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Benchmark calculations of Atom+Triatom and Diatom+Triatom rigid rotor inelastic scattering with MCTDH

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Dynamical Methods for COld Molecular collisions
Orsay, France

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Republic of Rwanda



Ministry of Education



1 (Molecular) Quantum Dynamics

2 Conclusion – Perspectives

The starting point in the study of microsystems is often the **Schrödinger Equation**.

Erwin Schrödinger (1887 – 1961)

Time Independent Schrödinger Equation

$$\mathcal{H}\psi = E\psi$$

Time Dependent Schrödinger Equation

$$\mathcal{H}\psi = i\hbar\frac{\partial}{\partial t}\psi$$



The Molecular Hamiltonian in the time independent formalism is written

$$\begin{aligned}
 \hat{H} &= \hat{T}_N + \hat{T}_e + \hat{V}_{NN} + \hat{V}_{ee} + \hat{V}_{Ne} \\
 &= - \sum_A^{nuclei} \frac{\hbar^2}{2M_A} \nabla_A^2 - \sum_i^{electrons} \frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_i^{electrons} \sum_A^{nuclei} \frac{e^2 Z_A}{4\pi\epsilon_0 r_{iA}} \\
 &\quad + \sum_{i>j}^{electrons} \frac{e^2}{4\pi\epsilon_0 r_{ij}} + \sum_{A>B}^{nuclei} \frac{e^2 Z_A Z_B}{4\pi\epsilon_0 r_{AB}}
 \end{aligned} \tag{1}$$

\hat{T}_N : Kinetic energy of the nuclei

\hat{V}_{NN} : nuclei-nuclei Coulomb interaction

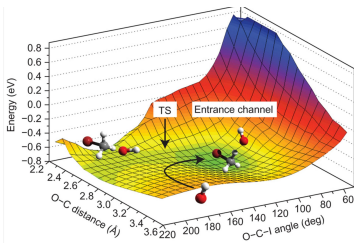
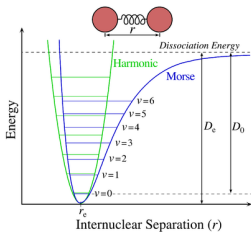
\hat{T}_e : Kinetic energy of the electrons

\hat{V}_{Ne} : nuclei-electrons Coulomb interaction

\hat{V}_{ee} : electrons-electrons Coulomb interaction

As the Schrödinger equation with the Molecular Hamiltonian **cannot be solved analytically**, one resorts to approximations. The most popular approximation used to solve the Schrödinger equation with the Molecular Hamiltonian is the **Born-Oppenheimer approximation**.

$$\left[\hat{T}_e + \hat{V}_{eN} + \hat{V}_{ee} \right] \Psi^{el}(\underline{R}, r) = E_{elect} \Psi^{el}(\underline{R}, r)$$



- The solution of the electronic Schrödinger equation provides the (Potential) Energies which are interpolated or extrapolated into **Potential Energy Surfaces^{ab}** (PES)
- The knowledge of electronic wavefunctions and energies is necessary to understand the **structure, electronic, magnetic, optical properties**, *dots* of molecules or materials.
- Two main categories of methods are used to solved the electronic energy problem: **wavefunction-based** (post Hartree-Fock) and **density-based** (DFT) methods.
- Various commercial, academic and open source programs are available to obtain those energies: MOLPRO, GAMESS, VASP, Quantum Espresso, Gaussian, Psi4, NWCHEM, Casino, QMCPACK, ...

^aM.Majumder, S.Ndengué, R.Dawes, Mol. Phys (2016) 114, 1.

^bR.Dawes, S.Ndengué, Int. Rev. Phys. Chem. (2016) 35, 441.

The Dynamics of the ions (nuclei) can be performed at 3 levels of sophistication: **classical**, **semi-classical** or **quantum-classical** and **quantum**

The Degrees of Freedom (DOF) of the ions could be treated with **classical mechanics**. This is referred as **Molecular Dynamics (MD)**, and described by Newton's 2nd Law:

$F = Ma$ where $F = -\nabla V$ with V the Potential Energy Surface. Various commercial and academic codes are available for this type of calculations: VENUS, CPMD, CP2K, LAMMPS, NAMD, NEWTON-X, AMBER, GROMACS, DLPOLY, ...

In a perfect world, all the DOF involved in the dynamics should be treated **quantum mechanically**: this is **Quantum Dynamics**.

Mainly various tailored homemade academic codes and the open source **MCTDH** program and its variants are available.

