Quantum Dynamics with the Multi-Configuration Time-Dependent Hartree (MCTDH) or the PODVR methods

Fabien Gatti.

Quantum Dynamics with the Multi-Configuration Time-Dependent Hartree (MCTDH) method or the PODVR methods
ISMO, University Paris-Saclay, Orsay, France

November, 2019

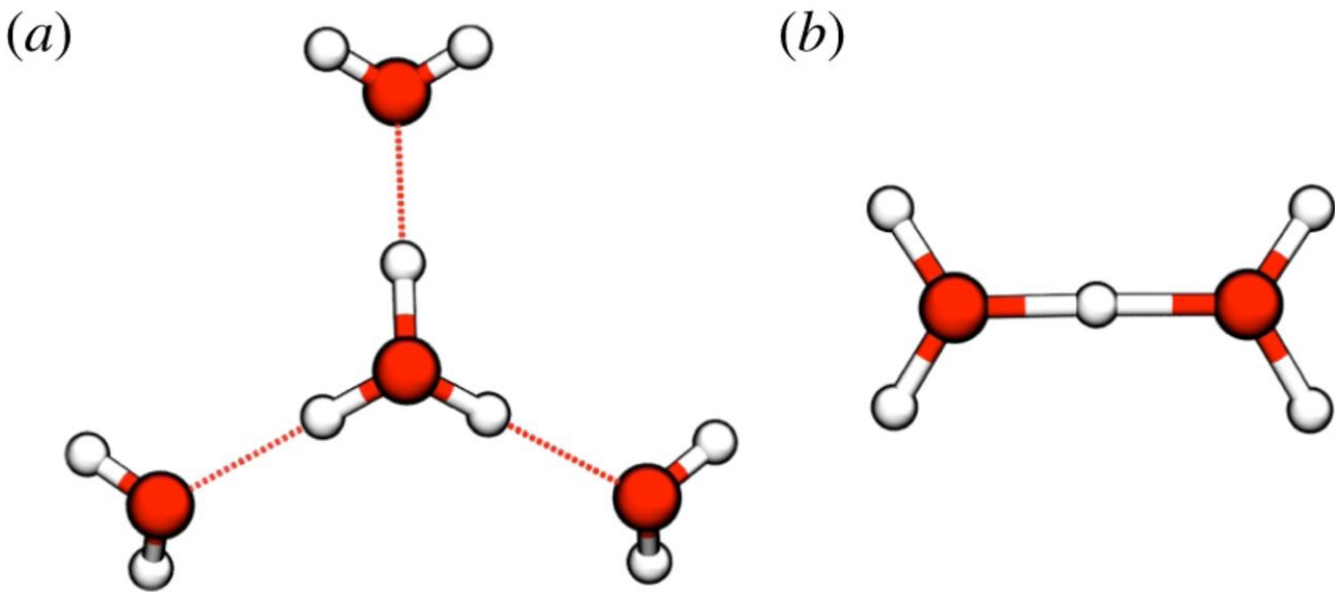
Molecular Quantum Dynamics, Springer, 2014, Ed. F. Gatti

Quantum Physics: applications in chemistry,
Lectures Notes in Chemistry, F. Gatti, B. Lasorne, H.-D. Meyer and A. Nauts,
Springer, 2017.

Full quantum mechanical time-dependent treatment

$$(H_2O)_3H_3O^+$$

Zundel and Eigen cations: the two "idealized" forms of an excess proton in liquid water. Essential to describe the diffusion of protons in water (Grotthuss mechanism).



Reactive collisions with 6 atoms

$H+CH_4 \rightarrow H_2 + CH_3$ Very accurate measurements of the cross sections of molecular

collisions (experimental group of Dalian)

Understanding of bi-molecular elementary reactions including all the most subtle quantum effects

Very large systems ?

Possible treatment of the quantum dynamics of systems with hundreds of atoms with the ML-MCTDH approach

One example on biological system

The Heidelberg Multi-Configuration Time-Dependent Hartree (MCTDH) package
http://www.pci.uni-heidelberg.de/cms/mctdh.html

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

Multidimensional Quantum Dynamics : MCTDH Theory and Applications Wiley-VCH
Edited by H.-D. Meyer, F. Gatti and G. Worth.

The MultiConfiguration Time Dependent Hartree (MCTDH) algorithm is a computational method to propagate wave packets. The MCTDH wavefunction *ansatz* writes

$$\begin{aligned}\Psi(q_1,\ldots,q_f,t) &\equiv \Psi(Q_1,\ldots,Q_p,t),\\ &= \sum_{m_1}^{n_1}\cdots\sum_{m_p}^{n_p} A_{m_1,\ldots,m_p}(t)\prod_{\kappa=1}^{p}\varphi_{m_\kappa}^{(\kappa)}(Q_\kappa,t),\\ &= \sum_{M} A_M \Phi_M, \end{aligned} \tag{1}$$

$$\varphi_{j_\kappa}^{(\kappa)}(Q_\kappa,t) = \sum_{l_1=1}^{N_{1,\kappa}}\cdots\sum_{l_d=1}^{N_{d,\kappa}} c_{j_\kappa l_1\cdots l_d}^{(\kappa)}(t)\,\chi_{l_1}^{(\kappa)}(q_{1,\kappa})\cdots\chi_{l_d}^{(\kappa)}(q_{d,\kappa}) \tag{2}$$

$$i\dot{A}_M = \sum_L \langle\Phi_M|H|\Phi_L\rangle A_L, \tag{3}$$

$$i\dot{\varphi}^{(\kappa)} = \left(1-P^{(\kappa)}\right)\left(\rho^{(\kappa)}\right)^{-1}\langle H\rangle^{(\kappa)}\varphi^{(\kappa)}. \tag{4}$$

Calculate the Potential and express it in an adequate form

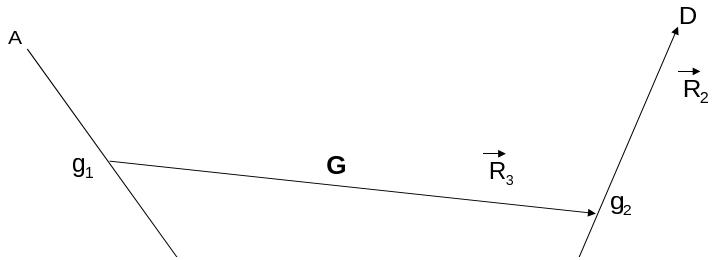
Sum of products of one-particle operators

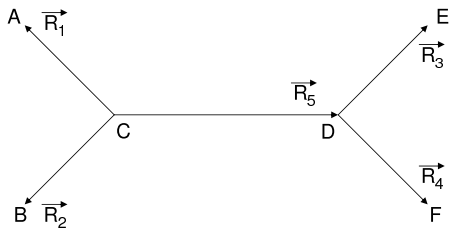
$$V(q_{i_1}^{(1)},\ldots,q_{i_p}^{(p)}) = \sum_{j_1=1}^{m_1}\cdots\sum_{j_p=1}^{m_p} C_{j_1\ldots j_p}\, v_{j_1}^{(1)}(q_{i_1}^{(1)})\cdots v_{j_p}^{(p)}(q_{i_p}^{(p)}) \tag{5}$$

The potential is in MCTDH form only when dealing with model problems
MCTDH form (potfit, Multigrid-potfit, Multilayer-potfit)
The MCTDH computation time grows linearly with the number of Hamiltonian terms

