Adiabatic and nonadiabatic molecular dynamics with multireference ab initio methods

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Outline

First Lecture: An introduction to molecular dynamics
1. Dynamics, why?
2. Overview of the available approaches

Second Lecture: Towards an implementation of surface hopping dynamics
1. Practical aspects to be addressed
2. The NEWTON-X program
3. Some applications: theory and experiment
Part II
Towards an implementation of surface hopping dynamics
Practical aspects to be addressed
Initial conditions

\[ P_{W}^{(0)}(R, P) = \frac{1}{\pi \hbar} \exp \left[ -2\alpha (R - R_e)^2 \right] \exp \left[ -\frac{P^2}{2\alpha \hbar} \right] \]

\[ \alpha = \frac{m \omega_{HO}}{2} \]

E

 accept
don’t accept

Wigner distribution

\[ E_0 \pm \Delta E \]
Any standard method can be used in the integration of the Newton equations.

A good one is the **Velocity Verlet** (Swope et al. JCP 76, 637 (1982)):

For each nucleus $I$

$$ R_I(t + \Delta t) = R_I(t) + v_I(t)\Delta t + \frac{1}{2}a_I(t)\Delta t^2 $$

$$ v_I\left(t + \frac{\Delta t}{2}\right) = v_I(t) + \frac{1}{2}a_I(t)\Delta t $$

$$ a_I(t) = -\frac{1}{M_I} \nabla_R E[R_I(t + \Delta t)] $$

$$ v_I(t + \Delta t) = v_I\left(t + \frac{\Delta t}{2}\right) + \frac{1}{2}a_I(t+\Delta t)\Delta t $$
## Time-step for the classical equations

### Table 1  Some typical vibrational modes

<table>
<thead>
<tr>
<th>Vibrational mode</th>
<th>Wavelength of absorption [cm(^{-1})] ((1/\lambda))</th>
<th>Absorption frequency [s(^{-1})] ((\nu = c/\lambda))</th>
<th>Period [fs] ((1/\nu))</th>
<th>Period/(\pi) [fs]</th>
</tr>
</thead>
<tbody>
<tr>
<td>O–H stretch</td>
<td>3200–3600</td>
<td>1.0 (\times) 10(^{14})</td>
<td>9.8</td>
<td>3.1</td>
</tr>
<tr>
<td>N–H stretch</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C–H stretch</td>
<td>3000</td>
<td>9.0 (\times) 10(^{13})</td>
<td>11.1</td>
<td>3.5</td>
</tr>
<tr>
<td>O–C–O asymmetric stretch</td>
<td>2400</td>
<td>7.2 (\times) 10(^{13})</td>
<td>13.9</td>
<td>4.5</td>
</tr>
<tr>
<td>C契约 C–N stretch</td>
<td>2100</td>
<td>6.3 (\times) 10(^{13})</td>
<td>15.9</td>
<td>5.1</td>
</tr>
<tr>
<td>C=O (carbonyl) stretch</td>
<td>1700</td>
<td>5.1 (\times) 10(^{13})</td>
<td>19.6</td>
<td>6.2</td>
</tr>
<tr>
<td>C=C stretch</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H–O–H bend</td>
<td>1600</td>
<td>4.8 (\times) 10(^{13})</td>
<td>20.8</td>
<td>6.4</td>
</tr>
<tr>
<td>C–N–H bend</td>
<td>1500</td>
<td>4.5 (\times) 10(^{13})</td>
<td>22.2</td>
<td>7.1</td>
</tr>
<tr>
<td>H–N–H bend</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C=C (aromatic) stretch</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C–N stretch (amines)</td>
<td>1250</td>
<td>3.8 (\times) 10(^{13})</td>
<td>26.2</td>
<td>8.4</td>
</tr>
<tr>
<td>Water Libration (rocking)</td>
<td>800</td>
<td>2.4 (\times) 10(^{13})</td>
<td>41.7</td>
<td>13</td>
</tr>
<tr>
<td>O–C–O bending</td>
<td>700</td>
<td>2.1 (\times) 10(^{13})</td>
<td>47.6</td>
<td>15</td>
</tr>
<tr>
<td>C=C–H bending (alkenes)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C=C–H bending (aromatic)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^{a}\)All values are approximate; a range is associated with each motion depending on the system. The value of \(c = 3.00 \times 10^{10}\) cm s\(^{-1}\). The last column indicates the timestep limit for leap-frog stability for a harmonic oscillator: \(\Delta t < 2/\omega = 2/(2\pi \nu)\).

