Methods of quantum dynamics and simulation of pump-probe spectra

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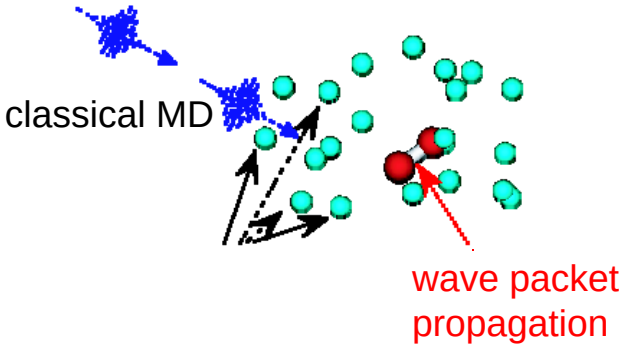
Methods of quantum dynamics and simulation of pump-probe spectra

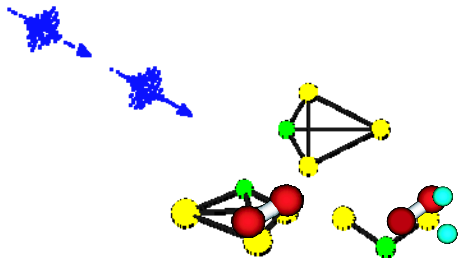
I. Introduction – Laser / molecule interaction
   -- electron / nuclei separation
   -- coupled channel equations
   -- simulation of pump probe spectra
   -- numerical implementation

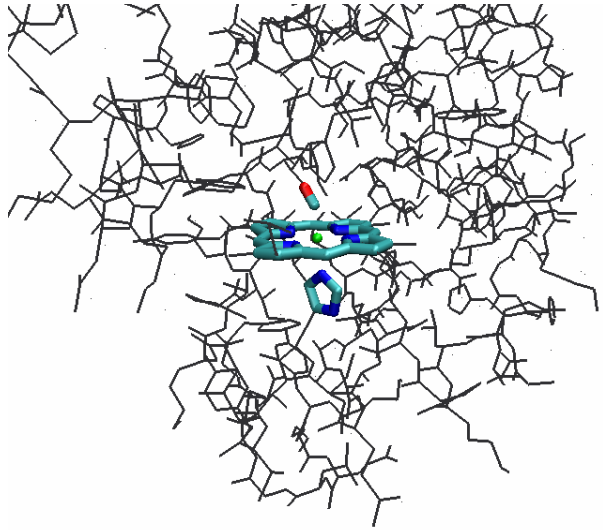
II. Methods of wave packet propagation
   -- standard methods: SOD, Crank-Nicholson, FFT-SO
   -- methods for high dimensional problems: TD-SCF, MCTDH

III. Outlook and further developments
   -- 6D quantum wp: vibrational predissociation of 4 atom complex
   -- Local control and within a mixed qu/classical propagation scheme

Context: Femtosecond laser interaction with atomic and molecular systems







dynamics subject to environments

dynamics of excited states

pulse shaped IR excitation

IVR, electronic / vibrational relaxation, predissociation...

experiment-----theory

Femtosecond spectroscopy in molecular systems

Aim: observation of elementary processes of chemical reactivity at the atomic scale in real time

We want to have access at:

- vibration, geometrical rearrangement
- breaking and formation of bonds
- isomerisation
- IVR
- transitions between electronic states: IC, ISC
- vibrational, electronic relaxation

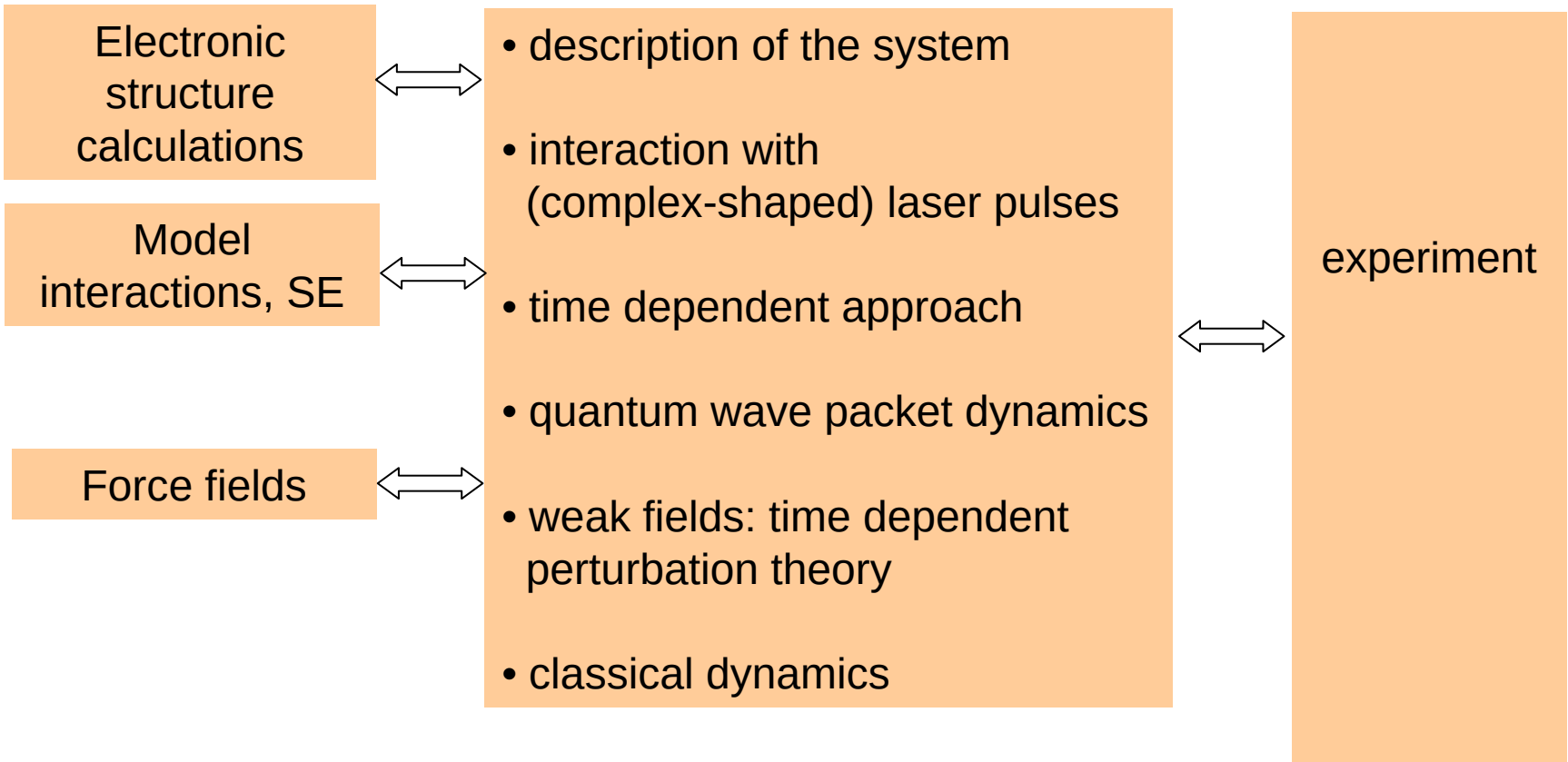
timescales:
femtosecond: 10^{-15} s
picosecond: 10^{-12} s

Principle of pump-probe experiments:

Two time-delayed ultrashort laser pulses

Pump pulse: triggers molecular dynamics
Probe pulse: probes quantum state at different delay times

Numerical simulatioins:



- system Hamiltonian:

$$H^{(s)} = \sum_n \frac{\mathbf{P}_n^{\,2}}{2m_n} + \sum_e \frac{\mathbf{P}_e^{\,2}}{2m_e} + V_c(\mathbf{r}_n, \mathbf{r}_e)$$

- dipole interaction Hamiltonian

$$H = H^{(s)} - \boldsymbol{\mu} \cdot \mathbf{E} \qquad \boldsymbol{\mu}(\mathbf{r}_n, \mathbf{r}_e) = \sum_\alpha q_\alpha \mathbf{r}_\alpha$$