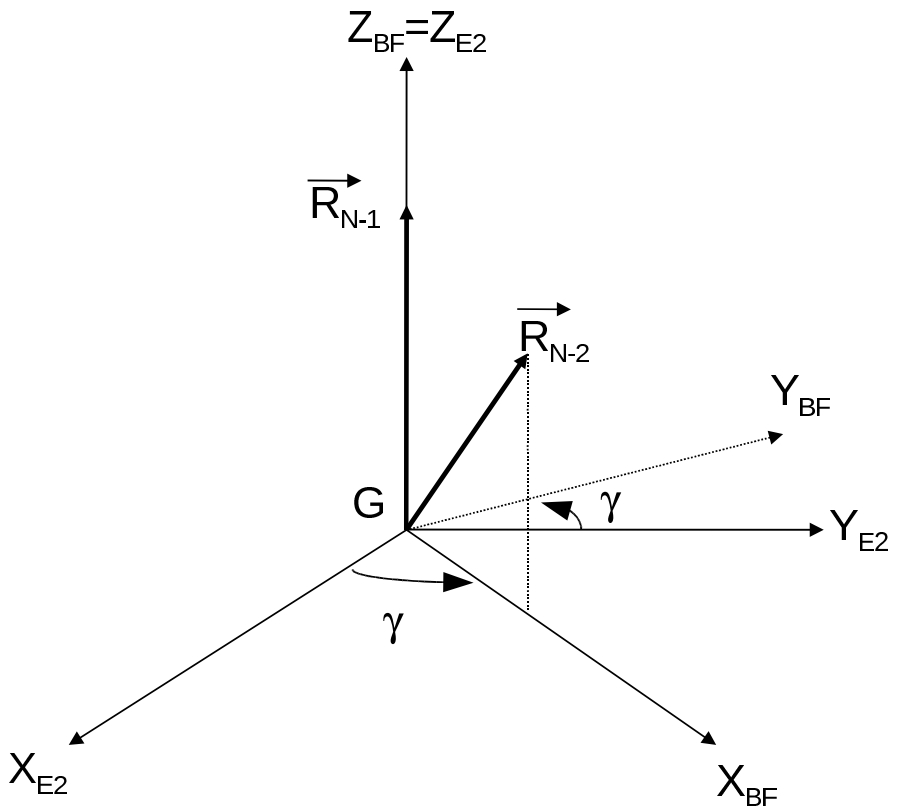
Polyspherical coordinates
F. Gatti and C. Iung Phys. Rep. (2009).

N-atoms, N-1 relative position vectors.

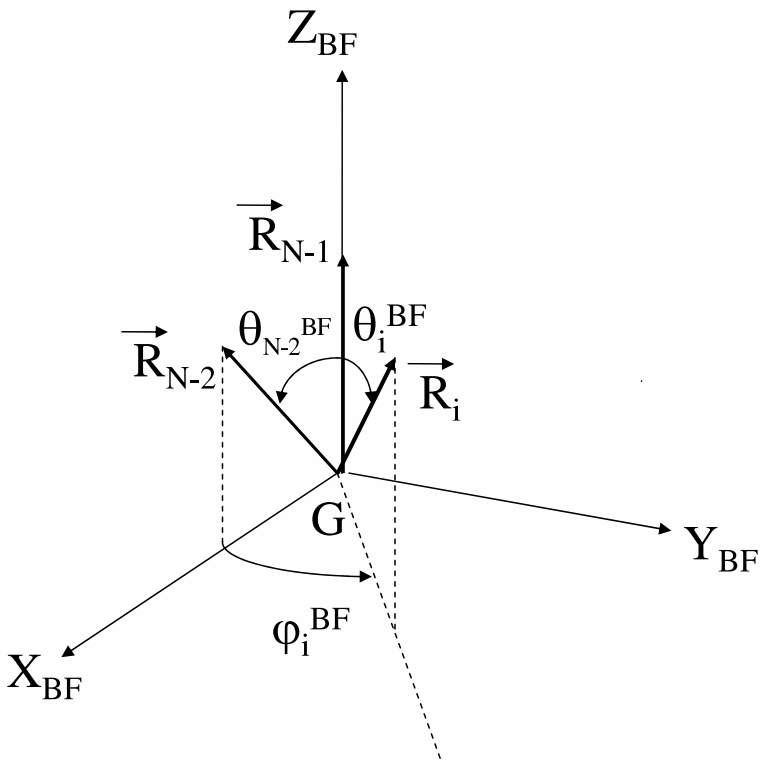




Definition of the Body-Fixed frame.



Definition of the polyspherical coordinates.



$$2\hat{T} = \sum_{i,j=1,\ldots,N-1} \sum_{\lambda=x,y,z} \hat{P}^{\dagger}_{i\,\lambda^{BF}} M_{ij} \hat{P}_{j\,\lambda^{BF}}$$

$$\hat{\vec{P}}_i = \hat{P}_{R_i} \vec{e}_i - \frac{\vec{e}_i \times \hat{\vec{L}}_i}{R_i} \tag{6}$$

M_{ij} is diagonal for "orthogonal" coordinates (Jacobi, Radau)

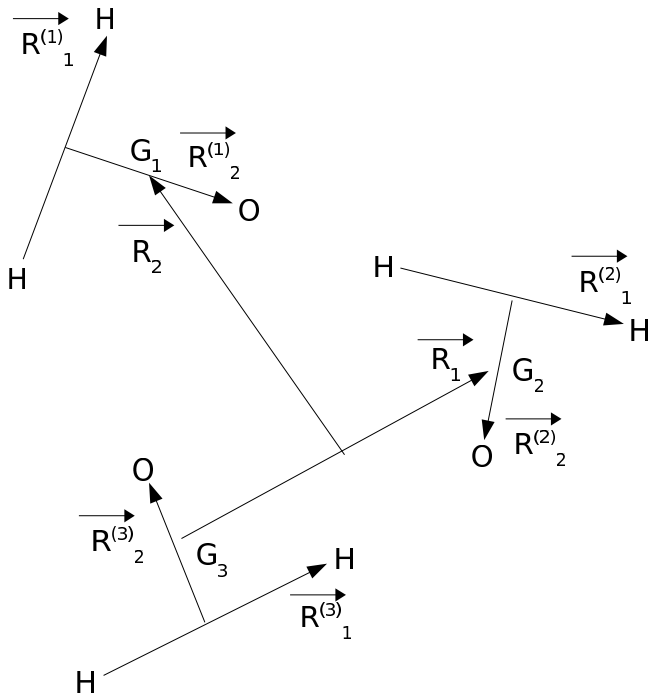
General expression of the KEO.

$$\begin{aligned}\hat{T} &= \sum_{l,m=1}^{3N-6} \frac{\hat{P}^{\dagger}_{q_l} \Sigma_{q_l q_m} \hat{P}_{q_m}}{2} + \sum_{l=1}^{3N-6} \sum_{\alpha=x,y,z} \frac{\hat{P}^{\dagger}_{q_l} \sigma_{q_l \alpha} \hat{J}_{\alpha BF} + \hat{J}_{\alpha BF} \sigma_{\alpha q_l} \hat{P}_{q_l}}{2} \\ &+ \sum_{\alpha=x,y,z} \sum_{\beta=x,y,z} \frac{\hat{J}_{\alpha BF} \Gamma_{\alpha\beta} \hat{J}_{\beta BF} + \hat{J}_{\beta BF} \Gamma_{\beta\alpha} \hat{J}_{\alpha BF}}{2} .\end{aligned} \tag{7}$$