Some DOF of the nuclei could be treated classically and other quantum mechanically. This type of methods are often referred as **Quantum-Classical Dynamics** or **Semi-Classical Dynamics** methods.

The most direct way to solve the (time dependent) Schrödinger equation is to expand the wavefunction on a (direct-product) basis and solve the resulting **matrix equations**.

The Wavefunction *Ansatz* which writes

$$\Psi(q_1, \dots, q_f, t) = \sum_{j_1=1}^{N_1} \dots \sum_{j_f=1}^{N_f} C_{j_1, \dots, j_f}(t) \chi_{j_1}^{(1)}(q_1) \dots \chi_{j_f}^{(f)}(q_f), \quad (2)$$

is plugged into the time-dependent Schrödinger equation.
After applying the **Dirac Frenkel variational principle**







$$\langle \delta\Psi | H - i\partial/\partial t | \Psi \rangle = 0, \quad (3)$$

we obtain the equation of motion:

$$i\dot{C}_{j_1, \dots, j_f} = \sum_{l_1, \dots, l_f} \langle \chi_{j_1}^{(1)} \dots \chi_{j_f}^{(f)} | H | \chi_{l_1}^{(1)} \dots \chi_{l_f}^{(f)} \rangle C_{l_1, \dots, l_f}. \quad (4)$$

For a molecular system made of N atoms, the number of nuclear Degrees of Freedom is: $f=3N-6$ for a general molecule and $f=3N-5$ for a linear molecule.

Then if we take 10 grid points per DOF, we have the following:

Molecule Type	Example	N	DOF	Hamiltonian Matrix size
Diatomic molecule	 H ₂	2	1	10×10
Triatomic molecule	 H ₂ O	3	3	$10^3 \times 10^3$
Linear Triatomic molecule	 CO ₂	3	4	$10^4 \times 10^4$
Tetratomic molecule	 NH ₃	4	6	$10^6 \times 10^6$
5-atoms molecule	 CH ₄	5	9	$10^9 \times 10^9$
12-atoms molecule	 C ₆ H ₆	12	30	$10^{30} \times 10^{30}$

The difficulty of the calculation increases exponentially with the number of atoms in the system. This is the **curse of dimensionality** encountered in quantum dynamics.

One of the simplest and most approximate propagation methods is the **Time-Dependent Hartree** (TDH) approach.

The Wavefunction *Ansatz* here writes

$$\Psi(q_1, \dots, q_f, t) = a(t)\varphi^{(1)}(q_1, t) \cdots \varphi^{(f)}(q_f, t), \quad (5)$$

where

$$\varphi^{(\kappa)}(q_\kappa) = \sum_{m_\kappa=1}^{N_\kappa} C_{m_\kappa} \chi_{m_\kappa}^{(\kappa)}(q_\kappa). \quad (6)$$

As the representation is not unique, some constraints are imposed on the functions; for example one may choose:

$$i\langle \dot{\varphi}^{(\kappa)} | \varphi^{(\kappa)} \rangle = g^{(\kappa)}(t). \quad (7)$$

We then arrive at the following equations of motion:

$$i\dot{a} = a \left(\frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle} - \sum_{\kappa=1}^f g^{(\kappa)} \right), \quad (8)$$

$$i\dot{\varphi}^{(\kappa)} = \mathcal{H}^{(\kappa)}\varphi^{(\kappa)} + \left(g^{(\kappa)} - \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle} \right) \varphi^{(\kappa)}. \quad (9)$$

The MultiConfiguration Time Dependent Hartree (MCTDH)^a algorithm is an approximate computational method used to propagate a wave packet. It combines the ideas of the Standard approach and the TDH method and is often thought as the Time Dependent version of the MCSCF methodology. The MCTDH wavefunction *ansatz* with $n_\kappa \ll N_\kappa$ writes

$$\begin{aligned} \Psi(q_1, \dots, q_f, t) &= \sum_{m_1=1}^{n_1} \cdots \sum_{m_f=1}^{n_f} A_{m_1, \dots, m_f}(t) \prod_{\kappa=1}^f \varphi_{m_\kappa}^{(\kappa)}(q_\kappa, t), \\ &= \sum_M A_M \Phi_M, \end{aligned} \quad (10)$$

where

$$\varphi_{m_\kappa}^{(\kappa)}(q_\kappa) = \sum_{j_{m_\kappa}=1}^{N_\kappa} C_{j_{m_\kappa}} \chi_{j_{m_\kappa}}^{(\kappa)}(q_\kappa) \quad (11)$$

and as the representation is not unique, some constraints are imposed on the functions; for example one may choose:

$$i\langle \dot{\varphi}^{(\kappa)} | \varphi^{(\kappa)} \rangle = g^{(\kappa)}(t). \quad (12)$$

