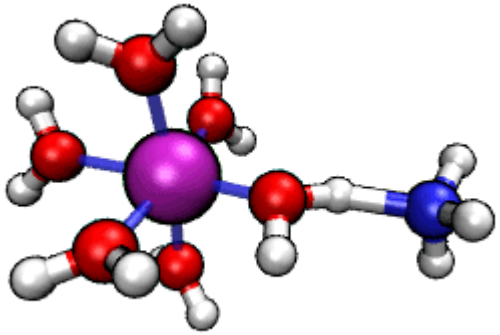
The ORCA MD Module



Martin Brehm

November 2020

https://brehm-research.de

Outline

1.) Features Already Implemented

2.) New Features in ORCA 5.0

- New Thermostats
- Restraints
- Metadynamics

The ORCA MD Module

Basic Idea:

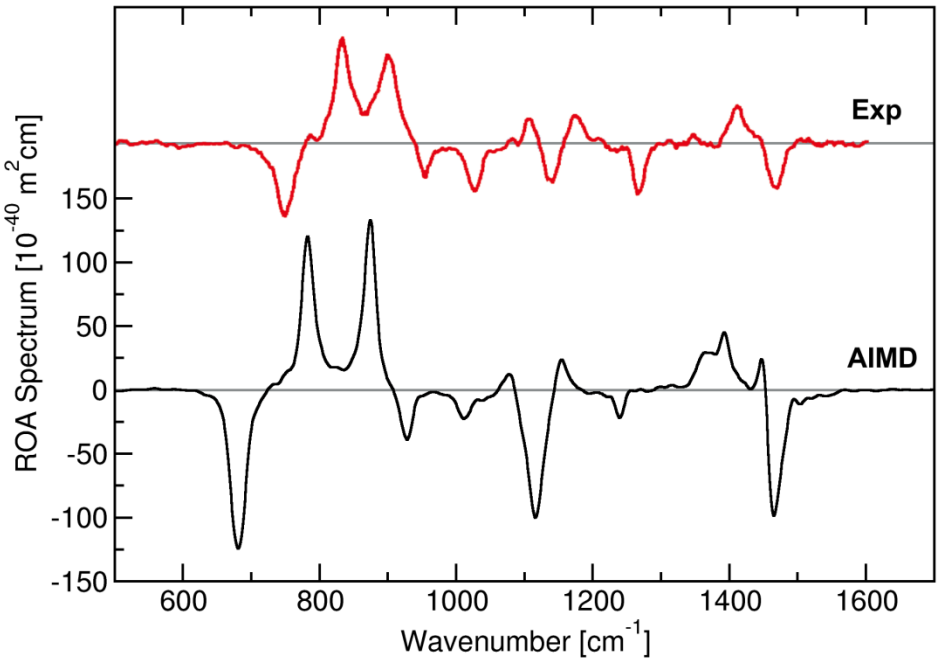
- ORCA offers a plethora of electron structure methods
- Many of them have analytic gradients
- Why not use them for molecular dynamics (MD)?

Advantages over static calculations:

- Includes entropy at desired temperature
  (much more precise than in harmonic approximation)
- Allows to treat full explicit solvent effect
- Intrinsic conformer sampling
- Accounts for many anharmonic effects *(hydrogen bonding, overtones, combination bands → vibrational spectroscopy)*

The ORCA MD Module

Example: Raman Optical Activity (ROA) spectrum of liquid propylene oxide [2]:



*(this spectrum was **not** calculated with ORCA; see [2])*

Computing vibrational spectra of bulk phase systems from AIMD:

IR and Raman spectra: [1] *Phys. Chem. Chem. Phys.* **2013**, *15*, 6608-6622.

Raman Optical Activity spectra: [2] *J. Phys. Chem. Lett.* **2017**, *8 (14)*, 3409-3414.

Resonance Raman spectra: [3] *J. Chem. Theory Comput.* **2019**, *15 (7)*, 3901-3905.

Spectroscopic functions in TRAVIS: [4] *J. Chem. Phys.* **2020**, *152 (16)*, 164105.