Time-step for the classical equations

Table 1  Some typical vibrational modes

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</table>

Time step should not be larger than 1 fs (1/10ν).

Δt = 0.5 fs assures a good level of conservation of energy most of the time.

Exception: dynamics close to the conical intersection may require 0.25 fs.
• Fourth-order Runge-Kutta (RK4)

Figure 16.1.3. Fourth-order Runge-Kutta method. In each step the derivative is evaluated four times: once at the initial point, twice at trial midpoints, and once at a trial endpoint. From these derivatives the final function value (shown as a filled dot) is calculated. (See text for details.)

• Bulirsch-Stoer

BS works better than RK4

Figure 16.4.1. Richardson extrapolation as used in the Bulirsch-Stoer method. A large spanned by different sequences of finer and finer substeps. Their results are extrapolated that is supposed to correspond to infinitely fine substeps. In the Bulirsch-Stoer method, that are done by the modified midpoint method, and the extrapolation technique is rational polynomial extrapolation.
Time-step for the **quantum** equations

\[
\Delta t/m_s
\]

\[
h(t+\Delta t) = h(t) + \frac{n}{m_s} (h(t+\Delta t) - h(t)) \quad (n=1..m_s-1)
\]

\[
\sum |c_i|^2
\]

\[
\Delta t = 0.5 \text{ fs}
\]
Fewest switches: two states

Population in $S_2$: $a_{22}(t) \rightarrow a_{22}(t + \Delta t)$

Trajectories in $S_2$: $N_2 = a_{22}N$

Minimum number of hoppings that keeps the correct number of trajectories:

$$n_{2\rightarrow 1}^{\text{hop}} = N_2(t) - N_2(t + \Delta t)$$

$$= (a_{22}(t) - a_{22}(t + \Delta t))N$$

$$n_{1\rightarrow 2}^{\text{hop}} = 0$$

Probability of hopping

$$P_{2\rightarrow 1}^{\text{hop}} = \frac{n_{2\rightarrow 1}^{\text{hop}}}{N_2(t)} \approx \begin{cases} \frac{\Delta t}{a_{11}(t)} \left( \frac{da_{11}}{dt} \right), & \frac{da_{11}}{dt} > 0 \\ 0, & \frac{da_{11}}{dt} \leq 0 \end{cases}$$
**Fewest switches: several states**

\[
\dot{a}_{kk} = \sum_{l \neq k} b_{kl} = \sum_{l \neq k} \left[ \frac{2}{\hbar} \text{Im}(a^*_{kl} H_{kl}) - 2 \text{Re}(a^*_{kl} d_{kl}) \right]
\]

\[P^\text{hop}_{k \rightarrow l} = \frac{b_{kl}}{a_{kk}} \Delta t \quad \text{Tully, JCP 93, 1061 (1990)}\]

Example: Three states \( \dot{a}_{33} = b_{32} + b_{31} \)

\[P^\text{hop}_{3 \rightarrow 2} = \frac{b_{32}}{a_{33}} \Delta t \quad \text{Only the fraction of derivative connected to the particular transition}\]
Forbidden hop makes the classical statistical distributions deviate from the quantum populations.

How to treat them:
• Reject all classically forbidden hop and keep the momentum.
• Reject all classically forbidden hop and invert the momentum.
• Use the time incertainty to search for a point in which the hop is allowed (Jasper et al. 116 5424 (2002)).
After hop, what are the new nuclear velocities?

