr>
</tbody>
</table>
The Hamiltonian for the \( \text{H}_2\text{O} – \text{Ar} \) system in Jacobi coordinates can be written as

\[
\hat{H} = -\frac{1}{2\mu_R} \frac{\partial^2}{\partial R^2} + \frac{\vec{L}_R^\dagger \cdot \vec{L}_R}{2\mu_R R^2} + \hat{T}_{\text{H}_2\text{O}} + V(R, \beta_{\text{H}_2\text{O}}, \gamma_{\text{H}_2\text{O}}, \alpha_{\text{H}_2\text{O}}, q_1, q_2, q_3)
\]  

(5)

with the reduced mass of the \( \text{H}_2\text{O}–\text{Ar} \) system writing

\[
\mu_R = \frac{m_{\text{Ar}} m_{\text{H}_2\text{O}}}{m_{\text{Ar}} + 2m_{\text{H}} + m_{\text{O}}}. 
\]

(6)

\( T_{\text{H}_2\text{O}} \) is the Kinetic Energy Hamiltonian of the \( \text{H}_2\text{O} \) molecule. Equation (1) rewrites after some transformations with BF referring to the Body-Fixed Frame and \( E_2 \) to the \( E_2 \) Frame as

\[
\hat{H} = -\frac{1}{2\mu_R} \frac{\partial^2}{\partial R^2} + \frac{\vec{J}^2_{BF} + \vec{L}^2_{\text{H}_2\text{O}E_2} - 2\vec{J}_{zBF} \hat{L}_{\text{H}_2\text{O},zBF} - \vec{J}_{-BF} \hat{L}_{\text{H}_2\text{O},+BF} - \vec{J}_{+BF} \hat{L}_{\text{H}_2\text{O},-BF}}{2\mu_R R^2}
+ \hat{T}_{\text{H}_2\text{O}} + V(R, \beta_{\text{H}_2\text{O}}, \gamma_{\text{H}_2\text{O}}, \alpha_{\text{H}_2\text{O}}, q_1, q_2, q_3)
\]

(7)

In reduced dimensionality (\( q_1, q_2 \) and \( q_3 \) taken to their equilibrium values), The KEO of \( \text{H}_2\text{O} \) is expressed as

\[
\hat{T}_{\text{H}_2\text{O}} = \left( \frac{A + C}{2} \right) \hat{j}^2 + \left[ B - \left( \frac{A + C}{2} \right) \right] \hat{j}_z^2 + \left( \frac{A - C}{4} \right) \left( \hat{j}_+^2 + \hat{j}_-^2 \right).
\]

(8)
The H$_2$O-Ar Dimer
Computational Approach

Bound States Calculations
- Reduced Dimensionality DVR calculations
- The PES expressed in the Sum-of-Product Form
- 256 FFT functions for the $R$ direction in the [5,20] a.u. range
- Wigner-DVR for the angular degrees of freedom with 34, 65 and 65 primitive basis functions respectively for the $\beta_{H_2O}$, $\gamma_{H_2O}$ and $\alpha_{H_2O}$ coordinates respectively.
- Block improved relaxation (wavepacket propagation of a block of wavefunctions in imaginary time) of 12 eigenstates without symmetry consideration on an optimized basis set of less than 500 combined functions.

Scattering Calculations
- TI (MOLSCAT) and TD (MCTDH) Reduced Dimensionality calculations
- The PES linked to the code was expanded on a basis of Associated Legendre polynomials
- Propagation with the hybrid modified Airy propagator of Alexander and Manolopoulos from 4 bohrs to 100 bohrs. The MCTDH $R$ grid instead covered the 5–45 bohrs range.
- TI and TD calculations done up to 3000 $cm^{-1}$ of total energy.
### Rovibrational Bound States for $J = 0$