The ORCA MD Module

History and Current State:

- Development started in 2016
- Has grown over time, many features now included
- Can be used with all ORCA methods that offer gradients
  (DFT, hybrid/double hybrid, MP2, semiempirics, TDDFT, ...)
- More features will be introduced with ORCA 5.0
  (see second half of my talk)

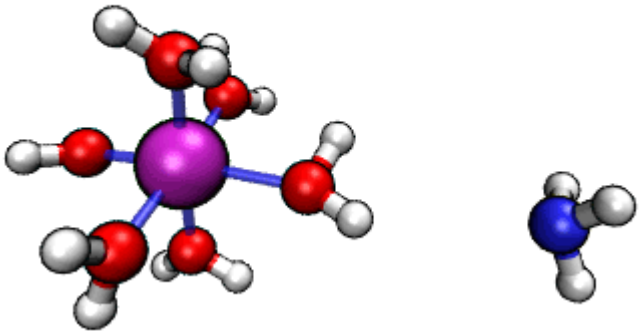
Input Format:

- The input in the **`%md`** section is executed line by line *(as a script)*, it is **not** keyword-based as the rest of the ORCA input
- Allows for arbitrarily complicated MD „experiments“ in one ORCA run

The ORCA MD Module

Example:

Proton abstraction from $[Al(H_2O)_6]^{3+}$ by NH_3



see
https://brehm-research.de

```
! MD BLYP D3 def2-SVP
%md
  Initvel 300_K
  Timestep 1.0_fs
  Thermostat Berendsen 300_K Timecon 20.0_fs
  Dump Position Stride 1 Filename "traj.xyz"
  Run 2000
end
* xyz 3 1
  Al    -1.69843    0.30039   -0.52660
  O     -1.75434    2.28860   -0.16768
  H     -1.06074    2.96658   -0.39426
  H     -2.57402    2.86004   -0.19067
  ...
*
```

The ORCA MD Module

A more complicated MD script

```
! MD BLYP D3 def2-SVP
%md
  Initvel 300_K
  Timestep 1.0_fs

  Thermostat Berendsen 300_K Timecon 10.0_fs Massive
  Dump Position Stride 1 Filename “equil.xyz"
  Run 1000

  Thermostat NHC 300_K Timecon 20.0_fs
  Dump Position Stride 1 Filename “prod.xyz"
  Run 2000

  Thermostat NHC Ramp 300_K 10_K Timecon 20.0_fs
  Dump Position Stride 1 Filename “anneal.xyz"
  Run 2000
end
* xyz 0 1
  ...
*
```

(„Thermostat NHC“ requires ORCA 5.0)

```
! MD
%md
  $verbose execute 1$  # reduce printlevel

  VAR tape : Character[]
      pos, p : Integer
      a : String

  a := "++++++++++[>+++++++>++++++++++>+++>+<<<<-]>++.>+.+++++++..+++.>++.<<++++++++
                          +++++++.>.+++.------.--------.>+.>."

  pos := 0
  p := 0
  tape.resize 1

  WHILE p < a.length DO
    IF       a[p] = ']' THEN IF tape[pos] <> 0 THEN WHILE a[p] <> '[' DO p-- ENDDO ENDIF
      ELSEIF a[p] = '+' THEN tape[pos]++
      ELSEIF a[p] = '-' THEN tape[pos]--
      ELSEIF a[p] = '.' THEN Print tape[pos]
      ELSEIF a[p] = '<' THEN pos--
      ELSEIF a[p] = '>' THEN pos++ IF pos >= tape.size THEN tape.add 0 ENDIF
    ENDIF
    p++
  ENDDO
end

* xyz 0 1
Ar 0.0 0.0 0.0
*
```

see **https://brehm-research.de/sanscript**

Features Already Implemented

Features Already Implemented

Thermostats

- Currently, only the **Berendsen thermostat** [1] is implemented
- Very robust, but does not sample the canonical ensemble well
- One Problem: „Flying ice cube effect“
- Available both as **global** *(one thermostat for whole system)* and **massive** *(one thermostat per degree of freedom)*

[1] H. J. C. Berendsen, J. P. M. Postma, W. F. van Gunsteren, A. DiNola, *J. Chem. Phys.* **1984**, *81*, 3684-3690.