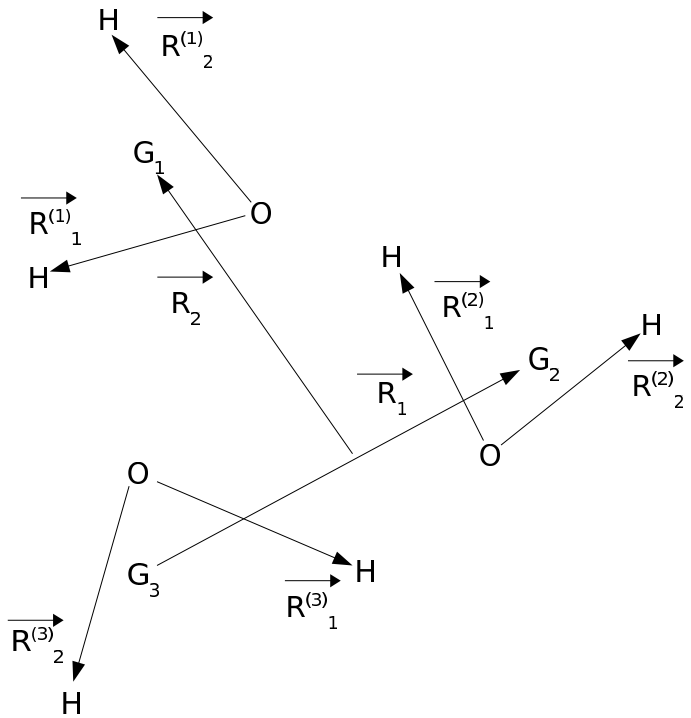
$$\hat{P}_{q_i} = \frac{1}{i} \frac{\partial}{\partial q_i}$$

$$M_{ij} \left(\hat{P}_{\varphi_i} \frac{\cos\varphi_i \cos\varphi_j}{R_i R_j \sin\theta_i \sin\theta_j} \hat{P}_{\varphi_j} + \hat{P}_{\varphi_j} \frac{\cos\varphi_i \cos\varphi_j}{R_i R_j \sin\theta_i \sin\theta_j} \hat{P}_{\varphi_i} \right) \tag{8}$$

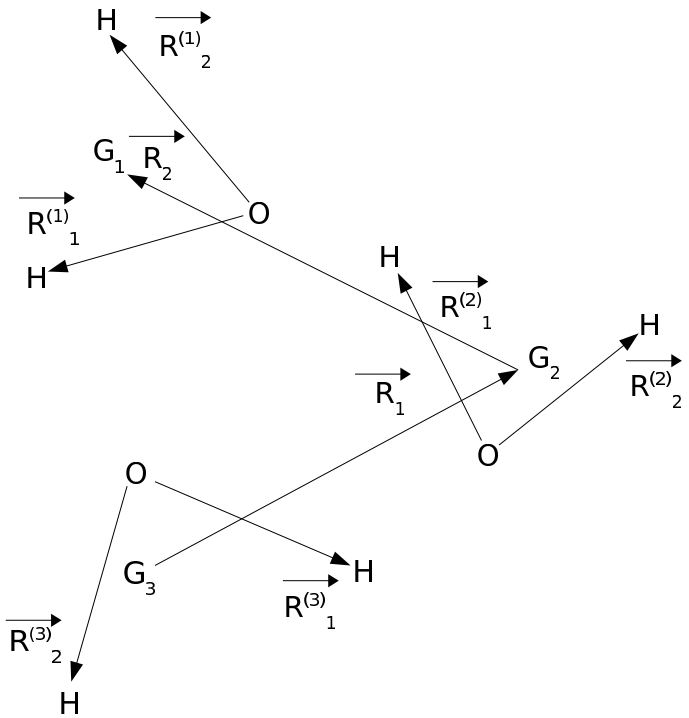
Separation into subsystems



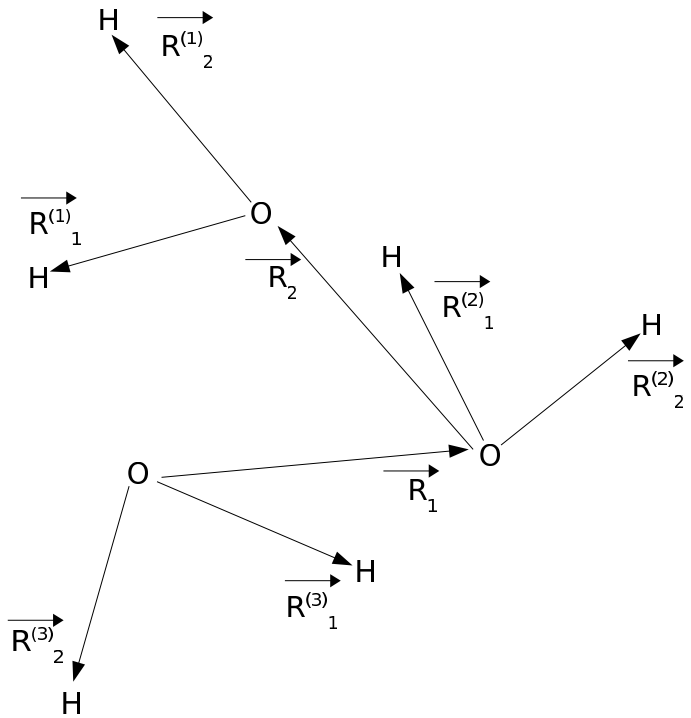
Separation into subsystems



Separation into subsystems



Separation into subsystems



Singularities.

$$-\frac{1}{2mR^2\sin^2\theta}\frac{\partial^2}{\partial\varphi^2} \tag{9}$$

An appropriate basis set that removes the singularities: a basis set of spherical harmonics: 2 dimensional DVR.

For the angular momentum of a body: Wigner 3D DVR

Kinetic Energy Operator:

Several advantages:

always a sum of products of one-dimensional operators

flexibility

one knows the solution if singularities appear

Disadvantages:

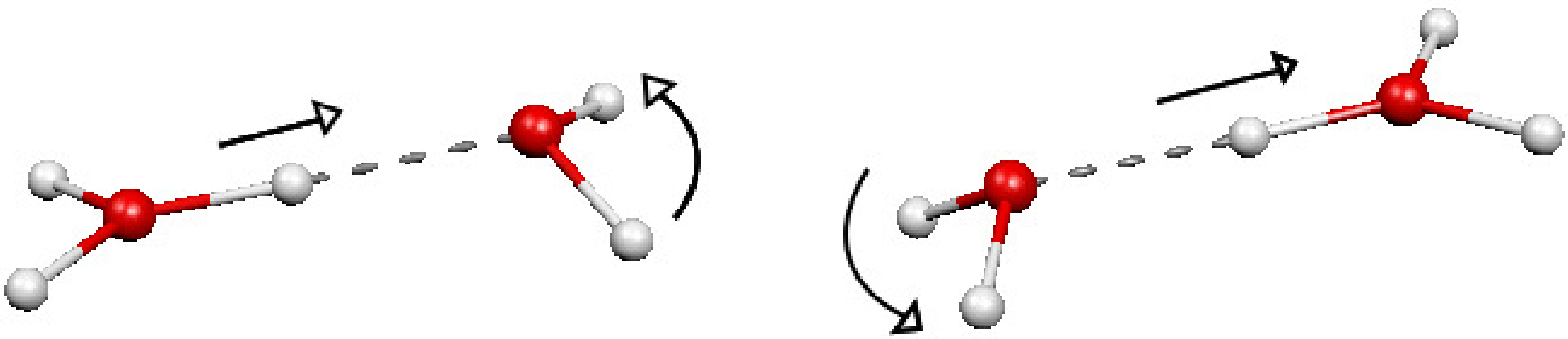
restrictions in the definition of the coordinates in particular for the BF frame