- Adjust the velocities components in the direction of the nonadiabatic coupling vector $h_{12}$. 
Phase control

Component $h_{1x}$

Before the phase correction

$\text{CNH}_4^+$: MRCI/CAS(4,3)/6-31G*$
Phase control

Component $h_{1x}$

- ■ Before the phase correction
- ○ After the phase correction

$CNH_4^+$: MRCI/CAS(4,3)/6-31G*

Time (fs)
Abrupt changes control

\[ h_{01} \]

11.75 fs

12.00 fs
Orthogonalization

\[ \tilde{g}_{ij} = -g_{ij} \cos \beta + h_{ij} \sin \beta \]
\[ \tilde{h}_{ij} = g_{ij} \sin \beta + h_{ij} \cos \beta \]
\[ \tan 2\beta = \frac{2g_{ij} \cdot h_{ij}}{h_{ij} \cdot h_{ij} - g_{ij} \cdot g_{ij}} \]

- The routine also gives the linear parameters:

\[ E = d_{gh} \left[ \sigma_x x + \sigma_y y \pm \left( \frac{1}{2} (x^2 + y^2) + \frac{\Delta_{gh}}{2} (x^2 - y^2) \right)^{1/2} \right] \]
Abrupt changes control

\[ h_{01} \]

\[ \tilde{h}_{01} \]

11.75 fs

12.00 fs
The Newton-X program
Adiabatic dynamics

Classical motion of the nuclei: **Velocity Verlet** [Swope et al. JCP 76, 637 (1982)]

- Fortran 90 routines
- Perl controller
Nonadiabatic dynamics

- Surface hopping: fewest switches

\[ |\psi(t)\rangle = \sum_k c_k(t) e^{-i\gamma_k(t)} |\phi_k(R)\rangle \]

\[ i\hbar \frac{\partial}{\partial t} |\psi(t)\rangle = H_{el} |\psi(t)\rangle \]

\[ \dot{c}_k(t) = -\sum_{l\neq k} c_l(t) e^{-i\gamma_l(t)} \mathbf{v} \cdot \mathbf{h}_{kl} \]

\[ a_{kl}(t) = c_k^*(t)c_l(t) \]

\[ P_{k\rightarrow l}(t) = \text{Max} \left( 0, \frac{\dot{a}_{lk}}{a_{kk}} \right) \]

Integration:

RK4 (with Granucci, Pisa)

Previous implementation:

Bulirsh-Stoer (Pittner, Prague)
Extensions to other methods

Presently:

- **COLUMBUS** (nonadiabatic dynamics)
  - MCSCF
  - MRCI

- **TURBOMOLE** (adiabatic dynamics)
  - TD-DFT
  - RI-CC2
## Current capabilities

<table>
<thead>
<tr>
<th>Features</th>
<th>Options</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dynamics</td>
<td><em>On-the-fly</em> adiabatic dynamics</td>
</tr>
<tr>
<td></td>
<td><em>On-the-fly</em> nonadiabatic dynamics with surface hopping (fewest switches)</td>
</tr>
<tr>
<td></td>
<td>Adjustment of momentum along the nonadiabatic coupling vector</td>
</tr>
<tr>
<td></td>
<td>Neglecting of forbidden hoppings</td>
</tr>
<tr>
<td></td>
<td>Phase control of the CI vector (overlapping / inner-product)</td>
</tr>
<tr>
<td></td>
<td>Yarkony orthogonalization of the nonadiabatic coupling vectors</td>
</tr>
<tr>
<td></td>
<td>Topographic analysis of the conical intersections</td>
</tr>
<tr>
<td></td>
<td>Damped dynamics (kinetic energy always null)</td>
</tr>
<tr>
<td></td>
<td>TDSE integrated in substeps of the classical equations</td>
</tr>
<tr>
<td>Portability</td>
<td>COLUMBUS (CASSCF, MRCI)</td>
</tr>
<tr>
<td></td>
<td>TURBOMOLE (TD-DFT, RI-CC2)</td>
</tr>
<tr>
<td></td>
<td>Analytical models</td>
</tr>
<tr>
<td>Initial conditions</td>
<td>Wigner distribution / classical harmonic oscillator</td>
</tr>
<tr>
<td>File management</td>
<td>Friendly input via nxinp. Automatic management of files and directories in multiple trajectories</td>
</tr>
<tr>
<td>Documentation</td>
<td>All options and routines are documented</td>
</tr>
<tr>
<td>Output and analysis</td>
<td>Statistical analysis of results (internal coordinates and forces, energies, wave function properties)</td>
</tr>
<tr>
<td></td>
<td>Recomputation of internal coordinates</td>
</tr>
<tr>
<td></td>
<td><em>On-the-fly</em> graphical outputs (MOLDEN, GNUPLOT)</td>
</tr>
</tbody>
</table>
NEWTON-X
Newton dynamics close to the crossing seam