Features Already Implemented

Restart of Simulations

- A restart file is automatically written after each simulation step
- Simulations which were aborted, crashed, or just ended normally can be easily restarted to continue at that point

  → Allows to split large simulations into multiple short runs
  (maximum job time of queuing system)
- You should call the **`Restart`** command only after all settings have been done as in the first run *(timestep, thermostat, ...)*

Features Already Implemented

Restart of Simulations

Running this input:

```
%md
  Timestep 0.5_fs
  Initvel 300_K
  Thermostat NHC 300_K Timecon 10.0_fs
  Dump Position Stride 1 Filename "traj.xyz"
  Run 1000
end
```

gives an **identical** trajectory to running this input 10 times in a row:

```
%md
  Timestep 0.5_fs
  Initvel 300_K
  Thermostat NHC 300_K Timecon 10.0_fs
  Dump Position Stride 1 Filename "traj.xyz"
  Restart IfExists
  Run 100
end
```

Features Already Implemented

Constraints

- Constraints hold some geometrical property fixed during MD
- They are „*hard*“, the degree of freedom is truly removed
- Solved via the RATTLE algorithm
- **Implemented constraint types:**
  - Distances
  - Angles
  - Dihedrals
  - Cartesian constraints
  - Center of mass position for groups of atoms

Features Already Implemented

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- **Implemented constraint types:**
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  - Angles
  - Dihedrals
  - Cartesian constraints
  - Center of mass position for groups of atoms
  - „Rigid“ constraints *(keep a molecule / group of atoms rigid)*

Features Already Implemented

Cartesian Minimization

- Implemented L-BFGS algorithm for energy minimization of huge systems (> 10 000 atoms)
- Not as effective as ORCA‘s standard optimization in internal coords, but linear scaling with system size
- Also a hybrid minimization approach available, which combines L-BFGS with simulated annealing runs
- Constraints and restraints can be active during minimization *(which is not possible with* **„!OPT“** *)*
- If **„!L-OPT“** is specified in ORCA, the L-BFGS minimizer from the MD module is called
- Can also optimize a subset of atoms *(e.g., H atoms in a crystal structure)* by adapting the active region

Features Already Implemented

Regions

- Certain parts of the system can be classified as „regions“
- Trajectories of regions can be independently written
- Regions can have individual thermostats, including different time constants and different target temperatures

  → allows for heat flow experiments

- **Typical example:**

  QM/MM simulations have a QM and a MM region

Features Already Implemented

Cells

- Can define a cell around the system which reflects atoms
- Useful to keep a system in a defined volume
- The walls are „soft“ *(harmonic)*; reflective walls are not available
- Periodic boundary conditions are not available
  (because ORCA does not do periodic calculations)
- Elastic cells which adapt their size to the pressure are available
  → constant-pressure simulations possible
- **Available cell geometries:**
  - Cubic / Orthorhombic
  - Prismatic
  - Spherical
  - Ellipsoids

Features Already Implemented

QM/MM

See separate talk :-)

2.) New Features in ORCA 5.0

New Features in ORCA 5.0

New Thermostats

1) **Nosé-Hoover Chain Thermostat (NHC)** [1]

   Extends the system by a chain of virtual particles

   Very good sampling of the canonical ensemble
   (no flying ice cube effect, etc.)

   → Thermostat of choice for most MD simulations

2) **Canonical Sampling through Velocity Rescaling (CSVR)** [2]

   Solves a stochastic differential equation to sample the canonical ensemble

   → Very modern method (2007) with growing applications

Both thermostats are available as **global** or **massive**.

[1] G. J. Martyna, M. L. Klein, M. Tuckerman, *J. Chem. Phys.* **1992**, *97*, 2635-2643.
[2] G. Bussi, D. Donadio, M. Parrinello, *J. Chem. Phys.* **2007**, *126*, 014101.