can create some artificial correlation and break the symmetry

TANA Package

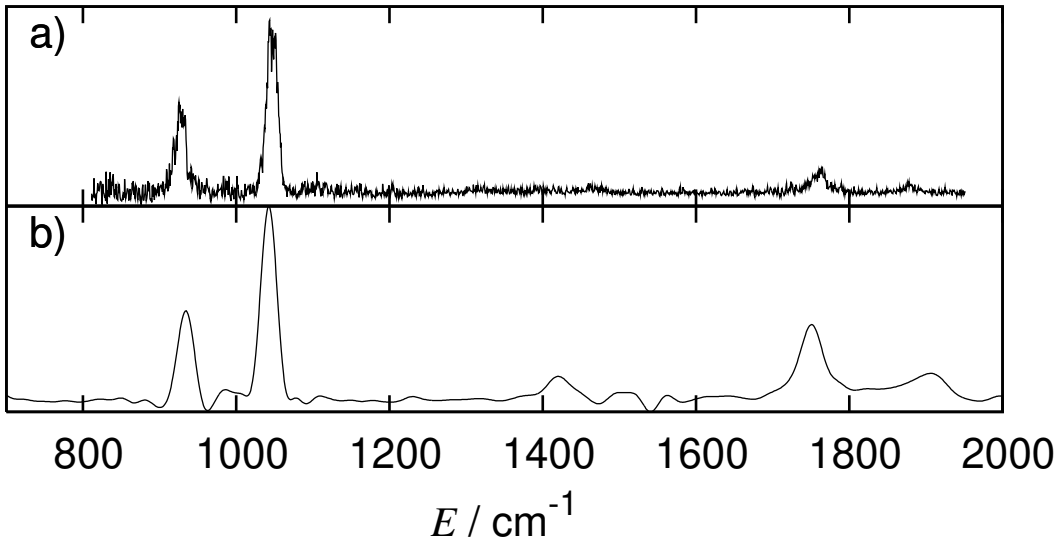
M. Dong, L. Joubert Doriol, H.-D. Meyer, A. Nauts F. Gatti , D. Lauvergnat JCP 139 (2013) 204107

Zundel cation



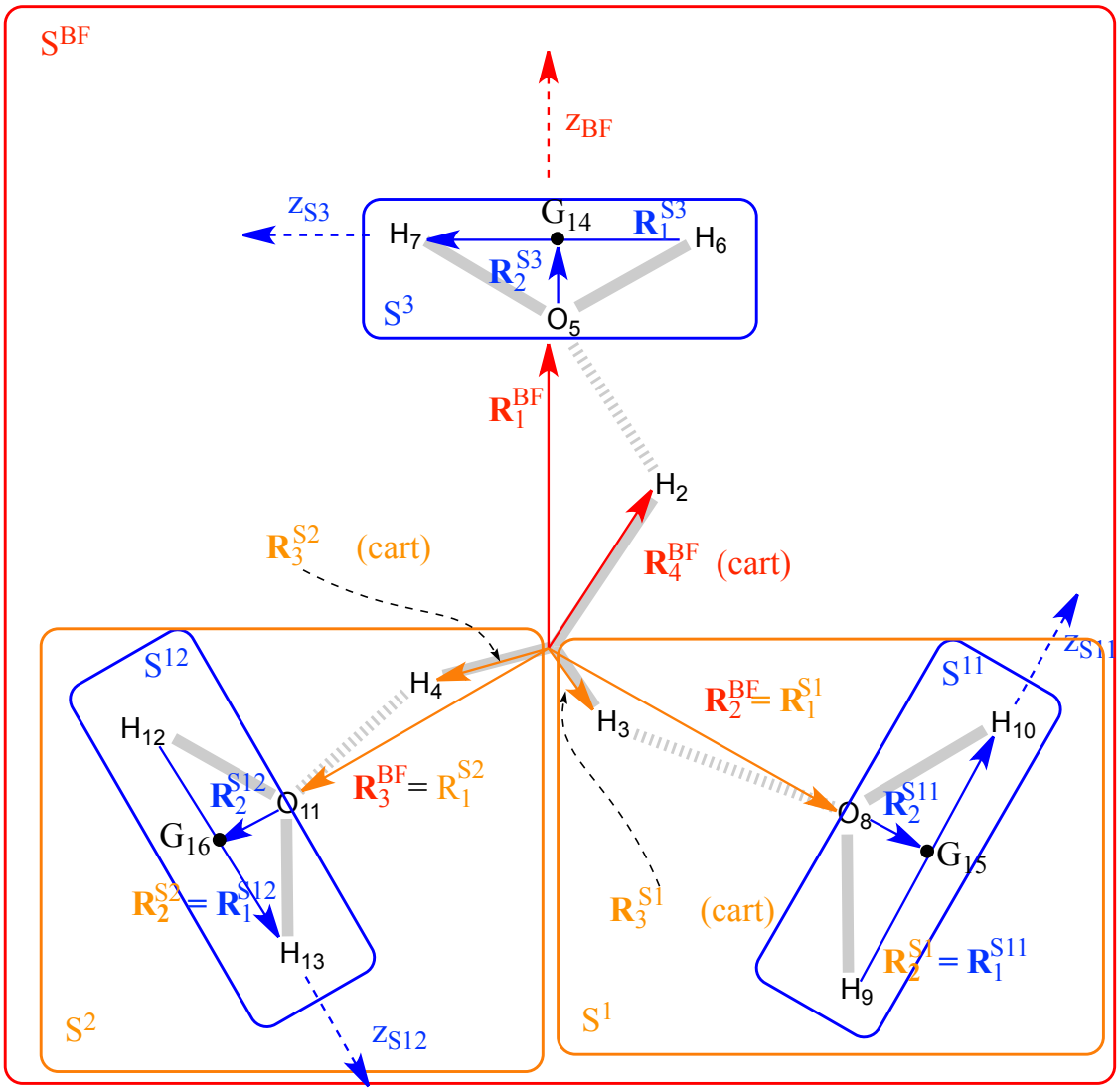
Strong coupling (Fermi resonance) between the proton-transfer motion and the wagging (or pyramidalization) bending mode of vibration. Description in terms of curvilinear (involving angles) coordinates.

Zundel cation



O. Vendrell, F. Gatti, and H.-D. Meyer, Angewandte Chemie Int. Ed (VIP) 46 (2007) 6918. "Dynamics and Infrared Spectroscopy of the Protonated Water Dimer."
S. S. Xantheas, Nature 457 (2009) 673.

Eigen cation.