MAIN MENU

1. GENERATE INITIAL CONDITIONS
2. SET BASIC INPUT
3. SET GENERAL OPTIONS
4. SET NONADIABATIC DYNAMICS
5. GENERATE TRAJECTORIES
6. SET STATISTICAL ANALYSIS
7. EXIT

Select one option (1-7):
SET BASIC OPTIONS

nat: Number of atoms.
There is no value attributed to nat
Enter the value of nat : 6
Setting nat = 6

nstat: Number of states.
The current value of nstat is: 2
Enter the new value of nstat : 3
Setting nstat = 3

nstatdyn: Initial state (1 - ground state).
The current value of nstatdyn is: 2
Enter the new value of nstatdyn : 2
Setting nstatdyn = 2

prog: Quantum chemistry program and method

0   - ANALYTICAL MODEL
1   - COLUMBUS
2.0 - TURBOMOLE RI-CC2
2.1 - TURBOMOLE TD-DFT
The current value of prog is: 1
Enter the new value of prog : 1
So many choices…
What method should I use?
<table>
<thead>
<tr>
<th>Method</th>
<th>Single/Multi Reference</th>
<th>Analytical gradients</th>
<th>Coupling vectors</th>
<th>Computational effort</th>
<th>Typical implementation</th>
</tr>
</thead>
<tbody>
<tr>
<td>MR-CISD</td>
<td>MR</td>
<td>√</td>
<td>√</td>
<td></td>
<td>Columbus</td>
</tr>
<tr>
<td>RI-CC2</td>
<td>SR</td>
<td>√</td>
<td>×</td>
<td></td>
<td>Turbomole</td>
</tr>
<tr>
<td>CASPT2</td>
<td>MR</td>
<td>×</td>
<td>×</td>
<td></td>
<td>Molcas / Molpro</td>
</tr>
<tr>
<td>MR-MP2</td>
<td>MR</td>
<td>×</td>
<td>×</td>
<td></td>
<td>Gamess</td>
</tr>
<tr>
<td>CISD/QCISD</td>
<td>SR</td>
<td>√</td>
<td>×</td>
<td></td>
<td>Molpro / Gaussian</td>
</tr>
<tr>
<td>CASSCF</td>
<td>MR</td>
<td>√</td>
<td>√</td>
<td></td>
<td>Columbus / Molpro</td>
</tr>
<tr>
<td>TD-DFT</td>
<td>SR</td>
<td>√</td>
<td>×</td>
<td></td>
<td>Turbomole</td>
</tr>
<tr>
<td>FOMO/AM1</td>
<td>MR</td>
<td>√</td>
<td>√</td>
<td></td>
<td>Mopac (Pisa)</td>
</tr>
</tbody>
</table>
Comparison among methods

RI-CC2

TD-DFT

CASSCF

Energy

Time (fs)

Time (fs)

Time (fs)

0 5 10 15 20 25 30

0 5 10 15 20 25 30

0 5 10 15 20 25 30

TD-DFT

MCSCF

0
t_c
t_final

Time
A basic protocol

• Use **TD-DFT** for large systems (> 10 heavy atoms) with one single configuration dominating the region of the phase space spanned by the dynamics. Test against **CASSCF** and **RI-CC2**.