New Features in ORCA 5.0

Restraints

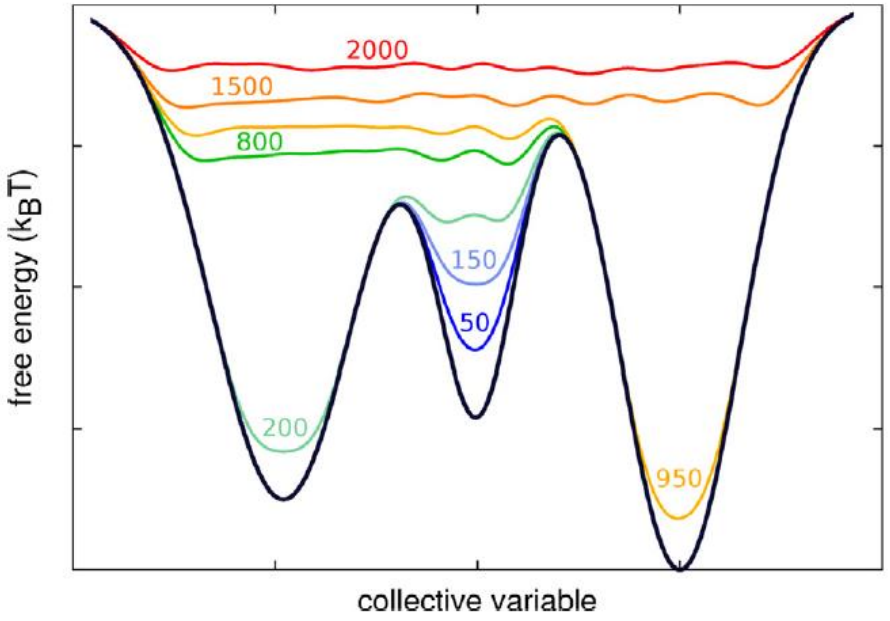
- In contrast to constraints, restraints are „soft“
- Implemented:
  - **Harmonic** restraints $E(x) = k/2 \cdot x^2$
  - **Gaussian** restraints $E(x) = A \cdot \exp(-\sigma^2/x^2)$

    Can be either hill or well *(depending on sign of A)*
- Can be applied to **distances**, **angles**, **dihedrals**
- Can be one-sided, *i. e.*, lower or upper walls
- Target value can be a ramp → Moving restraint
- Allows for enhanced sampling techniques such as umbrella sampling

New Features in ORCA 5.0

Metadynamics

- Method to explore **free energy profiles** of processes / reactions *(in contrast to surface scans)*
- Developed by Parrinello in 2002 [1]
- **Basic idea:** Slowly fill up energy surface with Gaussian hills



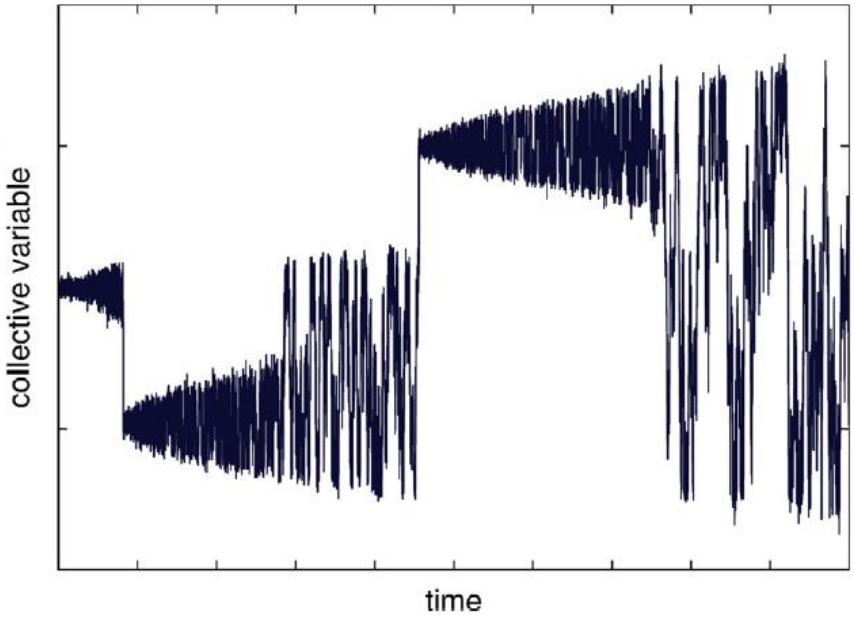


Image from *Rev. Phys.* **2017**, *2*, 32-45. (Creative Commons License)

[1] A. Laio, M. Parrinello, *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 12562-12566.

New Features in ORCA 5.0

Metadynamics

- The process of interest is defined via collective variables („Colvars“)
- ORCA 5.0 can run **one- and two-dimensional** Metadynamics
- **Implemented Colvar types:**
  - **Distances** *(including center-of-mass distances for groups, projections into planes or onto vectors)*
  - **Angles**
  - **Dihedral Angles**
  - **Coordination Numbers** [1]
- The latter has been successfully applied to predict pK_A values of weak acids under solvent influence [2,3]

[1] M. Iannuzzi, A. Laio, M. Parrinello, *Phys. Rev. Lett.* **2003**, *90*, 238302.
[2] A. K. Tummanapelli, S. Vasudevan, *J. Phys. Chem. B* **2014**, *118*, 13651-13657.
[3] A. K. Tummanapelli, S. Vasudevan, *Phys. Chem. Chem. Phys.* **2015**, *17*, 6383-6388.