MCTDH operator file provided by the TANA program

D. Lauvergnat (Orsay)

4370 terms

The IR Eigen cation spectrum (33D)

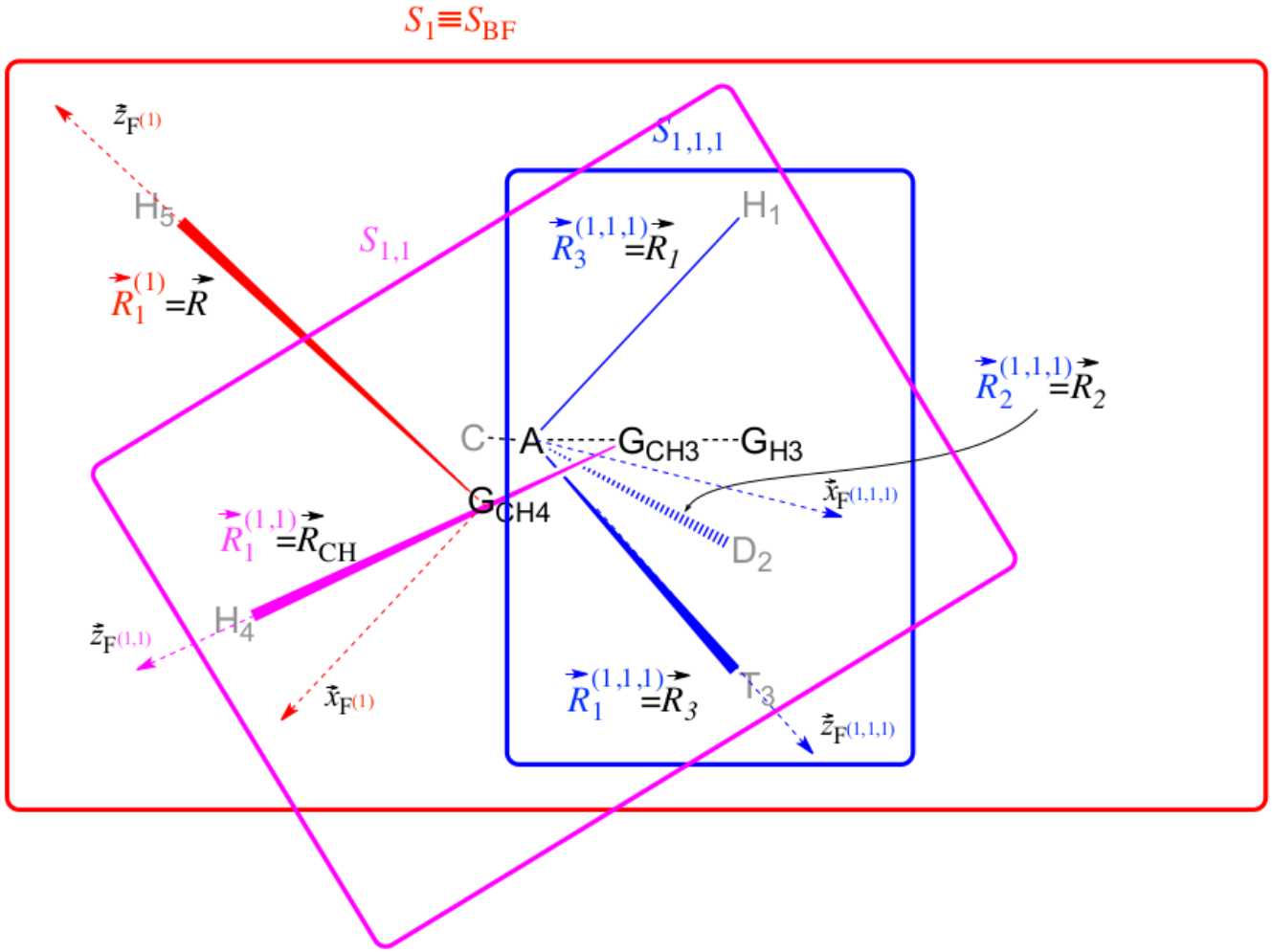
Collaboration with Dong-Hui Zhang (Dalian)

Goal : Accurate calculations of the cross-sections of $H+CH_4$

PODVR approach for the degrees of freedom

Not too many terms: necessity to be 100 % sure that the operator is perfectly implemented in the code of Dalian

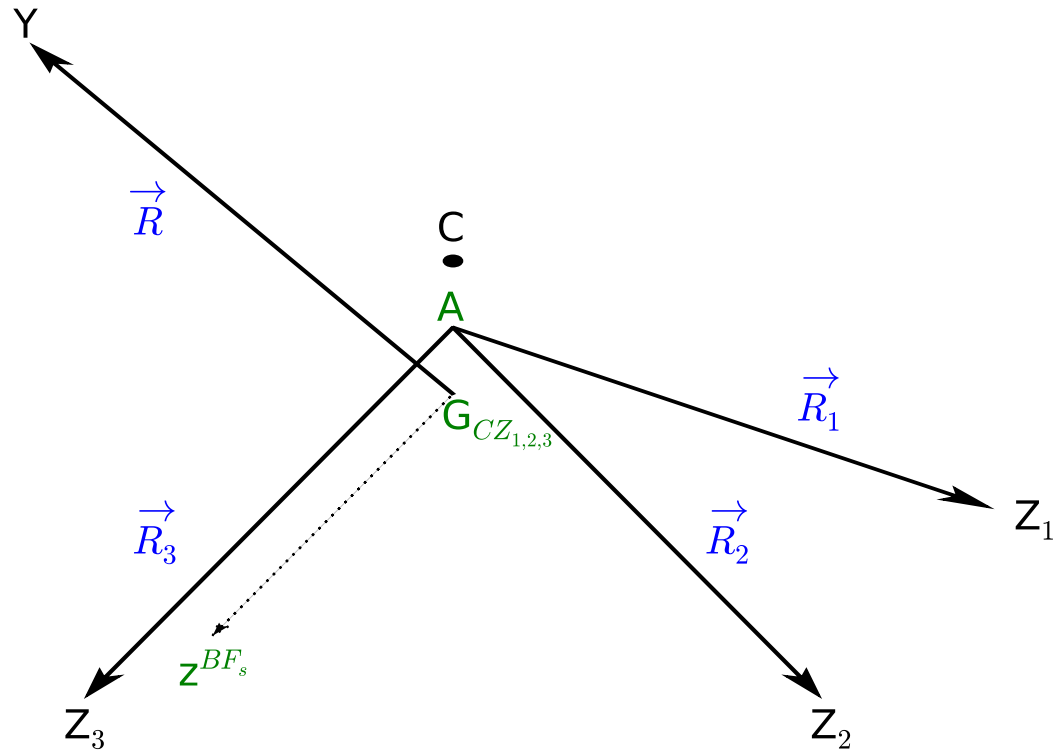
H+CH_4.



Other coordinates: Evenhuis C, Nyman G, Manthe U (2007) Journal of Chemical Physics 127(14): 144302/ Schapers D, Zhao B, Manthe U Chem. Phys. 509 (2009) 37.

Application to H + CHD_3

C3v symmetry and several coordinate transformations to avoid any singularity


Y
$\overrightarrow{R}$
C
A
$\overrightarrow{R_1}$
$G_{CZ_{1,2,3}}$
Z_1
$\overrightarrow{R_3}$
$\overrightarrow{R_2}$
z^{BF_s}
Z_3
Z_2

Comparison with Xiao-Gang Wang and T. Carrington
(Eckhart frame, contraction for the bend and stretch motions, use of symmetry).