- electronic/nuclear separation:

$$\left|\Psi(\mathbf{r}_n, \mathbf{r}_e, t)\right\rangle = \sum_i \chi_i(\mathbf{r}_n, t) \left|\varphi_i(\mathbf{r}_e; \mathbf{r}_n)\right\rangle$$

- electronic structure calculation ⇒

$$\begin{cases} H^{(e)} \left|\varphi_i(\mathbf{r}_e; \mathbf{r}_n)\right\rangle = V_i(\mathbf{r}_n) \left|\varphi_i(\mathbf{r}_e; \mathbf{r}_n)\right\rangle \\ \boldsymbol{\mu}_{ij} = \left\langle \varphi_i(\mathbf{r}_e; \mathbf{r}_n) \right| \boldsymbol{\mu} \left| \varphi_j(\mathbf{r}_e; \mathbf{r}_n) \right\rangle \end{cases}$$

$$i\left|\dot{\Psi}\right\rangle = \left(H^{(s)} - \boldsymbol{\mu} \cdot \mathbf{E}(t)\right)\left|\Psi\right\rangle$$

$$\sum_i i\dot{\chi}_i(\mathbf{r}_n, t) \left|\varphi_i(\mathbf{r}_e; \mathbf{r}_n)\right\rangle = H^{(s)} \sum_i \chi_i(\mathbf{r}_n, t) \left|\varphi_i(\mathbf{r}_e; \mathbf{r}_n)\right\rangle - \mathbf{E}(t)\boldsymbol{\mu} \sum_i \chi_i(\mathbf{r}_n, t) \left|\varphi_i(\mathbf{r}_e; \mathbf{r}_n)\right\rangle$$

also:

$$H^{(s)} = \sum_n \frac{\mathbf{P}_n^{\,2}}{2m_n} + \sum_e \frac{\mathbf{P}_e^{\,2}}{2m_e} + V_c(\mathbf{r}_n, \mathbf{r}_e) = \underbrace{-\sum_n \frac{1}{2m_n} \nabla_n^2}_{T_N} + H^{(e)}$$

$$i\dot{\chi}_j(\mathbf{r}_n, t) = -\sum_i \sum_n \frac{1}{2m_n} \left\langle \varphi_j(\mathbf{r}_e; \mathbf{r}_n) \right| \nabla_n^2 \; \chi_i(\mathbf{r}_n, t) \left| \varphi_i(\mathbf{r}_e; \mathbf{r}_n) \right\rangle + V_j(\mathbf{r}_n)\chi_j(\mathbf{r}_n, t) - \mathbf{E}(t) \sum_i \boldsymbol{\mu}_{ij} \; \chi_i(\mathbf{r}_n, t)$$

$$i\dot{\chi}_j(\mathbf{r}_n,t) = -\sum_i \sum_n \underbrace{\frac{1}{2m_n}\left\langle \varphi_j(\mathbf{r}_e;\mathbf{r}_n)\middle|\nabla_n^2\ \chi_i(\mathbf{r}_n,t)\middle|\varphi_i(\mathbf{r}_e;\mathbf{r}_n)\right\rangle}_{\left\langle \varphi_j(\mathbf{r}_e;\mathbf{r}_n)\middle|\varphi_i(\mathbf{r}_e;\mathbf{r}_n)\right\rangle = \delta_{ij}} + V_j(\mathbf{r}_n)\chi_i(\mathbf{r}_n,t) - \mathbf{E}(t)\sum_i \boldsymbol{\mu}_{ij}\ \chi_i(\mathbf{r}_n,t)$$

$$\left\langle \varphi_j(\mathbf{r}_e;\mathbf{r}_n)\middle|\varphi_i(\mathbf{r}_e;\mathbf{r}_n)\right\rangle \frac{1}{2m_n}\nabla_n^2\ \chi_i(\mathbf{r}_n,t) + \frac{1}{m_n}\left\langle \varphi_j(\mathbf{r}_e;\mathbf{r}_n)\middle|\nabla_n\varphi_i(\mathbf{r}_e;\mathbf{r}_n)\right\rangle \nabla_n\chi_i(\mathbf{r}_n,t)$$

$$+ \frac{1}{2m_n}\cancel{\left\langle \varphi_j(\mathbf{r}_e;\mathbf{r}_n)\middle|\nabla_n^2\varphi_i(\mathbf{r}_e;\mathbf{r}_n)\right\rangle \chi_i(\mathbf{r}_n,t)}$$

Properties of $\left\langle \varphi_j(\mathbf{r}_e;\mathbf{r}_n)\middle|\nabla_n\varphi_i(\mathbf{r}_e;\mathbf{r}_n)\right\rangle$ **:**

$$\nabla_n\left\langle \varphi_j(\mathbf{r}_e;\mathbf{r}_n)\middle|\varphi_i(\mathbf{r}_e;\mathbf{r}_n)\right\rangle = \left\langle \nabla_n\varphi_j(\mathbf{r}_e;\mathbf{r}_n)\middle|\varphi_i(\mathbf{r}_e;\mathbf{r}_n)\right\rangle + \left\langle \varphi_j(\mathbf{r}_e;\mathbf{r}_n)\middle|\nabla_n\varphi_i(\mathbf{r}_e;\mathbf{r}_n)\right\rangle = 0$$

$$= \left\langle \varphi_i(\mathbf{r}_e;\mathbf{r}_n)\middle|\nabla_n\varphi_j(\mathbf{r}_e;\mathbf{r}_n)\right\rangle + \left\langle \varphi_j(\mathbf{r}_e;\mathbf{r}_n)\middle|\nabla_n\varphi_i(\mathbf{r}_e;\mathbf{r}_n)\right\rangle = 0$$

$$\Rightarrow \left\langle \varphi_j(\mathbf{r}_e;\mathbf{r}_n)\middle|\nabla_n\varphi_i(\mathbf{r}_e;\mathbf{r}_n)\right\rangle = -\left\langle \varphi_i(\mathbf{r}_e;\mathbf{r}_n)\middle|\nabla_n\varphi_j(\mathbf{r}_e;\mathbf{r}_n)\right\rangle$$

and specifically : $\left\langle \varphi_i(\mathbf{r}_e;\mathbf{r}_n)\middle|\nabla_n\varphi_i(\mathbf{r}_e;\mathbf{r}_n)\right\rangle = 0$

$$i\dot{\chi}_j(\mathbf{r}_n,t) = \underbrace{\left(T_n + V_j(\mathbf{r}_n)\right)}_{\hat{H}_j}\chi_j(\mathbf{r}_n,t) + \sum_{i\neq j}\underbrace{\left(\sum_n \frac{1}{m_n}\left\langle \varphi_j(\mathbf{r}_e;\mathbf{r}_n)\middle|\nabla_n\varphi_i(\mathbf{r}_e;\mathbf{r}_n)\right\rangle \nabla_n\right)}_{V_{ij}^{(na)}}\chi_i(\mathbf{r}_n,t) - \mathbf{E}(t)\sum_i \boldsymbol{\mu}_{ij}\ \chi_i(\mathbf{r}_n,t)$$

non-adiabatic couplings

$$i\frac{\partial}{\partial t}\chi_j(\mathbf{r}_n,t)=\left(\hat{H}_j-\underbrace{\mathbf{E}(t)\boldsymbol{\mu}_{jj}}\right)\chi_j(\mathbf{r}_n,t)+\sum_{i\neq j}\left(\underbrace{V_{ij}^{(na)}}-\underbrace{\mathbf{E}(t)\boldsymbol{\mu}_{ij}}\right)\chi_i(\mathbf{r}_n,t)$$