Examples what can be done with Metadynamics:

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Dissociation Constants of Weak Acids from ab Initio Molecular Dynamics Using Metadynamics: Influence of the Inductive Effect and Hydrogen Bonding on pK_a Values

Anil Kumar Tummanapelli and Sukumaran Vasudevan*

View Author Information

Cite this: *J. Phys. Chem. B* 2014, 118, 47, 13651–13657
Publication Date: November 6, 2014
https://doi.org/10.1021/jp5088898

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From the journal:
Physical Chemistry Chemical Physics

Estimating successive pK_a values of polyprotic acids from *ab initio* molecular dynamics using metadynamics: the dissociation of phthalic acid and its isomers†

Check for updates

Anil Kumar Tummanapelli[a] and Sukumaran Vasudevan*[a]

Author affiliations

New Features in ORCA 5.0

Example for one-dimensional Metadynamics:

Polymer strand dissociation free energy in solvent

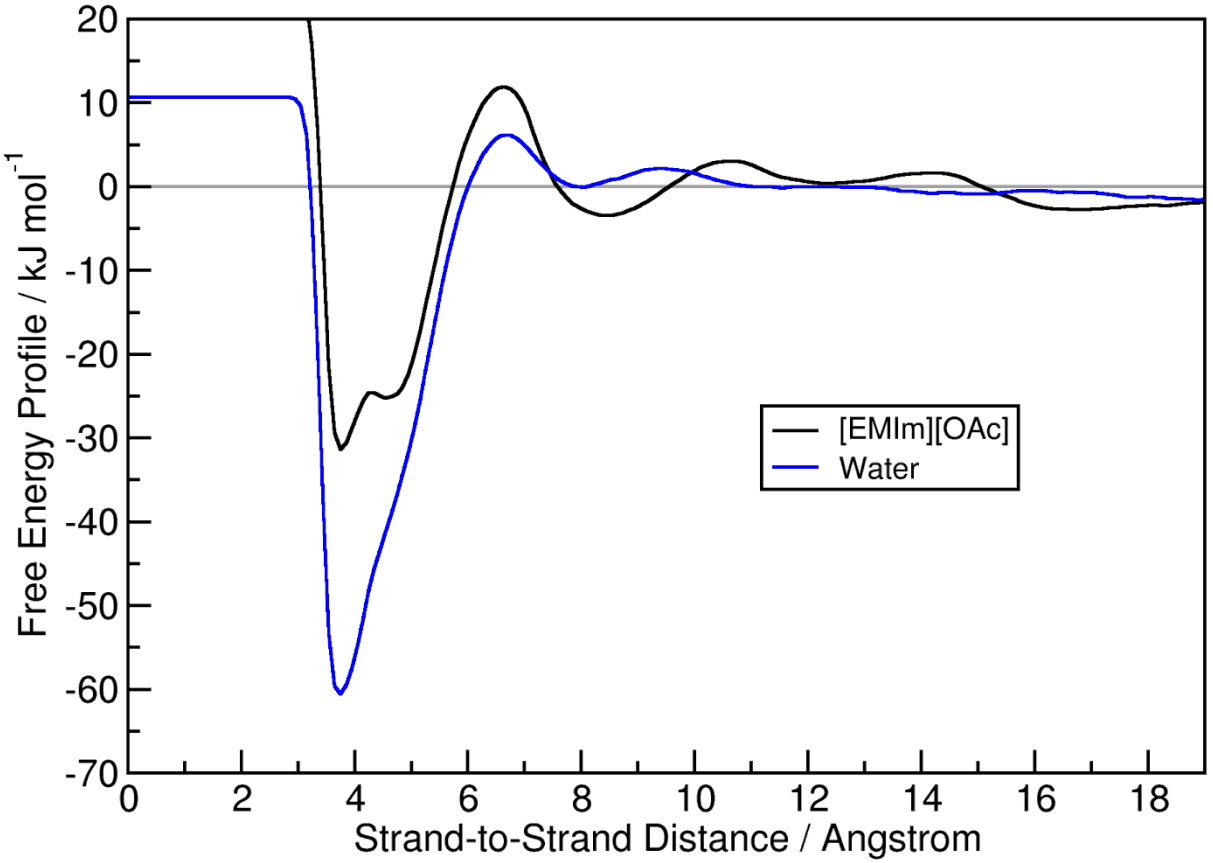
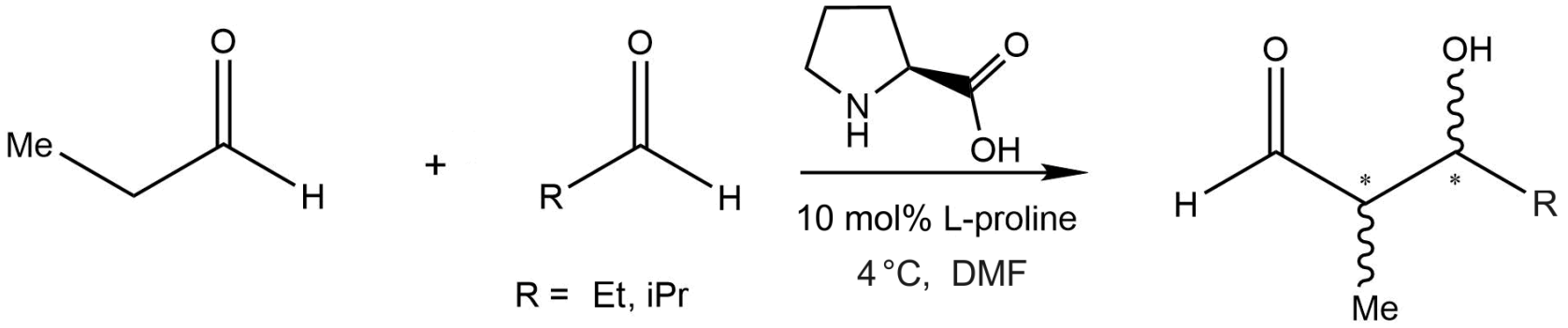