Basis set		R_1,R_2,R_3	θ_1,θ_2	φ	β_s	γ_s	R
	PODVR	7	7	7	7	7	7

State	Exp.	SSDP	NEKCB
(5,1)F_1	157.124	157.094 $\pm$ 0.002	157.088
(5,1)F_2	157.128	157.102 $\pm$ 0.005	157.092
(5,1)E	157.137	157.115 $\pm$ 0.008	157.101
(5,2)F_2	157.139	157.137 $\pm$ 0.014	157.103

Z. Zhao *at al.* JCP 148 (2018) 074113

$HCH_4/CHD_3/CH_3D/FCH_4$: Zhiqiang Zhao

Vib	(K)Sym	Exp.	SSDP	NEKCB
(002000)A_1	(1)E	2606.65	2608.18 ± 0.01	2606.08
(000011)E	(1)E	2629.05	2629.70 ± 0.01	2628.86
(000011)E	(0)E	2631.27	2631.91 ± 0.67	2631.06
(000011)A_1	(1)E	2634.30	2634.65 ± 0.01	2634.11
(000011)E	(1)A_2	2636.12	2637.74	2635.90
(000011)E	(1)A_1	2636.12	2637.75	2635.90
(000011)A_1	(0)A_2	2640.99	2642.75	2640.81
(000011)A_2	(0)A_1	2642.69	2643.34	2642.49
(000011)A_2	(1)E	2652.04	2653.09 ± 0.03	2651.85
(001010)E	(1)E	2782.51	2782.69 ± 0.00	2782.27
(001010)E	(0)E	2783.97	2784.19 ± 0.58	2783.73
(001010)E	(1)A_1	2788.17	2788.41	2787.94
(001010)E	(1)A_2	2788.26	2788.50	2788.02

12 D results to be published

Reaction probabilities for $H+CH_4 \rightarrow H_2 + CH_3$

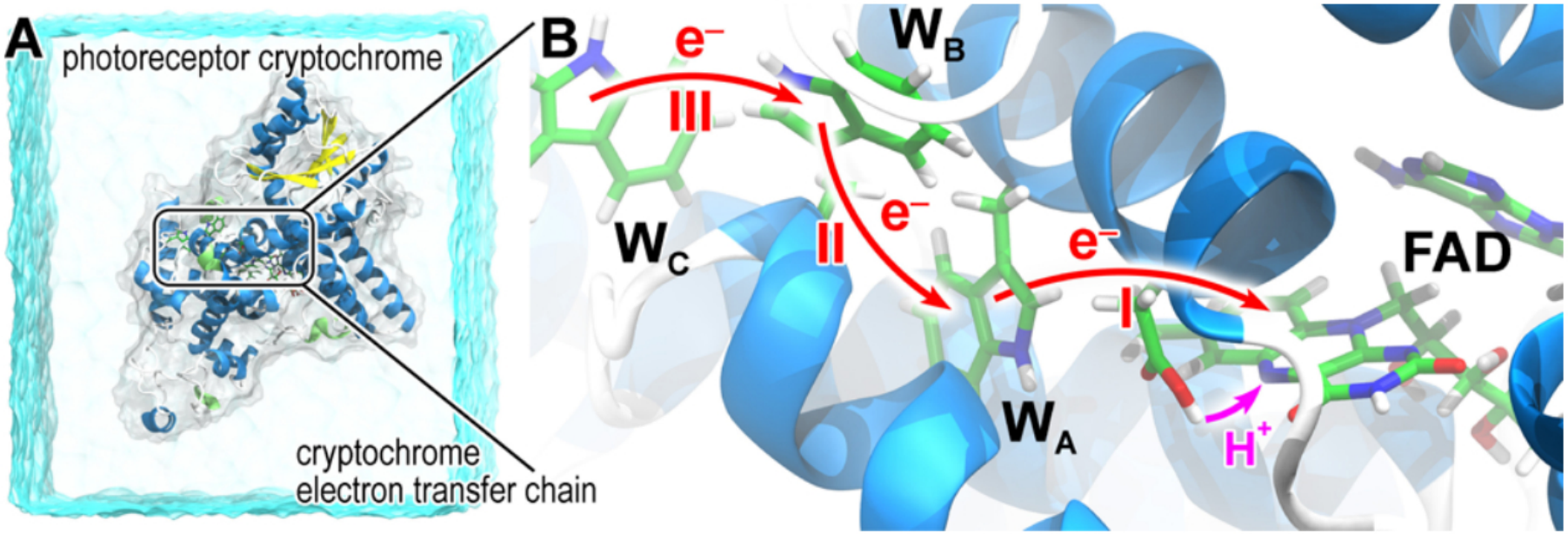
Zhaojun Zhang and Dong-Hui Zhang (Dalian)

$$\Psi(q_1,q_2,q_3,t) = \sum_{j_1=1}^{n_1}\sum_{j_2=1}^{n_2}\sum_{j_3=1}^{n_3} A_{j_1,j_2,j_3}(t)\varphi_{j_1}^{(1)}(q_1,t)\varphi_{j_2}^{(2)}(q_2,t)\varphi_{j_3}^{(3)}(q_3,t)$$

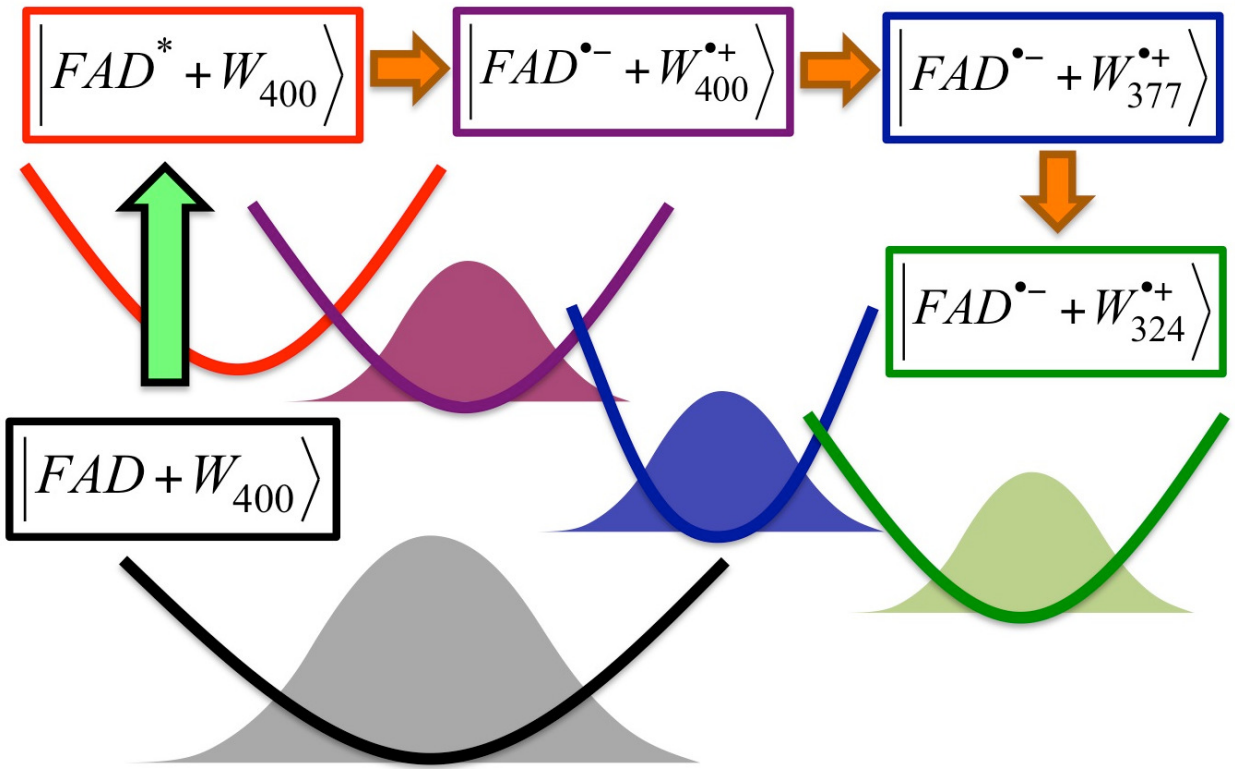
$$\varphi_{j_1}^{(1)}(q_1,t) = \sum_{i_1=1}^{N_1} c_{i_1}^{(1,j_1)}(t)\chi_{i_1}^{(1)}(q_1)$$

$$\Psi(q_1,q_2,q_3,t) = \sum_{j_{12}=1}^{n_{12}}\sum_{j_3=1}^{n_3} A_{j_{12},j_3}(t)\varphi_{j_{12}}^{(12)}(q_1,q_2,t)\varphi_{j_3}^{(3)}(q_3,t)$$

$$\varphi_{j_{12}}^{(12)}(q_1,q_2,t) = \sum_{k_1=1}^{n_1}\sum_{k_2=1}^{n_2} B_{k_1,k_2}^{(12,j_{12})}(t)\xi_{k_1}^{(1)}(q_1,t)\xi_{k_2}^{(2)}(q_2,t)$$