Vibrational excitation, IR

non-adiabatic couplings

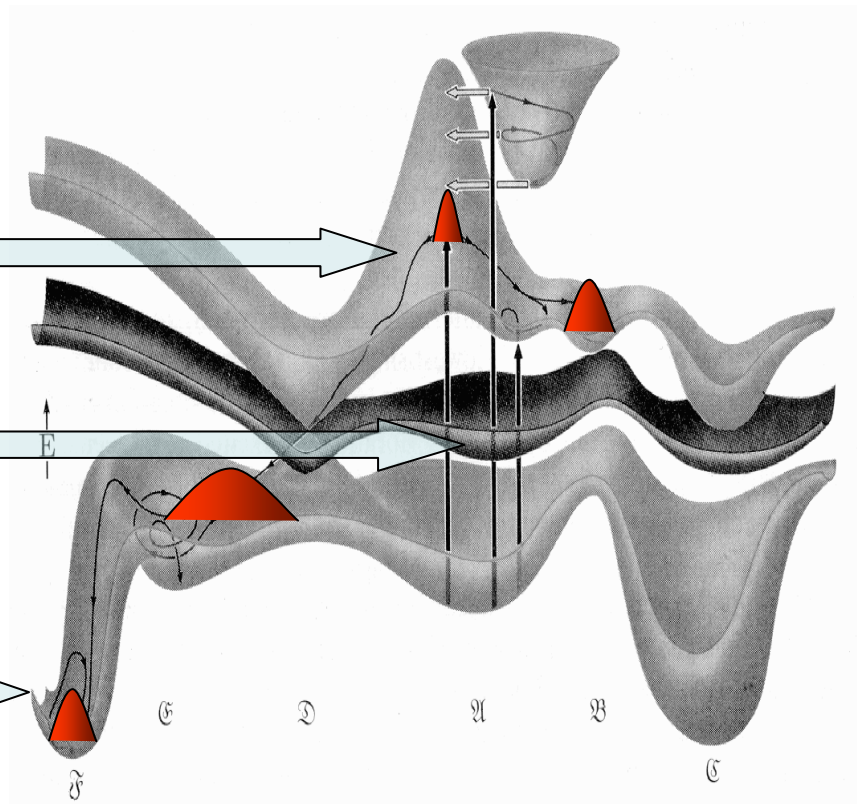
Electronic excitation vis-UV

⇩ ⇩ ⇩

Nuclear dynamics ion the electronic ground state

Non-radiative transition

Nuclear dynamics in excited states



reminder:

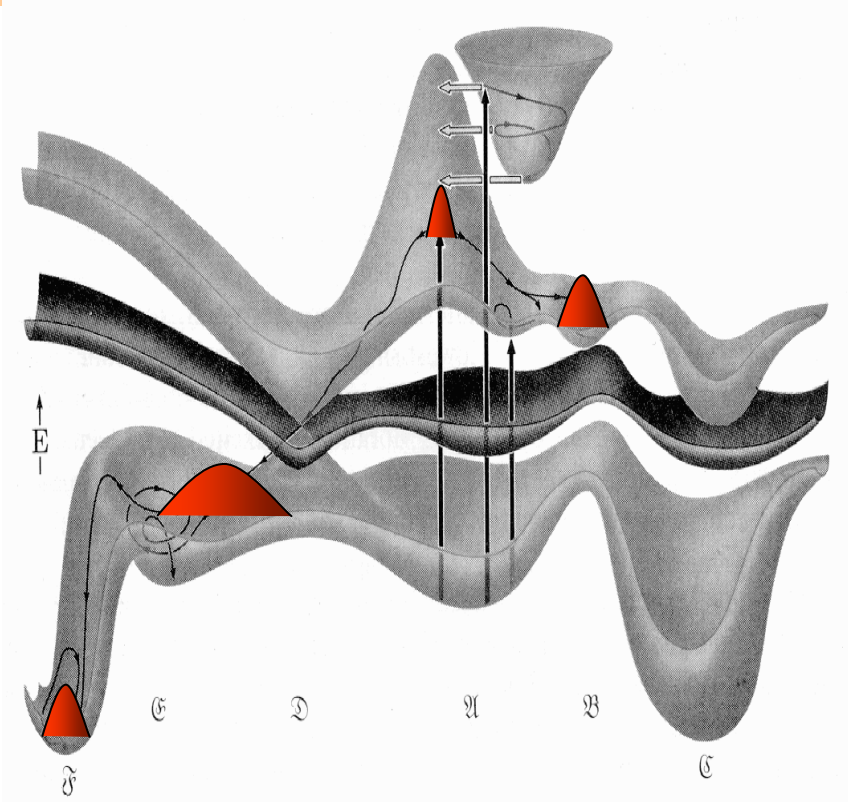
$\chi_j(\mathbf{r}_n,t)=$ **nuclear wave function on el. surface** $V_j(\mathbf{r}_n)$

Expression valid for high intensities

Nuclear dynamics ion the electroonic ground state

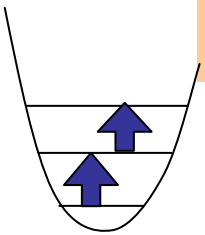
Non-radiative transition

Nuclear dynamics in excited states



- **Aim pump probe: choose two laser pulses with variable delay to study the combined electronic / nuclear dynamics**
- **Aim coherent control: choose (complex–shaped) laser pulses to induce a predifined dynamics (wrt a specific exit channel)**

$$i\frac{\partial}{\partial t}\chi_j(\mathbf{r}_n,t) = \left(\hat{H}_j - \underbrace{\mathbf{E}(t)\boldsymbol{\mu}_{jj}}_{\text{Vibrational excitation, IR}}\right)\chi_j(\mathbf{r}_n,t) + \sum_{i\neq j}\left(\underbrace{V_{ij}^{(na)}}_{\text{non-adiabatic couplings}} - \underbrace{\mathbf{E}(t)\boldsymbol{\mu}_{ij}}_{\text{Electronic excitation vis-UV}}\right)\chi_i(\mathbf{r}_n,t)$$

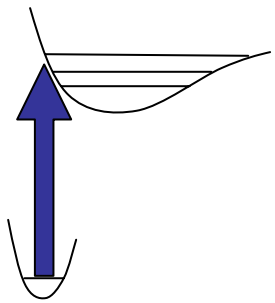


Nuclear dynamics in electronic ground state

$$i\partial_t\chi_g = \hat{H}_g\chi_g - \mathbf{E}\boldsymbol{\mu}_{gg}\chi_g$$

$$\chi_g(t) = Te^{-i\int_0^t(\hat{H}_g-\mathbf{E}\boldsymbol{\mu})dt'}\chi_g(0)$$

$$\chi_g(t+\delta t) = e^{-i(\hat{H}_g-\mathbf{E}\boldsymbol{\mu})\delta t}\chi_g(t)$$



Nuclear dynamics in electronically excited states

pert th..

$$i\partial_t\chi_g = \hat{H}_g\chi_g - \mathbf{E}\boldsymbol{\mu}_{ge}\chi_e$$

$$i\partial_t\chi_e = \hat{H}_e\chi_e - \mathbf{E}\boldsymbol{\mu}_{eg}\chi_g$$

$$\chi_e(t) = i\int_0^t e^{-i\hat{H}_e(t-t')}\left(\mathbf{E}\boldsymbol{\mu}_{eg}\right)e^{-i\hat{H}_g t'}\chi_g(0)\,dt'$$

$$\chi_e(t+\delta t) = e^{-i\hat{H}_e\delta t}\chi_e(t) + i\delta t\,\mathbf{E}\boldsymbol{\mu}_{eg}e^{-i\hat{H}_g\delta t}\chi_g(t)$$

In both cases:

$$\chi_i(t+\delta t) = e^{-i\hat{H}_i(t)\delta t}\chi_i(t)$$

"quantum propagator"

II. Methods of wave packet propagation

Methods of wave packet propagations have a wide range of applications, well beyond laser pulse interactions with atomic / molecular systems

e.g:

- **atomic and molecular physics:**
  [see also: D. J. Tannor, Introduction to Quantum Mechanics: A Time Dependent Perspective (University Science Press, Sausalito, 2006)]

  -- elastic / inelastic collisions, reactive scattering
  -- spectroscopy via correlation functions
  -- explicit time dependent perturbations, laser interactions, coherent control