• Use **TD-DFT** for large systems until a multireference region of the phase space be reached. Switch to **CASSCF** to continue the dynamics.

• Use **RI-CC2** for medium systems (6-10 heavy atoms) under the same conditions as in the previous two points.

• Use **CASSCF** for medium systems with strong multireference character in all phase space. Test against **MRCI**.

• Use **MRCI** for small systems (< 6 heavy atoms).

• In all cases, when the number of relevant internal coordinates is small (2-4) and they can easily be determined, test against wave-packet dynamics.
Some applications: theory and experiment
On the ambiguity of the experimental raw data
Analysis of the experimental results

The lifetime of ethylene

Barbatti, Granucci, Persico and Lischka, CPL 401, 276 (2005)
Survey of theoretical and experimental predictions

<table>
<thead>
<tr>
<th>Method</th>
<th>Lifetime (fs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DTSH [1]</td>
<td>$S_1 \rightarrow S_2, S_0$</td>
</tr>
<tr>
<td>DTSH [1]</td>
<td>$S_1, S_2 \rightarrow S_0$</td>
</tr>
<tr>
<td>DTSH [2]</td>
<td>$S_1 \rightarrow S_2, S_0$</td>
</tr>
<tr>
<td>AIMS [3]</td>
<td>$S_1 \rightarrow S_2, S_0$</td>
</tr>
<tr>
<td>AIMS [4]</td>
<td>$S_1 \rightarrow S_2, S_0$</td>
</tr>
<tr>
<td>MCDTH [5]</td>
<td>$S_1 \rightarrow S_2, S_0$</td>
</tr>
<tr>
<td>Experimental [6]</td>
<td>$S_1 \rightarrow S_2, S_0$</td>
</tr>
<tr>
<td>Experimental [7]</td>
<td>$S_1 \rightarrow S_2, S_0$</td>
</tr>
<tr>
<td>Experimental ($\tau_1 + \tau_2$) [8]</td>
<td>$S_1 \rightarrow S_2, S_0$</td>
</tr>
</tbody>
</table>

$^a E_v = 6.2 \pm 0.3$ eV.
$^b E_v = 7.4 \pm 0.15$ eV.

The time-window question

Radloff has a rather distinct explanation!

On how the initial surface can make a difference
Basic scenery expected:
Torsion + decay at twisted MXS

This and other movies are available at: homepage.univie.ac.at/mario.barbatti

Large momentum along CN stretch is acquired in the $S_2-S_1$ transition.

Stretching + pyramidalization dominate
If $S_1 (\sigma\pi^*)$ is directly populated, the torsion should dominate the dynamics.

This and other movies are available at: homepage.univie.ac.at/mario.barbatti
Intersection?
Which of them?
The $S_0/S_1$ crossing seam

Barbatti, Paier and Lischka, JCP 121, 11614 (2004).

Ohmine 1985
Freund and Klessinger 1998
Ben-Nun and Martinez 1998
Laino and Passerone 2004
First $S_1 \rightarrow S_0$ hopping.
Conical intersections in ethylene

\[ \tau \sim 100-140 \text{ fs} \]

~7.6 eV

60%

23%

11%

Ethylidene MXS

Pyram. MXS

H-migration

Torsion + Pyramid.

Barbatti, Ruckenbauer and Lischka, JCP 122, 174307 (2005)
Readressing the DNA bases problem
Experimental lifetimes of the excited state of DNA/RNA basis: $\sim 1$ ps

What has theory to say?

• The decay can be due to $\pi\sigma^*/S_0$ crossing

• Or maybe due to the $\pi\pi^*/S_0$ crossing
  Marian, JCP 122, 104314 (2005).