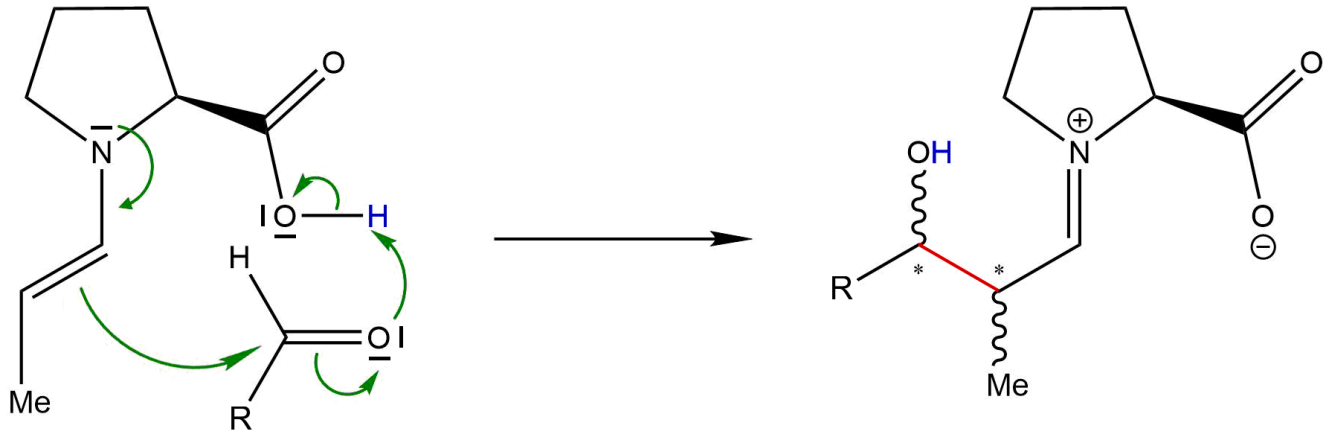
Figure: M. Brehm, unpublished results.

New Features in ORCA 5.0

Example for two-dimensional Metadynamics:

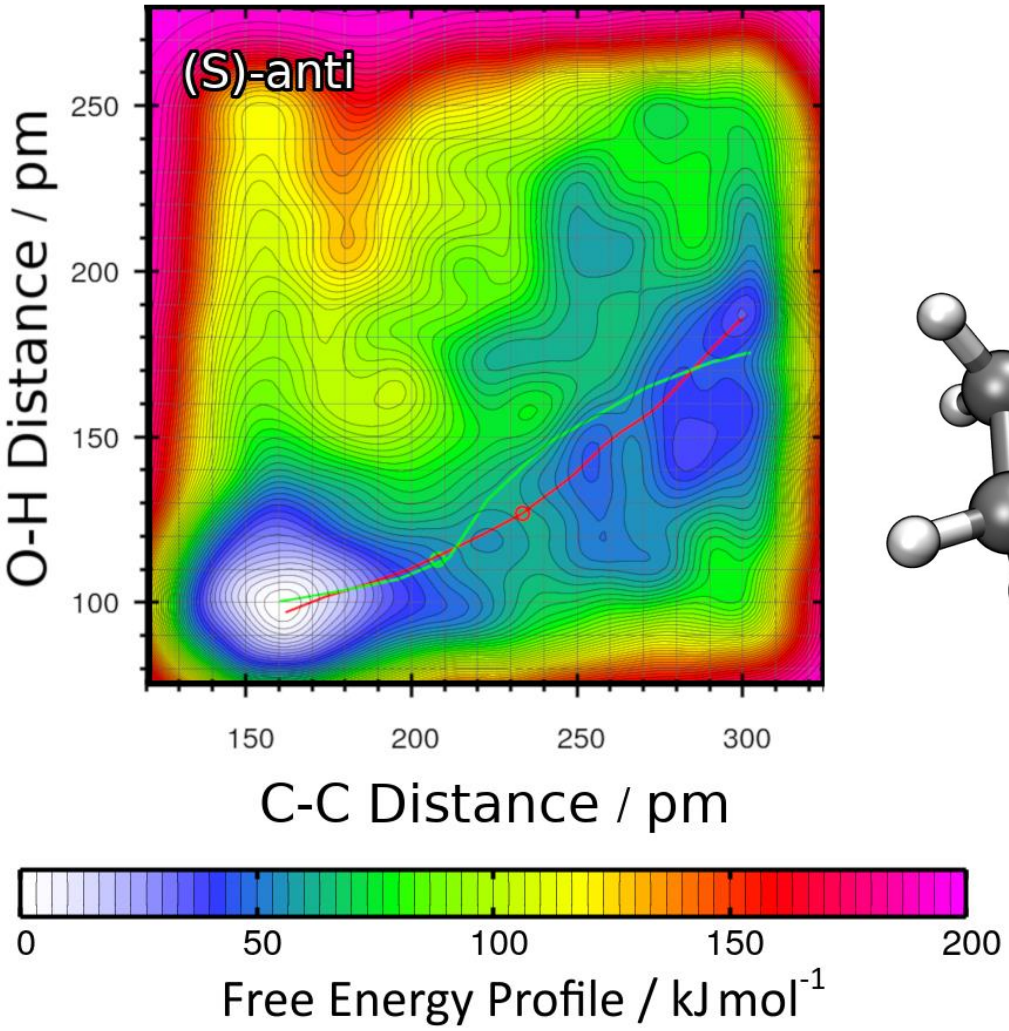
Organocatalytic enantioselective Aldol reaction in explicit solvent





New Features in ORCA 5.0

Example for a result of two-dimensional Metadynamics:



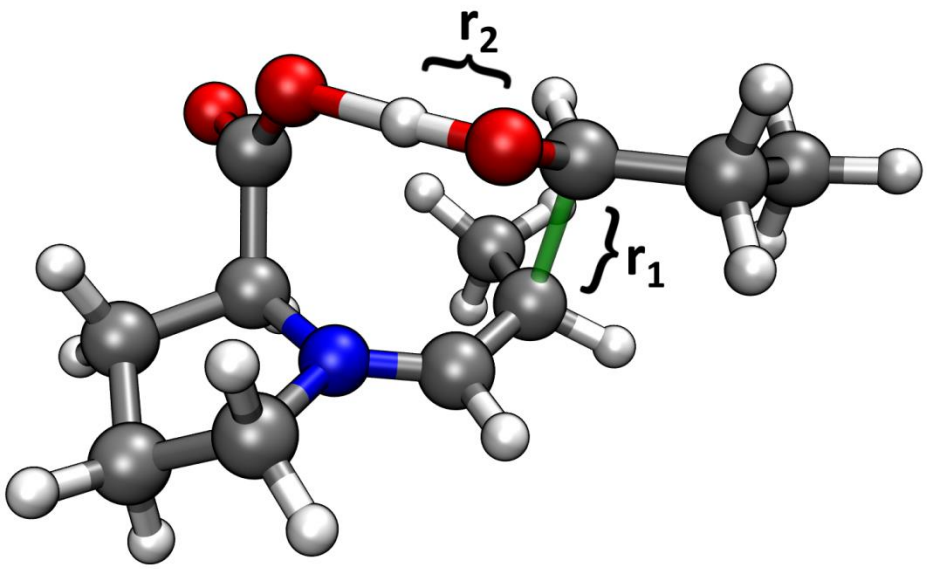
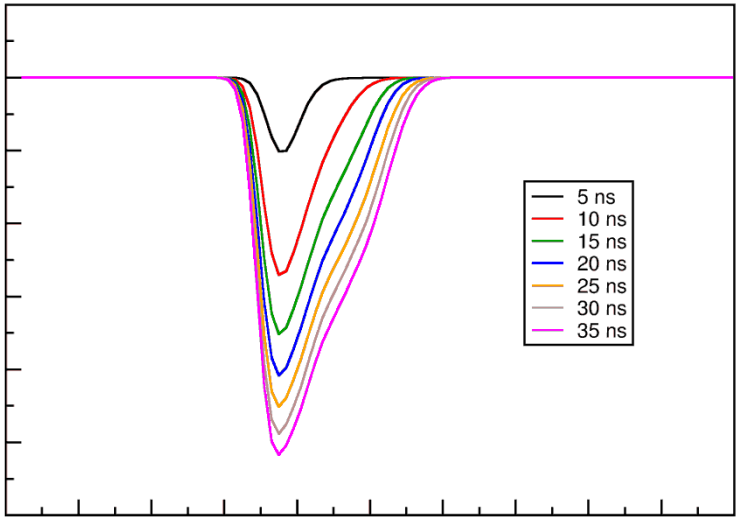


Figure: M. Brehm, unpublished results.

New Features in ORCA 5.0

Metadynamics

- Implementation has full restart ability → multiple short runs
- Implemented **well-tempered Metadynamics** [1] which converges smoothly towards the result:



- Implemented **extended Lagrangian Metadynamics** [2], where a virtual particle is coupled to the Colvars by a spring

[1] A. Barducci, G. Bussi, M. Parrinello, *Phys. Rev. Lett.* **2008**, *100*, 020603.
[2] M. Iannuzzi, A. Laio, M. Parrinello, *Phys. Rev. Lett.* **2003**, *90*, 238302.

New Features in ORCA 5.0

Metadynamics

Example ORCA input for 2D well-tempered extended Lagrangian Metadynamics *(requires ORCA 5.0)*:

```
%md

 Timestep 0.5_fs
 Initvel 350_K
 Thermostat NHC 350_K Timecon 100.0_fs
 Dump Position Stride 1 Filename "trajectory.xyz"

 Manage_Colvar Define 1 Distance Atom 0 Atom 1
 Manage_Colvar Define 2 Distance Atom 2 Atom 3

 Metadynamics Colvar 1 Scale 1.0 Wall Lower 3.0 10.0 Upper 10.0 10.0 Range 0.0 15.0 100
 Metadynamics Colvar 2 Scale 1.0 Wall Lower 1.0 10.0 Upper  8.0 10.0 Range 0.0 13.0 100

 Metadynamics HillSpawn 40 0.5 0.5 Store 2000
 Metadynamics WellTempered 6000_K
 Metadynamics Lagrange 100.0 10.0 200.0_K 10.0_fs

 Restart IfExists
 Run 100000

end
```

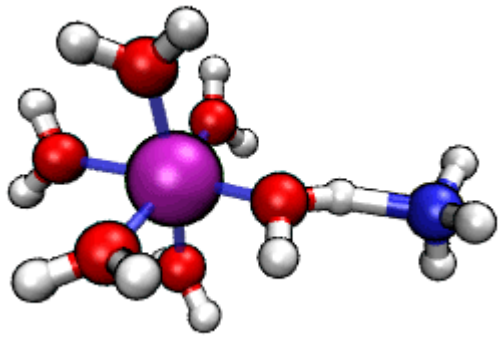
You can find this example in the manual of ORCA 5.0.

New Features in ORCA 5.0

Small Improvements

- There is now a meaningful error message if the SCF does not converge during MD
- Can now print population analysis in every MD step
- Can now use a ramp for the target value of constraints
- Can now keep the system‘s center of mass fixed during MD
- Fixed several small bugs

Thanks for your attention!



Ideas for new features in the MD module?

Please suggest them in the ORCA forum!