- **Optics: Maxwell's equation**
- **....**

Example:

propagation of electromagnetic waves in nanostructures

$$\dot{\mathbf{D}} = c\nabla \times \mathbf{H} \qquad \mathbf{D} = \varepsilon \mathbf{E}$$

$$\dot{\mathbf{B}} = -c\nabla \times \mathbf{E} \qquad \mathbf{B} = \mu \mathbf{H}$$

$$\psi = \begin{pmatrix} \mathbf{E} \\ \mathbf{H} \end{pmatrix} \qquad H = \begin{pmatrix} 0 & i\frac{c}{\varepsilon}\nabla \times \\ -i\frac{c}{\mu}\nabla \times & 0 \end{pmatrix} \qquad i\dot{\psi} = H\psi$$

- can be scaled to be hermitian
- Can be formulated for dispersive media
- Application: light transmission through nanostructured apertures

[A. G. Borisov, S. V. Shabanov, J. Comp. Phys. 209 643 (2005)]

$$\chi_i(t+\delta t) = \underbrace{e^{-i\hat{H}_i(t)\delta t}}_{U_i(t)}\chi_i(t)$$

quantum propagator

$$\left[U_i^{(app)}\right]^{\dagger} U_i^{(app)} = 1$$

norm should be conserved

$$\left\langle \chi_e(t+\delta t) \middle| \chi_e(t+\delta t) \right\rangle = \left\langle U_i^{(app)}\chi_e(t) \middle| U_i^{(app)}\chi_e(t) \right\rangle = \left\langle \chi_e(t) \middle| \chi_e(t) \right\rangle$$

- propagation not exact, discretisation error, should always be converged for $\delta t \to 0$

- second order differening
- (implicit) Cayley
- Split-Operator
- short iterative Lanczos

- time-dependent self consistent field (TD-SCF)
- Multiconfiguration time dependent Hartree (MCTDH)

- Lanczos
- Chebycheff

Can also be used fore the propagation of density matrices

Second order differencing (SOD):

- derivation:

$$\chi(t+\Delta t) = \left(1 - i\hat{H}\Delta t\right)\chi(t)$$
$$\chi(t-\Delta t) = \left(1 + i\hat{H}\Delta t\right)\chi(t)$$
$$\chi(t+\Delta t) - \chi(t-\Delta t) = -2i\hat{H}\Delta t\chi(t)$$

- method:

$$\chi(t+\Delta t) = \chi(t-\Delta t) - 2iH\Delta t\chi(t)$$

- characteristics:

-- storage: $\chi(t), \chi(t-\Delta t)$

-- operations: $\hat{H}\chi(t)$

-- stablility: $\Delta t < {}^{1}\!/_{E_{\max}}$

Cayley (Crank-Nicholson) :

- derivation:

$$e^{i\frac{\Delta t}{2}\hat{H}}\chi(t+\Delta t) = e^{-i\frac{\Delta t}{2}\hat{H}}\chi(t)$$

$$\left(1+i\hat{H}\,\tfrac{\Delta t}{2}\right)\chi(t+\Delta t) = \left(1-i\hat{H}\,\tfrac{\Delta t}{2}\right)\chi(t)$$

$$\chi(t+\Delta t) = \underbrace{\left(1+i\hat{H}\,\tfrac{\Delta t}{2}\right)^{-1}}\left(1-i\hat{H}\,\tfrac{\Delta t}{2}\right)\chi(t)$$

problem: inversion

$$\chi(t+\Delta t) - \chi(t) = -i\Delta t\hat{H}\left(\tfrac{\chi(t+\Delta t)+\chi(t)}{2}\right)$$

- method:

$$\chi(t+\Delta t) = \chi(t) + \xi$$

$$\xi = -i\tfrac{\Delta t}{2}\hat{H}\left(\xi + 2\chi(t)\right)$$

- characteristics:

-- storage: $\chi(t), \xi$

-- operations: $\hat{H}\chi(t)$

-- norm-conserving

-- symetric wrt. $\Delta t \to -\Delta t$

FFT-Split Operator (FFT-SO) :

- derivation: $\hat{H} = T(\frac{\partial}{\partial \mathbf{r}_n}) + V(\mathbf{r}_n)$

$$\chi(t+\Delta t) = e^{-i\Delta t\hat{H}}\chi(t) \approx e^{-i\frac{\Delta t}{2}V} e^{-i\Delta t T} e^{-i\frac{\Delta t}{2}V}\chi(t)$$

- Fourier representation:

$$\chi(t+\Delta t) = \underbrace{e^{-i\frac{\Delta t}{2}V(r_n)}}_{e^{-i\frac{\Delta t}{2}V}} \underbrace{\sum_{j=0}^{N-1}\frac{1}{\sqrt{N}} e^{2\pi i\left(\frac{jn}{N}\right)}}_{FFT^{-1}} \underbrace{e^{-i\Delta t\left(\frac{\hbar^2}{2m}k_j^2\right)}}_{e^{-i\Delta t T}} \underbrace{\left(\sum_{n'=0}^{N-1}\frac{1}{\sqrt{N}} e^{2\pi i\left(\frac{jn'}{N}\right)} e^{-i\frac{\Delta t}{2}V(r_n)}\chi(t)\right)}_{FFT}$$

- method:

$$\chi(t+\Delta t) = e^{-i\frac{\Delta t}{2}V} \xleftarrow{FFT^{-1}} e^{-i\Delta t T} \xleftarrow{FFT} e^{-i\frac{\Delta t}{2}V}\chi(t)$$

- characteristics:

  -- storage: χ

  -- operations: multiplications, FFT, no $\hat{H}\chi$!

  -- stable, norm-conserving

  -- symetric wrt $\Delta t \rightarrow -\Delta t$

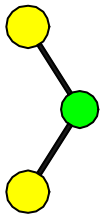
[M. D. Feit, J. A. Fleck, A. Steiger, J. Comput. Phys. 47, 412 (1982)]

Overview / comparison:

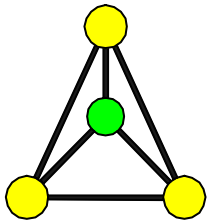
	avantages	désavantages
SOD	• flexible: any representation • H time dependent	• small timestep
Crank-Nicolson (implicit)	• flexible: any representation • H time dependent • unitary	• iteration at every timestep
FFT-SO	• FFT: efficient • no matrix-vector multiplication • H time dependent • unitary	• equidistant grids • *H* : no cross-terms

Quantum wave packet for high-dimensional problems:

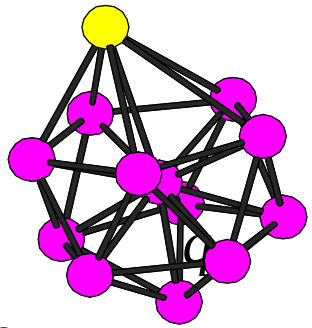
- N particles, 3N-6 internal DoF, (10 points/basis fcts per DoF)
- calculation of spectrum / dynamics
- exponential scaling



N=3
16 Mb
CPU time: 1sec



N=4
16000Gb
CPU time:10 days



N~10
~10^{40} Gb
CPU time: ~10^{20} years

→ Approximations

- approximate dynamics: TD-SCF, MCTDH
- dynamics in reduced dimensionality
- symmetry, periodicity
- harmonic approximation
- classical mechanics (trajectoires)
- mixed quantum/classical dynamics

consider 2 DoF for the presentation of the basic idea, but the usefulness lies in the extension to many DoF

- TD-SCF: suppose wf can be described by a product

$$\chi(x,y,t) = a(t)\,\phi^{(x)}(x,t)\,\phi^{(y)}(y,t)$$

- Rem: this decomposition is not unique !
  → constraints

$$\left\langle \dot{\phi}^{(x)} \middle| \phi^{(x)} \right\rangle = \left\langle \dot{\phi}^{(y)} \middle| \phi^{(y)} \right\rangle = 0$$

- Schrödinger equation becomes:

$$i\dot{a}(t) = \overline{H}a(t)$$
$$i\dot{\phi}^{(x)}(x,t) = \left(H^{(x)} - \overline{H}\right)\phi^{(x)}(x,t)$$
$$i\dot{\phi}^{(y)}(y,t) = \left(H^{(y)} - \overline{H}\right)\phi^{(y)}(y,t)$$

- Schrödinger eq. in 2D is replaced by 2 coupled 1D equations
- Dynamics in one DoF is determined by the dynamic mean field over the other DoF
- even if H is time independent, $H^{(x)}$ and $H^{(y)}$ are time-dependent !

$$\overline{H} = \left\langle \phi^{(x)} \middle| \left\langle \phi^{(y)} \middle| H \middle| \phi^{(x)} \right\rangle \middle| \phi^{(y)} \right\rangle$$
$$H^{(x)} = \left\langle \phi^{(y)} \middle| H \middle| \phi^{(y)} \right\rangle$$
$$H^{(y)} = \left\langle \phi^{(x)} \middle| H \middle| \phi^{(x)} \right\rangle$$

- can be used for up to ~100 DoF !