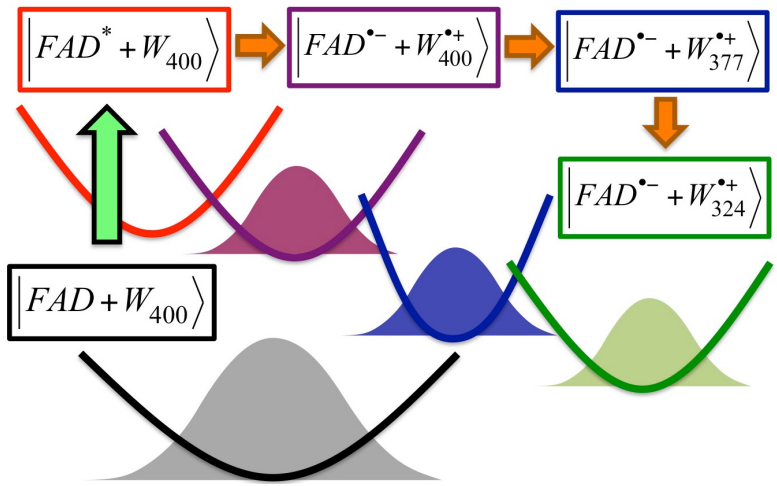


Spin-Boson Models
CDFT QM/MM calculations 110 000 atom
including 34 000 water molecules, 298.15 K
Parameters provided by QM/MM calculations (Aurélien de la Lande and M. Desouter Lecomte)



Absorption of light by the chromophore Flavin Adenine Dinucleotide (FAD) triggers an electron transfer to tryptophan residue

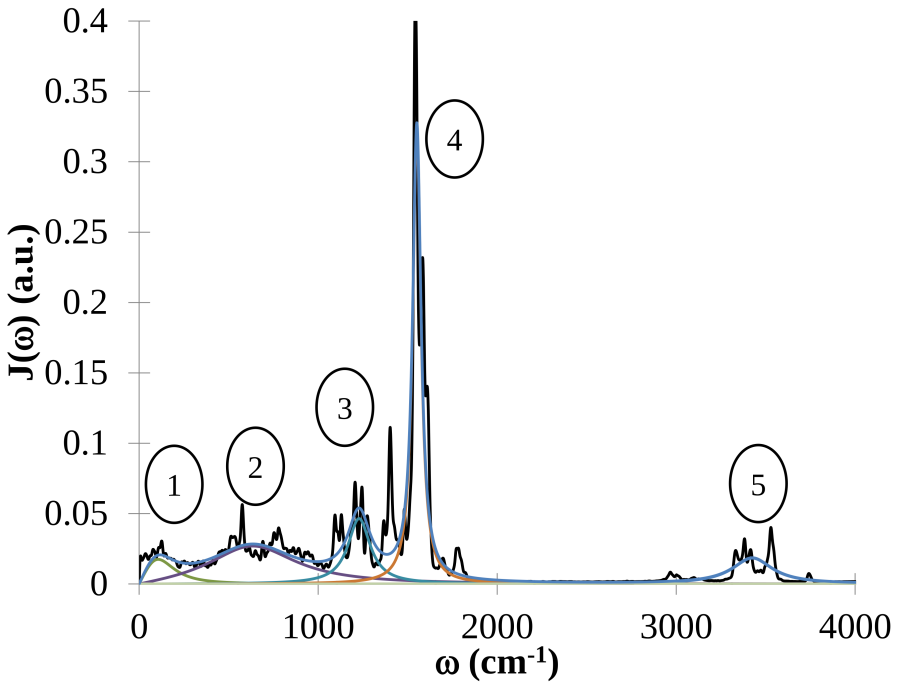
Electron transfers



	Time constant τ (ps)
Electron transfer	Experiment [1]
$W_{400} \rightarrow FAD$	0.4
$W_{377} \rightarrow W_{400}^{\cdot+}$	4 - 15
$W_{324} \rightarrow W_{377}^{\cdot+}$	30 - 50

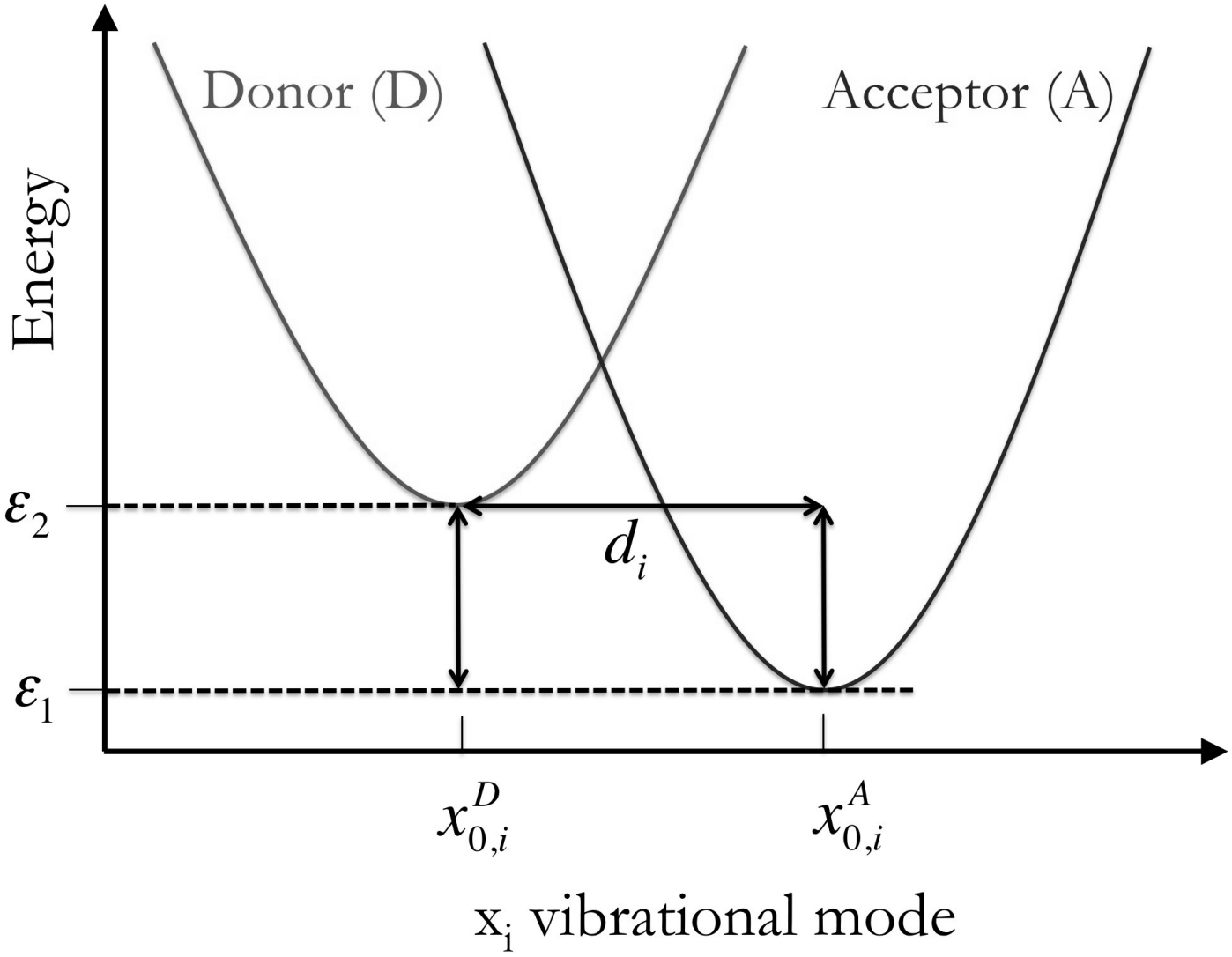
Difficulty to distinguish ET and vibrational cooling in the experiments