^aH.-D. Meyer, U. Manthe and L.S. Cederbaum, Chem. Phys. Lett. 165, 73 (1990)

Those are used to solve the time-dependent Schrödinger equation by the following equations of motion

$$i\dot{A}_M = \sum_L \langle \Phi_M | H | \Phi_L \rangle A_L, \quad (13)$$

$$i\dot{\varphi}^{(\kappa)} = \left(1 - P^{(\kappa)}\right) \left(\rho^{(\kappa)}\right)^{-1} \langle H \rangle^{(\kappa)} \varphi^{(\kappa)}. \quad (14)$$

The MCTDH algorithm can also be 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 (14) to the following Eqn (15):

$$\dot{\varphi}_m^{(\kappa)} = -(1 - P^{(\kappa)}) \sum_{k,l=1}^{n_\kappa} (\rho^{(\kappa)})_{mk}^{-1} \langle H^{(\kappa)} \rangle_{kl} \varphi_l^{(\kappa)} = 0. \quad (15)$$

The numerical effort of a calculation using the Standard Method is approximately:

$$\text{effort}_{St.Method} = c_0 \cdot f \cdot N^{f+1}$$

The numerical effort of an MCTDH calculation is approximately:

$$\text{effort}_{MCTDH} = c_1 \cdot s \cdot f \cdot n \cdot N^2 + c_2 \cdot s \cdot f^2 \cdot n^{f+1}$$

The memory demand (in bytes) of a Standard Method calculation is approximately:

$$\text{Memory}_{\text{St.Method}} = 3 \times N^f \times \text{complex16}$$

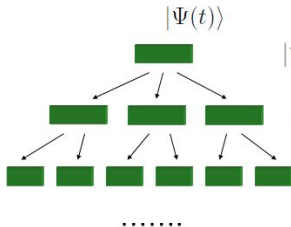
The memory demand (in bytes) of an MCTDH calculation is approximately:

$$\text{Memory}_{\text{MCTDH}} = 12 \times (n^f + f \cdot n \cdot N) \times \text{complex16}$$

If we have for example $N = 32$ grid points with $n = 7$ SPFs for each degree of freedom we would obtain:

f	St. Method	MCTDH	n^f	$f \cdot n \cdot N$
3	1.54 MB	190 KB	343	672
4	48 MB	620 KB	2401	896
6	48 GB	22 MB	$117 \cdot 10^3$	1344
9	1.54 PB	7.2 GB	$40 \cdot 10^6$	2016

The Multilayer MCTDH Theory



$$|\Psi(t)\rangle = \sum \sum \dots \sum A_{j_1 j_2 \dots j_p}(t) \prod^P |\varphi_{j_\kappa}^{(\kappa)}(t)\rangle$$

$$|\varphi_{j_\kappa}^{(\kappa)}(t)\rangle = \sum_{i_1} \sum_{i_2} \dots \sum_{i_{Q(\kappa)}} B_{i_1 i_2 \dots i_{Q(\kappa)}}^{\kappa, j_\kappa}(t) \prod_{q=1}^{Q(\kappa)} |v_{i_q}^{(\kappa, q)}(t)\rangle$$

$$|v_{i_q}^{(\kappa, q)}(t)\rangle = \sum_{\alpha_1} \sum_{\alpha_2} \dots \sum_{\alpha_{M(\kappa, q)}} C_{\alpha_1 \alpha_2 \dots \alpha_{M(\kappa, q)}}^{\kappa, q, i_q}(t) \prod_{\tau=1}^{M(\kappa, q)} |\xi_{\alpha_\tau}^{\kappa, q, i_q}(t)\rangle$$

$$i|\dot{\Psi}(t)\rangle_{L1 \text{ coefficients}} = \hat{H}(t)|\Psi(t)\rangle,$$

$$i|\dot{\underline{\varphi}}^k(t)\rangle_{L2 \text{ coefficients}} = [1 - \hat{P}^{(\kappa)}(t)][\hat{\rho}^{(\kappa)}(t)]^{-1} \langle \hat{H} \rangle^{(\kappa)}(t) |\underline{\varphi}^{(\kappa)}(t)\rangle,$$