Other formulations exist

- **disavantage**: approximate, error hard to estimate

consider 2 DoF for the presentation of the basic idea, but the usefulness lies in the extension to many DoF

- MCTDH: multi-configurational expansion of the wavefunction

$$\chi(x,y,t) = \sum_{n=1}^{N}\sum_{m=1}^{M} a_{nm}(t)\,\phi_n^{(x)}(x,t)\,\phi_m^{(y)}(y,t)$$

Rem: this is not unique !
→ constraints

$$\left\langle \phi_n^{(x)} \middle| \phi_{n'}^{(x)} \right\rangle = \delta_{nn'} \qquad \left\langle \phi_m^{(y)} \middle| \phi_{m'}^{(y)} \right\rangle = \delta_{mm'}$$

- Schrödinger equation becomes:
  -- coupled equations for the $a_{nm}(t), \phi_n^{(x)}(x,t), \phi_m^{(y)}(y,t)$
  -- for $N \to \infty$ and $M \to \infty$, $\phi_n^{(x)}(x,t), \phi_m^{(y)}(y,t)$ become complete:
  → MCDTH becomes an exact standard method
  → $\phi_n^{(x)}(x,t), \phi_m^{(y)}(y,t)$ become time independent

- flexible, any representation is possible, different representations for different DoF possible
- gain in storage requirements: for N_b and M_b basis fcts/grid points
  N* N_b+M* M_b + N*M vs. N_b*M_b
  generally: $N \ll N_b$ $M \ll M_b$,

U. Manthe, H.-D. Meyer, L. S. Cederbaum, J. Chem. Phys. 97, 3199 (1992);
H.-D. Meyer, U. Manthe, L.S. Cederbaum, Chem. Phys. Letters 165, 73 (1990).

consider 2 DoF for the presentation of the basic idea, but the usefulness lies in the extension to many DoF

- MCTDH: multi-configurational expansion of the wavefunction

$$\chi(x,y,t) = \sum_{n=1}^{N}\sum_{m=1}^{M} a_{nm}(t)\,\phi_n^{(x)}(x,t)\,\phi_m^{(y)}(y,t)$$

Rem: this is not unique !
→ constraints

$$\left\langle \dot{\phi}_n^{(x)} \middle| \phi_{n'}^{(x)} \right\rangle = \delta_{nn'} \qquad \left\langle \dot{\phi}_m^{(y)} \middle| \phi_{m'}^{(y)} \right\rangle = \delta_{mm'}$$

- Schrödinger becomes:

$$i\dot{a}_{n'm'}(t) = \sum_{n=1}^{N}\sum_{m=1}^{M} \overline{H}_{n'nm'm}\, a_{nm}(t)$$

$$i\sum_{n=1}^{N} \rho_{n'n}^{(x)} \left| \dot{\phi}_n^{(x)} \right\rangle = \left(1 - P^{(x)}\right) \sum_{n=1}^{N} H_{n,n'}^{(x)} \left| \phi_n^{(x)} \right\rangle$$

$$i\sum_{m=1}^{m} \rho_{m'm}^{(y)} \left| \dot{\phi}_m^{(y)} \right\rangle = \left(1 - P^{(y)}\right) \sum_{m=1}^{M} H_{m,m'}^{(y)} \left| \phi_m^{(y)} \right\rangle$$

$$\overline{H}_{n'nm'm} = \sum_{n=1}^{N}\sum_{m=1}^{M} \left\langle \phi_{n'}^{(x)} \middle| \left\langle \phi_{m'}^{(y)} \middle| H \middle| \phi_m^{(y)} \right\rangle \middle| \phi_n^{(x)} \right\rangle$$

$$P^{(x)} = \sum_{n=1}^{N} \left| \phi_n^{(x)} \right\rangle \left\langle \phi_n^{(x)} \right| \qquad \rho_{nn'}^{(x)} = \sum_{m=1}^{M} a_{n'm}^{*} a_{nm} \qquad H_{n'n}^{(x)} = \sum_{m=1}^{M}\sum_{m'=1}^{M} a_{n'm'}^{*} a_{nm} \left\langle \phi_{m'}^{(y)} \middle| H \middle| \phi_m^{(y)} \right\rangle$$

$$P^{(y)} = \sum_{m=1}^{M} \left| \phi_m^{(y)} \right\rangle \left\langle \phi_m^{(y)} \right| \qquad \rho_{mm'}^{(y)} = \sum_{n=1}^{N} a_{nm}^{*} a_{nm'} \qquad H_{m'm}^{(y)} = \sum_{n=1}^{N}\sum_{n'=1}^{N} a_{n'm'}^{*} a_{nm} \left\langle \phi_{n'}^{(x)} \middle| H \middle| \phi_n^{(x)} \right\rangle$$

- quantum wave packet methods
- errors: representation errors, errors in the calculation of the propagator
- avantages / disadvantages
- feasible for moderate number of DoF: 1-3
- for more than 3 DoF: MCTDH, else: → approximations

References:

Méthodes de propagation de paquets d'ondes:

C. Cerjan, N umerical Grid methods and their application to the Schrödinger equation, Kluwer, 1993.
C. Leforestier, R. H. Bisseling, C. Cerjan, M. D. Feit, R. Friesner, A. Guldberg, A. Hammerich, G.Jolicard, W. Karrlein, H.-D. Meyer, N. Lipkin, O. Roncero, R. Kosloff J. Comp. Phys. 94, 59 (1991)
R. Kosloff, J. Chem. Phys. 92, 2087 (1988)

Multiconfiguration time-dependent Hartree:

M. H. Beck, A. Jäckle, G. A. Worth, H.-D. Meyer, Phys. Reports, 324, 1 (2000);
U. Manthe, H.-D. Meyer, L. S. Cederbaum, J. Chem. Phys. 97, 3199 (1992);
H.-D. Meyer, U. Manthe, L.S. Cederbaum, Chem. Phys. Letters 165, 73 (1990).

III. Outlook + future developments

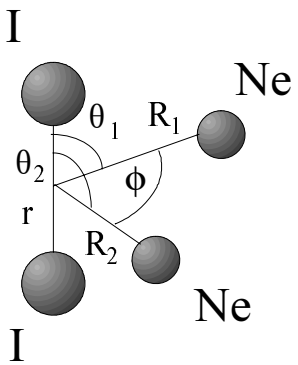
→ **Dynamical processes of more complex systems**

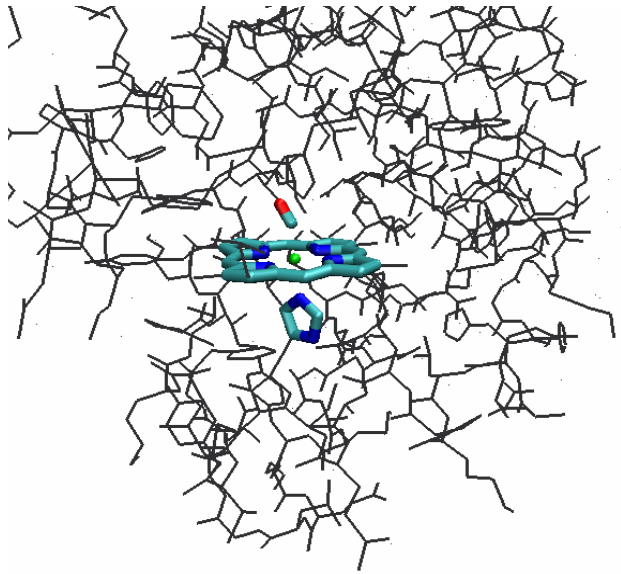
-- More degrees of freedom

-- Non-isolated systems (effects of environment, decoherence…)