**Table:** Rovibrational Bound states of ortho and para-$\text{H}_2\text{O}$-Ar for $J = 0$.

<table>
<thead>
<tr>
<th>Assignment</th>
<th>$\text{V}_{\text{AW}2}$</th>
<th>$\text{V}_{\text{MLR}}$</th>
<th>$\text{V}_{\text{IMLS}}$</th>
<th>Assignment</th>
<th>$\text{V}_{\text{AW}2}$</th>
<th>$\text{V}_{\text{MLR}}$</th>
<th>$\text{V}_{\text{IMLS}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$0,\Sigma(000)$</td>
<td>-98.330</td>
<td>-93.494 (-93.499)</td>
<td>-97.017</td>
<td>$0,\Sigma(101)$</td>
<td>-81.583</td>
<td>-76.646 (-76.639)</td>
<td>-80.790</td>
</tr>
<tr>
<td>$1,\Sigma(000)$</td>
<td>-68.083</td>
<td>-63.776 (-63.507)</td>
<td>-65.677</td>
<td>$0,\Pi(101)$</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$0,\Pi(111)$</td>
<td>-57.650</td>
<td>-53.223 (-53.315)</td>
<td>-56.919</td>
<td>$1,\Sigma(101)$</td>
<td>-47.608</td>
<td>-43.547 (-43.149)</td>
<td>-45.525</td>
</tr>
<tr>
<td>$2,\Sigma(000)$</td>
<td>-39.253</td>
<td>-36.151 (-35.719)</td>
<td>-36.858</td>
<td>$1,\Pi(101)$</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$0,\Sigma/\Pi(202)$</td>
<td>-32.858</td>
<td>-28.264 (-28.246)</td>
<td>-31.905</td>
<td>$0,\Sigma(212)$</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$1,\Sigma(111)$</td>
<td>-27.130</td>
<td>-23.562 (-23.804)</td>
<td>-25.901</td>
<td>$0,\Sigma(212)$</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$1,\Pi(1311)$</td>
<td>-18.177</td>
<td>-16.172 (-15.665)</td>
<td>-16.777</td>
<td>$2,\Sigma(101)$</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$3,\Sigma(000)$</td>
<td>-18.177</td>
<td>-16.172 (-15.665)</td>
<td>-16.777</td>
<td>$1,\Sigma(101)$</td>
<td>-13.352</td>
<td>-10.229 (-10.039)</td>
<td>-11.313</td>
</tr>
<tr>
<td>$0,\Pi(111)$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>$0,\Pi(101)$</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$0,\Pi(202)$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>$0,\Sigma(110)$</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$1,\Pi(111)$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>$1,\Pi(101)$</td>
<td>0</td>
<td>0</td>
<td>0</td>
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<tr>
<td>$1,\Pi(110)$</td>
<td>0</td>
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<td>0</td>
<td>$1,\Pi(110)$</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$1,\Pi(212)$</td>
<td>0</td>
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<td>0</td>
<td>$1,\Pi(212)$</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$1,\Sigma(110)$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>$1,\Sigma(110)$</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
Table: Excitation cross section from the $0_{00}$ to \textit{para}-states at 480 cm$^{-1}$.

<table>
<thead>
<tr>
<th>Final State $J_K_aK_c$</th>
<th>$\Delta E$(cm$^{-1}$)</th>
<th>AW2 XS(Å$^2$)</th>
<th>SAPT XS(Å$^2$)</th>
<th>IMLS XS(Å$^2$)</th>
<th>Expt XS(Å$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>111</td>
<td>37.137</td>
<td>16.6</td>
<td>19.0</td>
<td>18.4</td>
<td>21(2)</td>
</tr>
<tr>
<td>202</td>
<td>70.091</td>
<td>3.21</td>
<td>2.29</td>
<td>3.42</td>
<td>8(1)</td>
</tr>
<tr>
<td>211</td>
<td>95.176</td>
<td>0.718</td>
<td>0.55</td>
<td>0.32</td>
<td>4.2(6)</td>
</tr>
<tr>
<td>220</td>
<td>136.164</td>
<td>7.18</td>
<td>6.81</td>
<td>5.29</td>
<td>6.2(6)</td>
</tr>
<tr>
<td>313</td>
<td>142.279</td>
<td>3.88</td>
<td>2.50</td>
<td>2.64</td>
<td>4.2(6)</td>
</tr>
<tr>
<td>322</td>
<td>206.301</td>
<td>0.14</td>
<td>0.11</td>
<td>0.027</td>
<td>0.7(2)</td>
</tr>
<tr>
<td>404</td>
<td>222.052</td>
<td>3.03</td>
<td>2.63</td>
<td>3.06</td>
<td>3.4(4)</td>
</tr>
<tr>
<td>413</td>
<td>275.497</td>
<td>0.084</td>
<td>0.090</td>
<td>0.019</td>
<td>2.4(8)</td>
</tr>
<tr>
<td>331</td>
<td>285.219</td>
<td>0.790</td>
<td>0.725</td>
<td>0.36</td>
<td>1.7(3)</td>
</tr>
<tr>
<td>422</td>
<td>315.779</td>
<td>0.047</td>
<td>0.172</td>
<td>0.130</td>
<td>0.5(2)</td>
</tr>
<tr>
<td>515</td>
<td>326.625</td>
<td>0.061</td>
<td>0.867</td>
<td>0.645</td>
<td>0.7(3)</td>
</tr>
<tr>
<td>431</td>
<td>385.842</td>
<td>0.007</td>
<td>0.010</td>
<td>0.001</td>
<td>0.0(2)</td>
</tr>
</tbody>
</table>
Figs.: TICC and MCTDH Inelastic scattering cross-sections from the $0_{00}$ to excited \textit{para} states.\textsuperscript{1}

The H$_2$O-HCN Dimer
• H$_2$O and HCN are common molecules in planetary environments and comets and it was recently proposed that the isomerization process between HCN and HNC can be catalyzed by H$_2$O molecules in the ISM.