$$i|\dot{\underline{v}}^{(\kappa, q)}(t)\rangle_{L3 \text{ coefficients}} = [1 - \hat{P}_{L2}^{(\kappa, q)}(t)][\hat{\rho}_{L2}^{(\kappa, q)}(t)]^{-1} \langle \hat{\mathcal{H}} \rangle_{L2}^{(\kappa, q)}(t) |\underline{v}^{(\kappa, q)}(t)\rangle,$$

$$i|\dot{\underline{\xi}}^{(\kappa, q, \gamma)}(t)\rangle_{L4 \text{ coefficients}} = [1 - \hat{P}_{L3}^{(\kappa, q, \gamma)}(t)][\hat{\rho}_{L3}^{(\kappa, q, \gamma)}(t)]^{-1} \langle \hat{\mathcal{H}} \rangle_{L3}^{(\kappa, q, \gamma)}(t) |\underline{\xi}^{(\kappa, q, \gamma)}(t)\rangle$$

Wang, Thoss, J. Chem. Phys. **119** (2003) 1289

Some problems solved with MCTDH Quantum Dynamics: <http://mctdh.uni-hd.de>

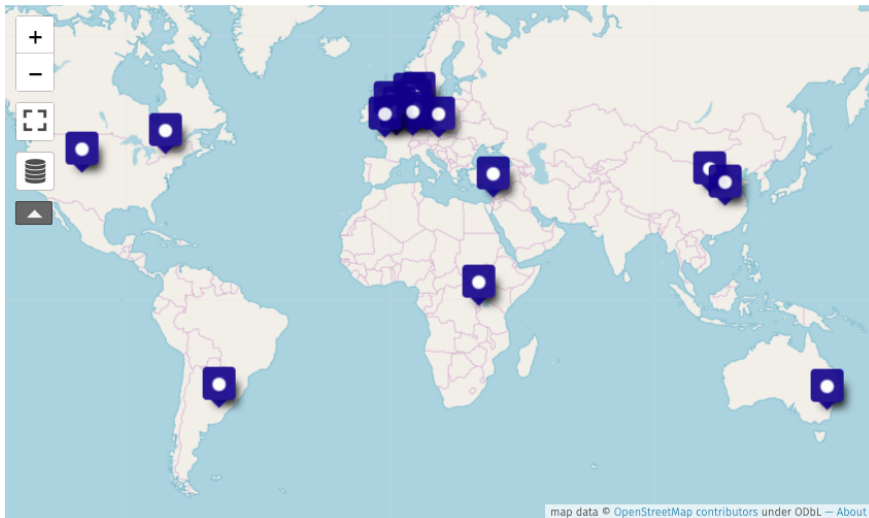
- **Photodissociation & Photoabsorption** (or ionisation) spectra
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- Vibrational Predissociation
- **Molecule–Surface scattering** (catalysis)
- **Inelastic Scattering**
- Reactive Scattering: cross-sections, thermal reaction rates
- **Computation of eigenstates**, phonon modes
- Spin-Boson model
- Nuclear dynamics during electron-scattering processes
- **Proton transfer reactions**
- Optimal control
- Electron-phonon Interaction
- Bose-Einstein Condensates & Ultracold Atoms



A small community of scientists from Germany, France, UK, Israel, China, US, Netherlands, . . . , Rwanda are contributing to the MCTDH package and exploring new avenues of the program.



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- MCTDH is a multipurpose **quantum dynamical toolbox** useful for various type of calculations that find applications in astrophysics, atmospheric chemistry, combustion, catalysis, ultracold physics, biological physics, etc . . .
- Contraction methods in general and the MCTDH algorithm in particular extends the range of what is computationally reachable in quantum dynamics. Calculations that were previously intractable are now becoming standard with new algorithms.
- This is amplified by **improved parallelization**, a **Multi-Layer** version of MCTDH or **Dynamical Pruning** of the basis which make this field exciting for the future.

-  Benchmarking Inelastic Scattering for various systems of astrophysical interest: $\text{H}_2\text{O}-\text{H}_2$, $\text{H}_2\text{O}-\text{H}_2\text{O}$, ... In particular we are interested in systems that are challenging with respect to their **computational cost**.
-  A **time-independent** description of scattering taking advantage of contraction scheme. Probably the best approach to study **cold scattering processes**.
-  Applying contraction ideas to study systems in high dimensionality and creating a bridge with **biological physics, material science**, ...
-  Writing a code to implement the time-independent treatment of collisions with contraction. The code will eventually be integrated in the MCTDH package.

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