→ **Control by complex shaped laser pulses, spectral regions IR, UV,XUV**

→ **Higher intensity**



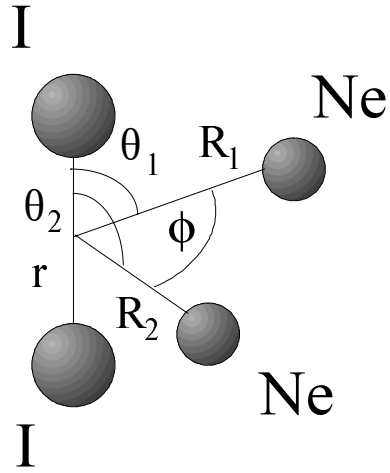


pulse shaped IR excitation Hb-CO

Vi

Local control scheme
Mixed qu/cl dynamics

Exemple: vibrational predissociation of I_2Ne_2



- model system to study the sovlant-solute interactions
- weak van der Waals interaction:

Challenges:

- zero-point energy effects important
- 1 quantum of vibration of I_2 is enough to dissociate one
- strongly correlated dynamics of the two Ne atoms

Quantum treatment in `full dimensionality'

- reference calculation for approximate schemes
- processus studied:

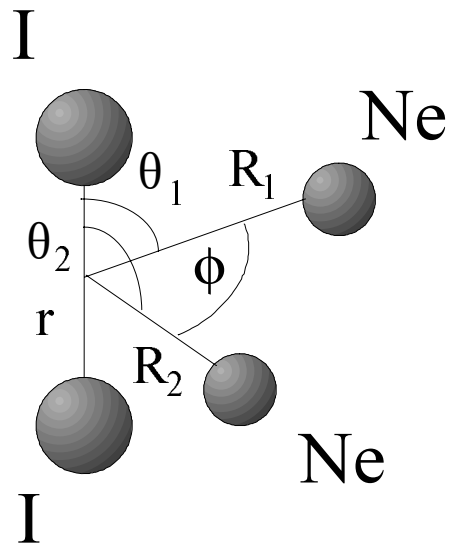
  vibrational predissociation of : $I_2(B,n=21)Ne_2 \rightarrow I_2(B,n=20)Ne + Ne$

  $\rightarrow I_2(B,n=19)Ne + Ne$

[C. Meier, U. Manthe, J. Chem. Phys. 115, 5477 (2001)]

Satellite coordonnées (non-orthogonal):

r	distance I-I
R_1, R_2	(centre of mass I_2)-Ne
θ_1, θ_2	angle ($r, R_{1,2}$)
ϕ	angle between the I-I-Ne planes



$$H(r,R_1,R_2,\theta_1,\theta_2,\phi) = -\frac{1}{2\mu_{I_2}}\left(\frac{1}{r}\frac{\partial^2}{\partial r^2}r\right) + \sum_{i=1,2} -\frac{1}{2\mu_i}\left(\frac{1}{R_i}\frac{\partial^2}{\partial {R_i}^2}R_i\right) + \left(\frac{1}{2\mu_{I_2}r^2} + \frac{1}{2\mu_i {R_i}^2}\right)\left(\frac{1}{\sin\theta_i}\frac{\partial}{\partial\theta_i}\sin\theta_i + \frac{1}{\sin^2\theta_i}\frac{\partial^2}{\partial\phi^2}\right)$$

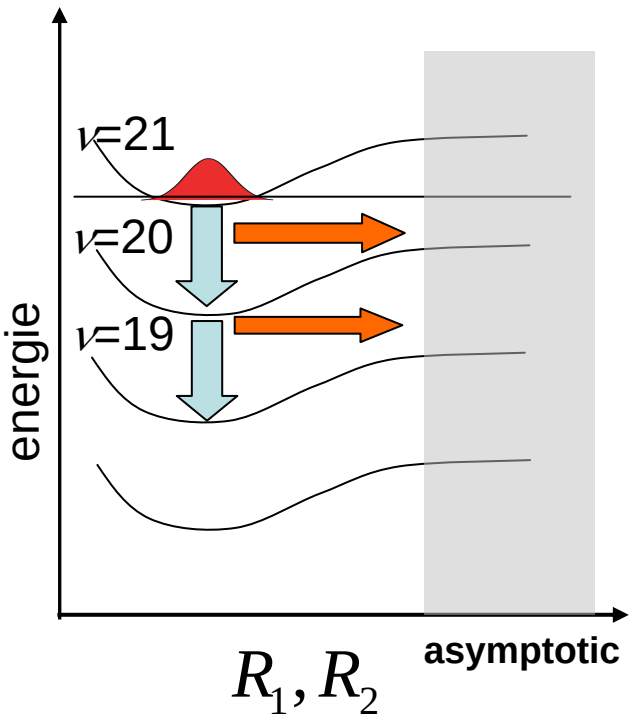
$$+ \sum_{\gamma,\lambda=R_1,R_2,\theta_1,\theta_2,\phi} C_{\gamma\lambda}\frac{\partial^2}{\partial\gamma\partial\lambda} + V(r,R_1,R_2,\theta_1,\theta_2,\phi)$$

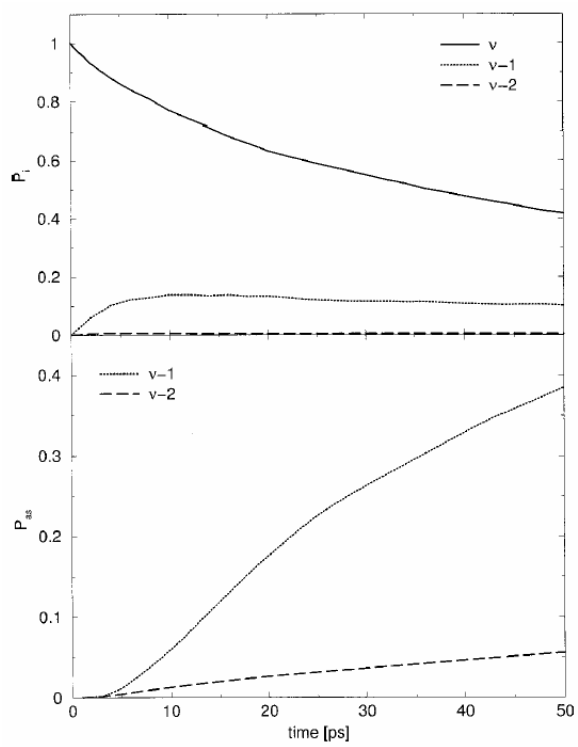
wave packet propagation using the MCTDH scheme in 6 D

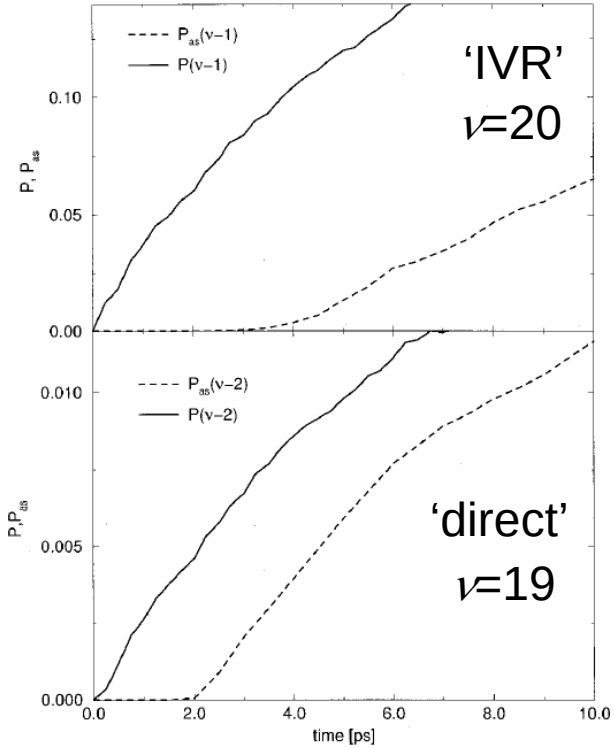
$$\psi(r,R_1,R_2,\theta_1,\theta_2,\phi,t) =$$
$$\sum_{n_1=1}^{N_1}\cdots\sum_{n_6=1}^{N_6} a_{n_1\cdots n_6}\ \chi_{n_1}^{(1)}(r,t)\ \chi_{n_2}^{(2)}(R_1,t)\ \chi_{n_3}^{(3)}(R_2,t)\ \chi_{n_4}^{(4)}(\theta_1,t)\ \chi_{n_5}^{(5)}(\theta_2,t)\ \chi_{n_6}^{(6)}(\phi,t)$$

coordinate	N_i (SPF)	nbr. of basis fct.	representation
r	5	49	fct. propres de I_2
R_1	20	384	FFT
R_2	20	384	FFT
θ_1	4	80	Legendre DVR
θ_2	4	80	Legendre DVR
ϕ	6	192	FFT

number of configurations: 192000
Hamiltonian matrix in standard method: ~10^{13} x 10^{13}