• HCN is one of the molecules used to carry out statistical studies on the composition of comets. The interpretation of HCN emission in comets requires the availability of spectroscopic and state-to-state rate coefficients for collisions with the local most abundant disturbers which are electrons and H$_2$O.
We use the PES of the H$_2$O-HCN dimer computed by Quintás Sanchez and Dubernet$^2$. The PES exhibits 2 planar minima displayed below with different well depths.

$R = 7.156$ bohrs, $\theta = 0^\circ$, $\theta' = 0^\circ$ and $D_e = 1814.51$ cm$^{-1}$

$R = 7.020$ bohrs, $\theta = 122.47^\circ$, $\theta' = 66.59^\circ$ and $D_e = 1377.30$ cm$^{-1}$

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$^2$EL Quintas Sanchez and ML Dubernet, PCCP (2017) 19, 6849
The Hamiltonian and frequencies

\[
H = -\frac{1}{2\mu_R} + T_{H_2O} + T_{HCN} + V \\
+ \frac{1}{2\mu R^2} \left( \hat{j}^2 + (\vec{L}_{H_2O} + \vec{L}_{HCN})^2 \right)_{E_2} \\
- \frac{1}{2\mu R^2} \left( 2(\vec{L}_{H_2O} + \vec{L}_{HCN}) \hat{j} \right)_{E_2}
\]

The potential initially written as:

\[
V(R, \theta, \varphi, \theta', \varphi') = \sum_i v_i(R) t_i(\theta, \varphi, \theta', \varphi'),
\]

is transformed to:

\[
V(R, \beta, \gamma, \alpha, \theta_1, \phi_1) = \sum_j w_j(R) f_j(\beta, \gamma, \alpha, \theta_1, \phi_1).
\]

Table 1: \(H_2O-CHN\) Rigid Rotor Harmonic and vibrational frequencies (in \(cm^{-1}\)).

<table>
<thead>
<tr>
<th>Mode</th>
<th>Heikkilä (H)</th>
<th>CCSD(T)-F12 (H)</th>
<th>This Work (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\nu_1) (HCN libration)</td>
<td>98.9</td>
<td>66.1</td>
<td>93.7</td>
</tr>
<tr>
<td>(\nu_2) (H(_2)O wagging)</td>
<td>101.6</td>
<td>88.8</td>
<td>111.4</td>
</tr>
<tr>
<td>(\nu_3) (O···C stretch)</td>
<td>139.9</td>
<td>118.6</td>
<td>130.3</td>
</tr>
<tr>
<td>(\nu_4) (H(_2)O torsion)</td>
<td>144.6</td>
<td>147.4</td>
<td>171.2</td>
</tr>
<tr>
<td>(\nu_5) (H(_2)O rocking)</td>
<td>243.1</td>
<td>240.5</td>
<td>208.1</td>
</tr>
<tr>
<td>ZPE (cm(^{-1}))</td>
<td>364.1</td>
<td>330.7</td>
<td>357.3</td>
</tr>
</tbody>
</table>
Excitations Transition probabilities ($J=0$): $(0_{00},0_0) \rightarrow (0_{00},n_0)$, $n = 1, \ldots, 5$
The (H$_2$O)$_2$ Dimer
• H₂O is a major molecule in planetary environments, comets and the ISM. A detailed account of the chemical kinetics in all those environments therefore require accurate collisional rate coefficients of H₂O with other abundant systems, which include H₂O itself.