• Or $n\pi^*/S_0$ crossing, who knows?
  Chen and Li, JPCA 109, 8443 (2005).

• Maybe, there’s no crossing at all!
  Langer and Doltsinis, PCCP 6, 2742 (2004)

• Our own dynamics simulations (TD-DFT(B3LYP)/SVP) do not show any crossing too…

• But the dynamics calculations are not reliable enough until now: or they miss the MR character, or the nonadiabatic character, or both!
An example: photodynamics of DNA bases

Amino pyrimidine as a model for adenine

9H-adenine

4-amino pyrimidine
An example: photodynamics of DNA bases

4-amino pyrimidine
SA-3-CAS(5,6)/6-31G*

The system moves toward the crossing seam with out-of-plane motions similar to that predicted by Marian for adenine (JCP 122, 104314 (2005))
An example: photodynamics of DNA bases

4-amino pyrimidine
SA-3-CAS(5,6)/6-31G*

If the H-atoms that replace the ring have a big isotopic mass, the out-of-plane motion is inhibited and there is no crossing.
An example: photodynamics of DNA bases

4-amino pyrimidine
SA-3-CAS(5,6)/6-31G*

Average probability is $4 \times 10^{-5}$ in each 0.05 fs.

In 1 ps, the probability is 0.8.

The system does not need a crossing to decay in 1 ps. The weak $S_1/S_0$ coupling is enough to induce the transfer.
Conclusions
Conclusions

Correlation Method

- Full-CI
- MRCI
- CASSCF
- HF

Basis set

DZ  TZ  ...  BS limit
Conclusions

Basis set

Correlation Method

DZ
TZ
BS limit

HF
CASSCF
MRCI
Full-CI

< 6 heavy atoms
6-10 heavy atoms

Dynamics method

Wavepacket dynamics

Surf. Hopping and Mean Field

Multiple Spawning

Adiabatic dynamics

Static calculations

< 6 heavy atoms
6-10 heavy atoms
Conclusions

Dynamics, Why?
• Ab initio dynamics can be used to characterize lifetimes, and relaxations paths in the ground and excited state, occurring in the time scale of sub-picosecond.
• Dynamics reveal features that is not easily found by static methods.
• Dynamics can be used to locate the important regions of the crossing seam.

Excited-state dynamics around the world (a very incomplete and biased inventory…)
• Semiclassical dynamics:
  Tully; Jasper and Thrular; Robb, Olivucci and Buss; Barbatti and Lischka; Marx and Doltsinis (Car-Parrinelo); Granucci and Persico (local diabatization); Martinez-Nuñez; Pittner and Bonačić-Koutecký; Neufeld.

• Multiple spawning
  Ben-Nun and Martínez

• Wave packet
  Gonzalez and Manz; Manthe and Cederbaum; Viel and Domcke; Jacubtz; de Vivie-Riedle and Hofmann; Schinke; Köppel.
Our contribution

Towards an implementation of surface hopping dynamics
• **NEWTON-X**: new implementation of on-the-fly surface hopping dynamics.
• Energies, gradients and nonadiabatic coupling vectors can be read from any quantum chemical package.
• For MRCI and CASSCF dynamics, COLUMBUS has been used.
• For TD-DFT and RI-CC2, TURBOMOLE.

Where are we going now?
• QM/MM: investigation of the influence of the environment on the relaxations paths, lifetimes and efficiency of the crossing seam.
Collaborators

Vienna:
Hans Lischka
Adélia Aquino
Matthias Ruckenbauer (Master student)
Gunther Zechmann (Master student, now at Warwick)
Daniela Raab

Pisa:
Giovanni Granucci

Prague:
Jiri Pittner

Zagreb:
Mario Vazdar
• References and additional information: homepage.univie.ac.at/mario.barbatti

• Support: CNPq (Brazil), Austrian Science Fund (Special project F16)