[1] Immeln *et al* JACS 134 (2012) 12536



CDFT QM/MM calculations 110 000 atom including 34 000 water molecules, 298.15 K

PCCP 12 (2016) 21442


Donor (D)
Acceptor (A)
Energy
ε_2
ε_1
d_i
$x^D_{0,i}$
$x^A_{0,i}$
x_i vibrational mode

A spin boson model Hamiltonian

$$\hat{H} = \hat{H}_S + \hat{H}_B + \hat{H}_{BS}$$

$$\hat{H}_S = \begin{bmatrix} \epsilon_1 & H_{12} \\ H_{12} & \epsilon_2 \end{bmatrix} = \epsilon_1 |D\rangle \langle D| + \epsilon_2 |A\rangle \langle A| + H_{12}(|D\rangle \langle A| + |A\rangle \langle D|)$$

$$\hat{H}_B = \sum_{i=1}^{N} \frac{\hbar w_i^D}{2} (\hat{p}_i^2 + \hat{x}_i^2) |D\rangle \langle D| + \sum_{i=1}^{N} \frac{\hbar w_i^A}{2} (\hat{p}_i^2 + \hat{x}_i^2) |A\rangle \langle A|$$

$$\hat{H}_{BS} = \sum_{i=1}^{N} k_i^D x_i |D\rangle \langle D| + \sum_{i=1}^{N} k_i^A x_i |A\rangle \langle A|$$

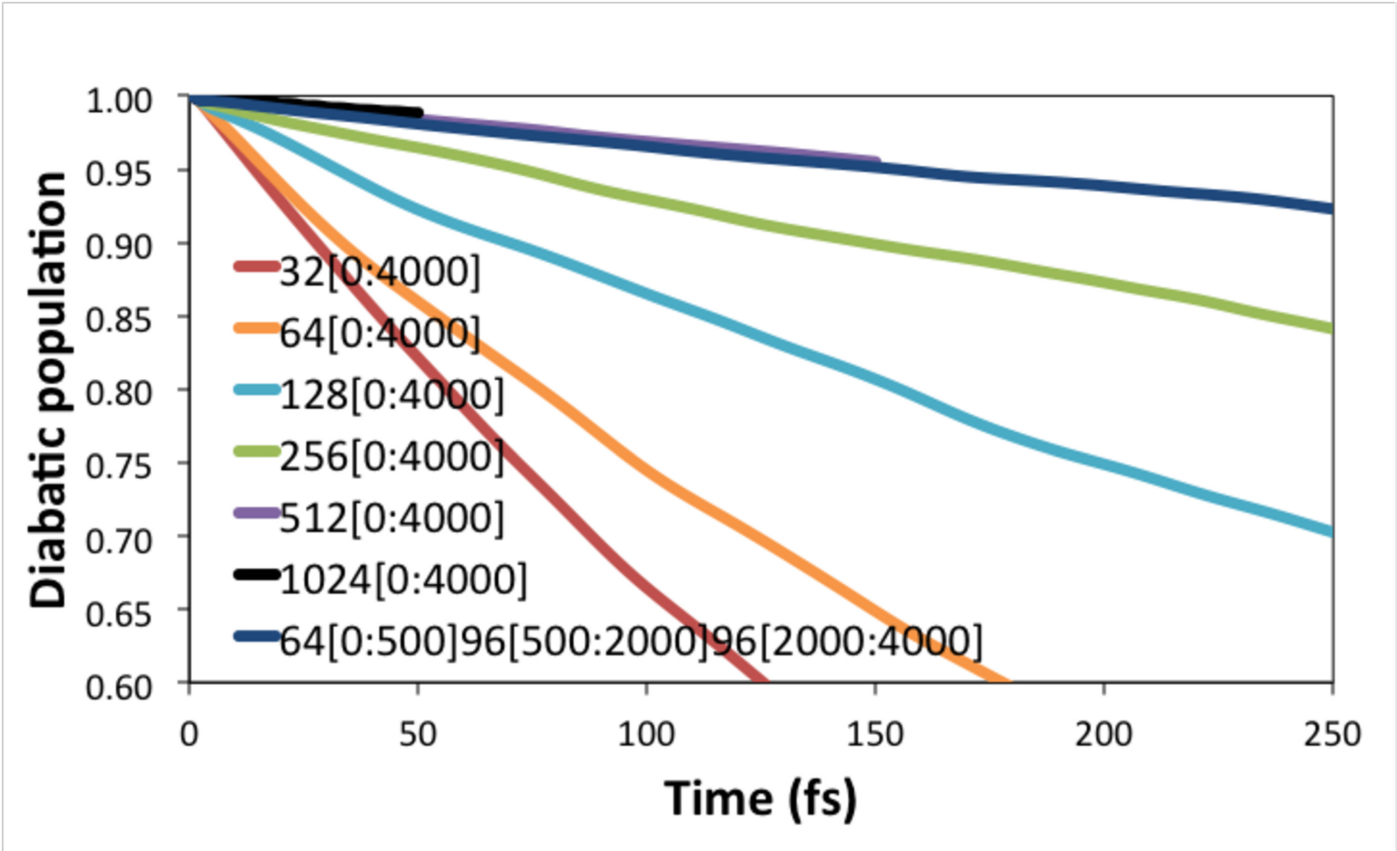
Initial condition

Difficulty to define the initial condition: two extreme cases
This initial state is thermalized

Slow bath relaxation:
Vertical instantaneous transition for the electronic degrees of freedom
Bath Centered on the ground state curve

Fast bath relaxation:
Bath relaxed onto the individual ET electronic state

Electron transfers



Experiment (ps)	Marcus Theory	HEOM	This work (fast)
4 - 15	4.97	0.82	3.3

HEOM : Hierarchical Equations of Motions

Fast and slow bath relaxations: in reality mixed scenario depending on the bath modes

Process seems to be dominated by low-frequency modes

Low-frequency modes partly linked to the molecules of water, which can relax fast

Full ab initio approach

The process strongly depends on the differences in the relaxation time-scale between electronic and nuclear (bath) degrees of freedom

Limits and problems

Necessity to have the potential and in the adapted form

Difficult for high accuracy (time-dependent)

Very slow processes: very difficult

Efficient: fast quantum process involving many eigenstates

Treatment of Fermionic and Bosonic systems

Acknowledgements

We would like to thank the following who contributed to this work:

- Z. Zhao, Z. Zhang, and D.-H. Zhang (Dalian, China).
- Hans-Dieter Meyer, Oriol Vendrell, Markus Schröder (Heidelberg Univ.).
- D. Lauvergnat (Orsay).

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