• On the fundamental viewpoint, characterizing the spectroscopy and the collisional dynamics quantum mechanically of dimers formed from non-linear fragments, even in the rigid rotor approximation is still a remarkable computational challenge. The water dimer case is in this respect a benchmark case and while its spectroscopy has been widely studied in the past decades, only few attempts to tackle the collisional dynamics have been made, and in most cases several (crude) approximations were made.
The traditional expression of the rigid rotor PES is

$$V(R, \omega_A, \omega_B) = \sum_{\Lambda} v_{\Lambda}(R) A_{\Lambda}(\omega_A, \omega_B)$$

with $$\Lambda = \{L_A, L_B, L, K_A, K_B\}$$ and where

$$A_{\Lambda}(\omega_A, \omega_B) = \sum_{M_A} (-1)^{(L_A+L_B+L)} \begin{pmatrix} L_A & L_B & L \\ M_A & -M_A & 0 \end{pmatrix} D_{M_AK_A}^{L_A}(\omega_A)^* D_{-M_AK_B}^{L_B}(\omega_B)^*$$

And

$$v_{\Lambda}(R) = \frac{(2L_A + 1)(2L_B + 1)(2L + 1)}{64\pi^4} \int d\omega_A d\omega_B A_{\Lambda}(\omega_A, \omega_B)V(R, \omega_A, \omega_B)$$

We selected an equivalent alternate representation expressed as

$$V(R, \omega_A, \omega_B) = \sum_{\lambda} w_{\lambda}(R) B_{\lambda}(\omega_A, \omega_B)$$

with $$\lambda = \{L_A, L_B, M_A, K_A, K_B\}$$ and where

$$B_{\lambda}(\omega_A, \omega_B) = D_{M_AK_A}^{L_A}(\omega_A)^* D_{-M_AK_B}^{L_B}(\omega_B)^*$$

$$= d_{M_AK_A}^{L_A}(\beta_A)d_{-M_AK_B}^{L_B}(\beta_B)\cos(M_A(\alpha_A - \alpha_B) + K_A\gamma_A + K_B\gamma_B)$$
The PES used for our study is the MB-Pol from the Paesani’s group\(^3\) considered to be one of the most accurate in the literature.

The rigid water dimer possesses several symmetries that have an impact on the multipolar expansion coefficients.

- **Inversion operation**
  This operation transforms each Wigner as
  \[
  \hat{D}^{L}_{M,K}(\omega) = (-1)^{(L+K)}D^{L}_{M,-K}(\omega)
  \]

- **Interchange operation** of the water molecules
  \[
  w_{L_A,M_A,K_A,L_B,-M_A,K_B}(R) = (-1)^{(L_A+L_B)}w_{L_B,-M_A,K_B,L_A,M_A,K_A}(R)
  \]

- **C\(_{2v}\) symmetry of rigid water**
  This imposes \(w_\lambda(R) = 0\) when \(K_A\) and/or \(K_B\) are odd.

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\(^{3}\)Babin et al, JCTC (2013) 9, 5395; JCTC (2014) 10, 1599
1D cut of the potential and error along the angular equilibrium position as a function of $R$ (in cm$^{-1}$). Expansion order $l = 6, 7$ and $8$ and Gauss-Legendre integration with $l+1$ and $2l+1$ points.
Comparison and Evaluation of the surface

1D cut of the potential along the angular equilibrium position as a function of $R$ (in cm$^{-1}$).
Expansion order $l = 6$ and Gauss-Legendre integration with $l' + 1$ and $2l' + 1$ points ($l' = 6, 7$ and $8$).
Conclusion and Perspectives
We presented a procedure, using the MCTDH algorithm, to obtain the rovibrational states and inelastic state-to-state cross-sections of a number of dimer interactions: Molecule/Atom, Molecule/Linear Molecule and Molecule/Molecule.

This procedure has been applied successfully on the Molecule/Atom case and our current work aim to extend it to more complex cases.

The MCTDH approach is a promising implementation for Molecule/Molecule collisions, which even in the rigid rotor approximations are out-of-reach for traditional Close-Coupling methods. Only very recently was the first Mixed Quantum Classical Trajectory (MQCT) calculations done in Babikov group on the $\text{H}_2\text{O}+\text{H}_2\text{O}$ collision with several limitations.
Works currently undergone and scheduled:

- Calculation of the rovibrational states \((J \geq 0)\) and state-to-state cross-sections for the \(\text{H}_2\text{O}-\text{HCN}\) dimer.

- Calculation of the state-to-state cross-sections for the \(\text{H}_2\text{O}+\text{H}_2\text{O}\) collision.

- Optimally we project to describe a \textit{generic procedure} to obtain inelastic cross-sections using the MCTDH approach.
We would like to thank the following who contributed to this work:

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- Dr Moumita Majumder (Texas Tech, PES).
- Dr Enersto Quintas Sanchez (Missouri S&T, PES).
- Prof Dr Hans-Dieter Meyer (Heidelberg Univ., MCTDH).
- Prof Fabien Gatti (Univ. Montpellier II, MCTDH).

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