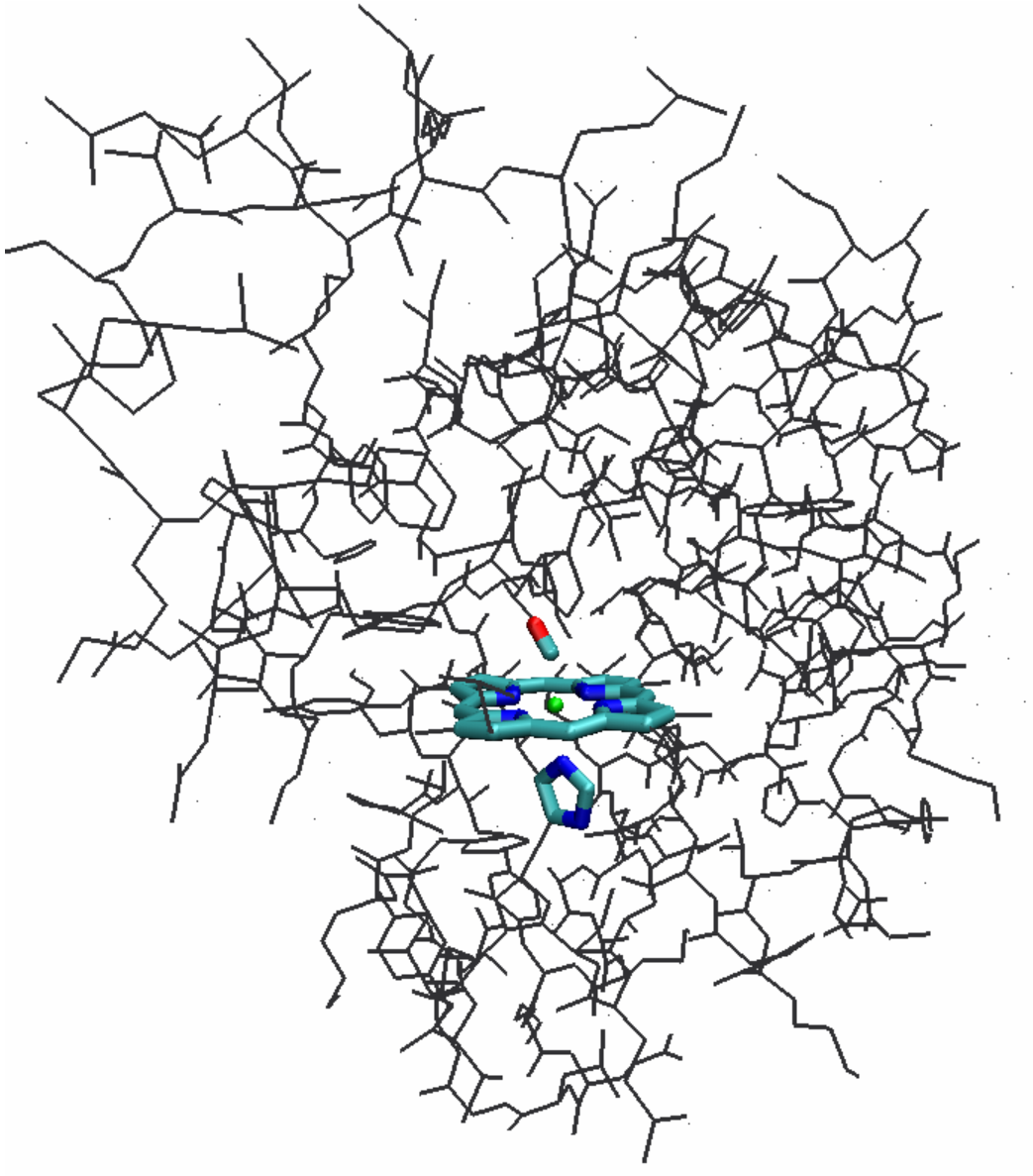


- life time of the resonance: I_2(B,n=21)Ne_2 : ~55 ps

  process: I_2(B,ν=21) Ne_2→ I_2(B, ν=20) Ne + Ne: IVR
  process: I_2(B,ν=21) Ne_2→ I_2(B,ν=19) Ne + Ne: direct

- dynamical process requires QM and full dimensionality !

Exemple: Multiphoton IR excitation of HbCO with shaped pulses



Why ?

- CO vibration as local probe of protein environment
- studies of vibrational relaxation: relaxation pathways – flow of energy
- inducing conformal changes ? “ground state chemistry”

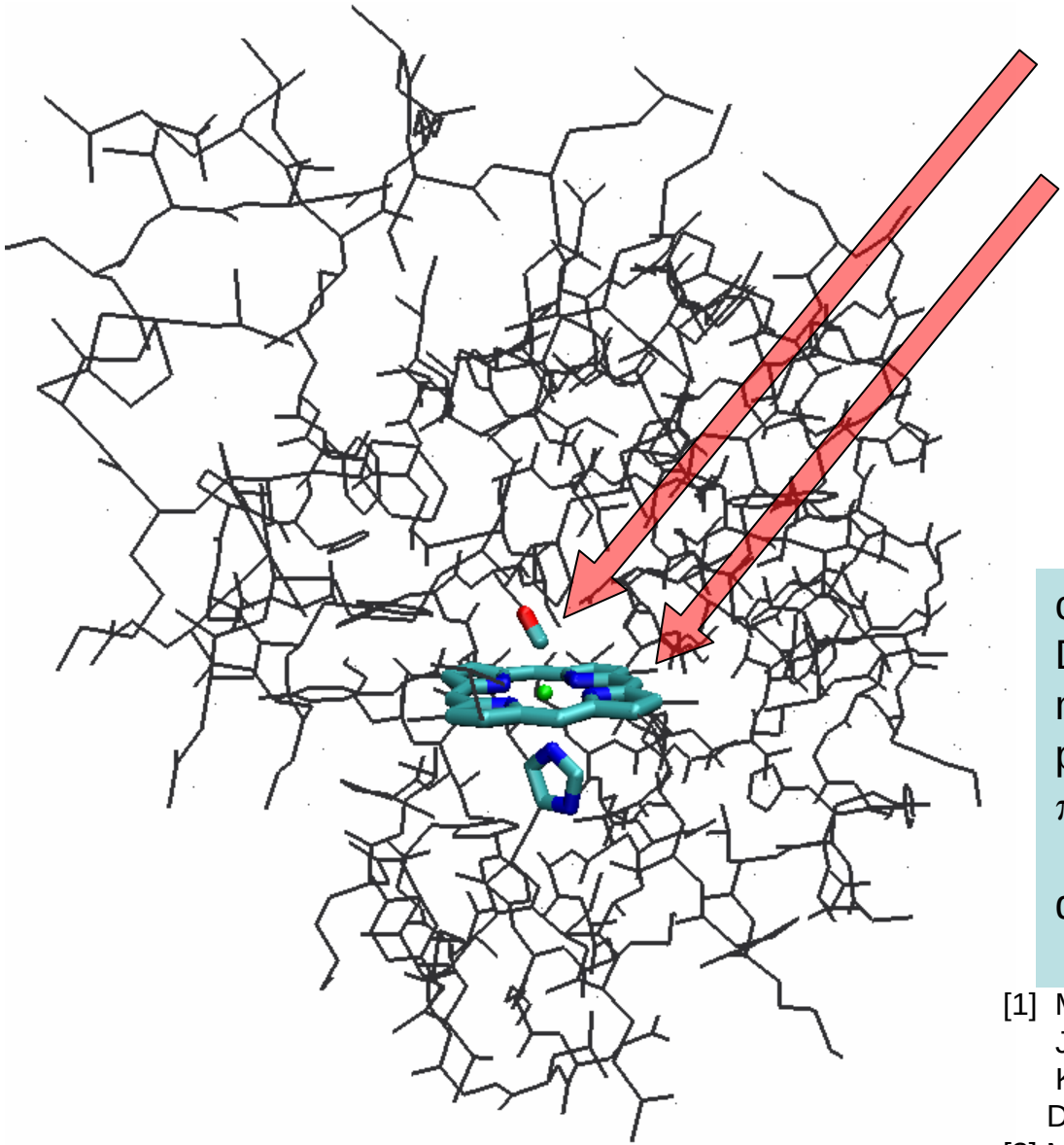
aim:

- depositing as much energy in the CO-stretch as possible :

➔ conformal changes ?
➔ ground state dissociation ?
➔ energy relaxation pathways

- exciting single vibrational states or coherent superpositions of states

➔ subsequent measures of state resolved relaxation times, decoherence: sensitive measure of environment / protein dynamics



anharmonic quantum oscillator CO

heme complex ~30 atoms
FeP(Im)-CO

sub-unit of protein ~2200 atoms
model: [1]

[future work: full protein, solvation]

CO FeP(Im) protein

close environment:
DFT (B3LYP)
metal-ligand
properties
π-backbonding [2]

dipole moment

protein:
Charmm

modifies FeP
entity

creates fluct.
electric fields

[1] M. D. Fayer, Annu. Rev. Phys. Chem, **52**, (2001)
J.R. Hill et al. J. Phys. Chem. **98**, 11213 (1996),
K. A. Merchant et al, JACS, **125**, 13804 (2003)
D.E. Sagnella, J.E Straub, Biophys. J. 77, 70 (1999)
[2] M. C. Heitz, C. M., J. Chem. Phys. **123**, 044504 (2005)

Mixed quantum-classical dynamics

quantum: $\psi(q,t)$

Schrödinger equation

q : CO stretch within FeP(Im)-CO complex

$$i\frac{\partial}{\partial t}\psi(q,t) = \left(-\frac{1}{2}\frac{\partial^2}{\partial q^2} + V(q,\mathbf{r}_1\cdots\mathbf{r}_N) + \vec{\mu}(q,\mathbf{r}_1\cdots\mathbf{r}_N)(\vec{E}_{prot}(t)+\vec{E}(t))\right)\psi(q,t)$$

$$\approx H_0(q) + H_f(q,\mathbf{r}_1\cdots\mathbf{r}_N) + \vec{\mu}(q,\mathbf{r}_1\cdots\mathbf{r}_N)\vec{E}(t)$$

classical: $\mathbf{r}_i(t)$

Newtons equations

$$\ddot{\mathbf{r}}_i(t) = -\frac{1}{m_i}\nabla_{\mathbf{r}_i} V(\bar{q},\mathbf{r}_1\cdots\mathbf{r}_N)$$

no back-reaction:
force is evaluated at CO equilibrium position $\bar{q}$

[include backreaction ➔ future]

➔2 step simulation: 1. Charmm with CO fixed
2. multiple quantum wave packet calculations
with **fluctuations in potential + dipole orientation**

Observables, density matrices and Local control

multiple WP propagations with different H_f ➔ $\psi_i(q,t)$

density matrix ➔ $\rho = \frac{1}{N}\sum_{i=1}^{N} |\psi_i\rangle\langle\psi_i|$

observables ➔ $A = tr(A\rho) = \frac{1}{N}\sum_{i=1}^{N}\langle\psi_i|A|\psi_i\rangle$

local control for $A = H_0$ ➔ $\frac{d\langle H_0\rangle}{dt} = tr([H, H_0]\rho)$

$$\approx E(t)\, i\, \frac{1}{N}\sum_{i=1}^{N}\cos\theta_i(t)\langle\psi_i(t)|[\mu, H_0]|\psi_i(t)\rangle$$

If one chooses: ➔

$$E(t) \approx -i\ f(t)\, \frac{1}{N}\sum_{i=1}^{N}\cos\theta_i(t)\langle\psi_i(t)|[\mu, H_0]|\psi_i(t)\rangle$$

then we have: ➔ $\frac{d\langle H_0\rangle}{dt} \geq 0$

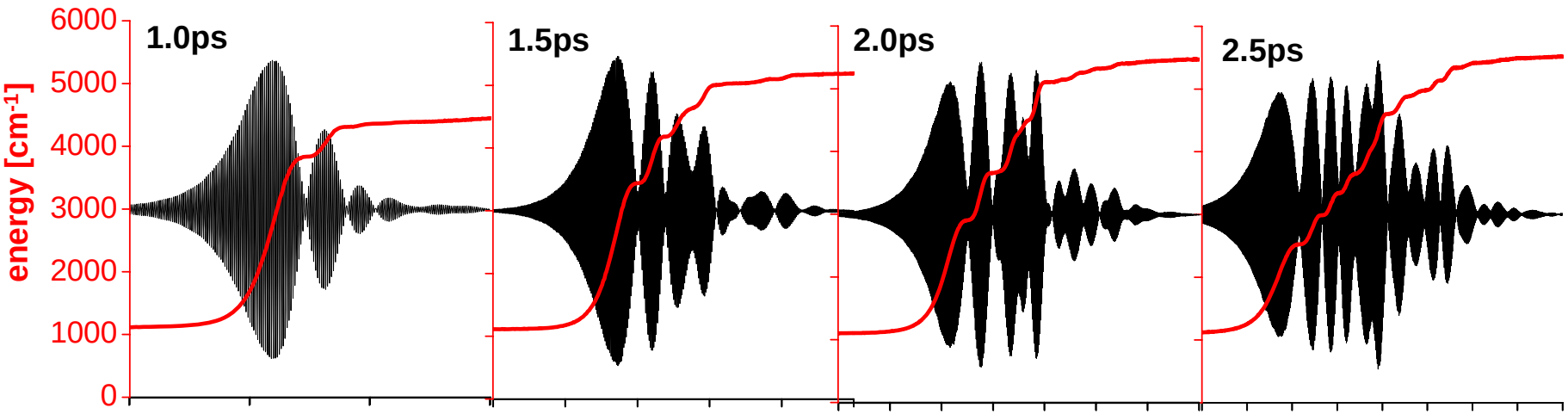
External field ensures heating of specific mode: Local control scheme within Q/C

[1] R. Kosloff, S. A. Rice, P. Gaspard, S. Tersigni, D. Tannor Chem. Phys. **139**, 201 (1989)
M. Sugawara Y. Fujimura, J. Chem. Phys. **100**, 5646 (1994)
P. Gross, H. Singh, H. Rabitz, K. Mease, G. M. Huang, Phys. Rev A. **47**, 4593 (1993),
and lots more...

• simulations: 1000 mixed qu/classical runs for isotropically oriented sample

$$E(t) \approx \pm i\ f(t)\ \frac{1}{N}\sum_{i=1}^{N}\cos\theta_i \left\langle \psi_i(t)\right| \left[\mu, H_0\right] \left|\psi_i(t)\right\rangle$$

$f(t)$ chosen to ensure pulse lengths of: 1ps, 1.5 ps, 2ps, 2.5 ps
and constant intensity: 1 μJ @ 40 μm
(parameters of IR pulse shape experiments of M. Joffre, LOB, Paris [1])



• Wigner plots of LCT pulses
• comparison with ➔ non-fluctuating system, isotropic

[1] C. Ventalon et al, PNAS, **101**, 13216 (2004)

• future + + :

-- development of mixed quantum / classical approaches

-- application to realistic systems

-- control in dissipative environments

-- combination of MCTDH and classical mechanics

• funding: ANR French ministry: → post doc position