



Molecular Dynamics and Monte-Carlo simulations in structural investigations of free molecules

Denis Tikhonov



Structural Studies of Free Molecules

Main Experimental Methods:

- Gas Electron Diffraction (**GED**)
- Rotational Spectroscopy (**RSp**)
- Vibrational Spectroscopy (**VSp**)

+ Theoretical Model based on Quantum
Chemistry (**QC**)

Theoretical model making

What do we want?



Perform one calculation



Get all the required properties at once

Conventional theoretical model

@ Born-Oppenheimer approximation:

$$(\hat{H}_{rot}^{(0)} + \hat{H}_{vib}^{(0)} + \hat{W})\psi = E\psi .$$

$$\hat{H}_{rot}^{(0)} = \frac{1}{2}\hat{\mathbf{j}}^\dagger \mathbf{I}^{-1} \hat{\mathbf{j}} . \text{ (rigid rotor)}$$

$$\hat{H}_{vib}^{(0)} = \frac{1}{2}\hat{\mathbf{p}}^\dagger \mathbf{G}\hat{\mathbf{p}} + \frac{1}{2}\hat{\mathbf{q}}^\dagger \mathbf{F}\hat{\mathbf{q}} . \text{ (harmonic oscillator)}$$

Perturbation:

$$\hat{W} = V_{anh.} + \hat{T}_{vib-rot} .$$

Large amplitude motions (LAM) $\rightarrow$ dynamic model

Sutable for VSp, RSp and GED.

Alternatives

Molecular Dynamics (MD):

$$m_i \ddot{\mathbf{r}}_i = -\nabla_i V_{QC}$$

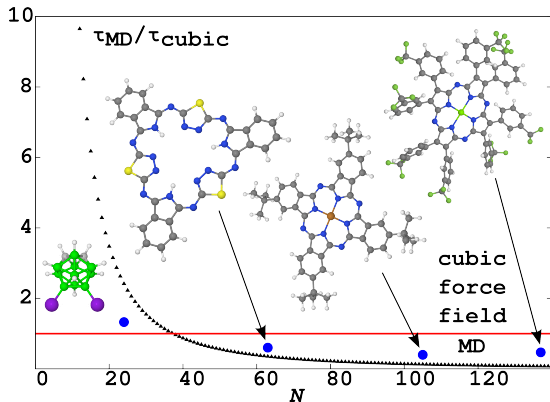
- classical MD
- quantum MD (PIMD, Q-CN-GLE)

Monte-Carlo (MC):

Random movement

- classical MC
- quantum MC (DMC, VMC, PIMC)

Why do we need alternatives?



$$\frac{\tau_{MD}}{\tau_{cubic}} \approx \frac{a \cdot b(\nu_{max}/\nu_{min})}{36N^2}$$

• Vishnevskiy Yu. et al.
// *Inorg. Chem.*, **54**, pp.
11868–11874 (2015)

• Zhabanov Yu. et al.
// *J. Porph. Phthal.*, **17**,
pp. 220–228 (2013)

• Pimenov O. et al. //
Struct. Chem., **26**, pp.
1531–1541 (2015)

• Zhabanov Yu. et al.
// *J. Mol. Struct.*, **1092**,
pp. 114–112 (2015)

Vishnevskiy Yu. et al. // *Theor. Chem. Acc.*,
135, p. 88 (2016)

Applications of MD simulations

MD in VSp: 😊

$$I_{\text{IR}}(\nu) \propto \frac{\nu \tanh\left(\frac{h\nu}{2k_B T}\right)}{n(\nu)} \text{Re} \int_0^\infty e^{-i2\pi\nu t} \langle \mathbf{d}(t), \mathbf{d}(0) \rangle dt ,$$

MD in GED: 😊

$$r_g = \langle r \rangle, \quad l^2 = \langle r^2 \rangle - \langle r \rangle^2, \quad r_a = \langle r^{-1} \rangle^{-1}.$$

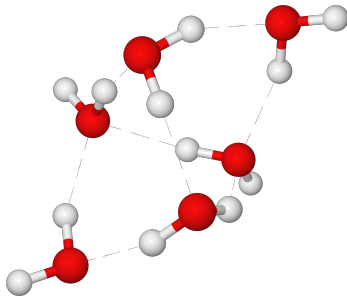
Iuchi S. et al. // *J. Phys. Chem. B* (2002), **106**, pp. 3466–3476

Tse J. // *Ann. Rev. of Phys. Chem.* (2002), **53**, pp. 249–290

Wann D. et al. // *J. Phys. Chem. A*, **113**, pp. 9511–9520 (2009)

Applications of MC simulations

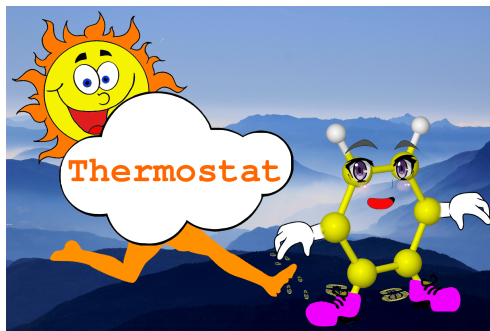
MC in RSp:



Structure of hexamer of H_2O ($B_e - B_0$ obtained with DMC).

Liu K. et al. // *Nature*, **381**, pp. 501-503 (1996)

Application of MD simulations in GED



Problems of usage of MD in GED



No quantum effects

PIMD, quantum colored-noise
thermostats



“Flying Ice Cube” Effect

Better thermostats

Harvey S. et al. // *J. Comput. Chem.*, **19**,
pp. 726–740 (1998)

Qassandra (QA)

10

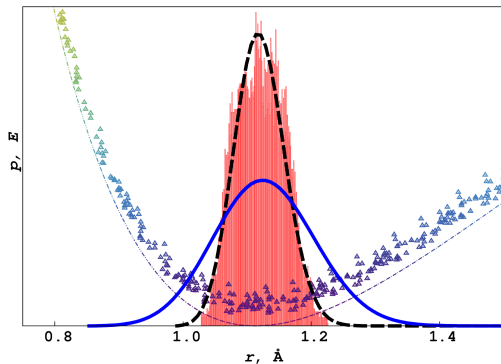
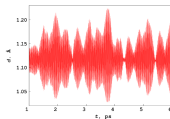
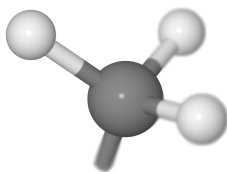
[QuAntum corrections to claSSical pArameters
for gas electroN DiffRAction]



Vishnevskiy Yu. et al. // *Theor. Chem. Acc.*, **135**, p. 88 (2016)

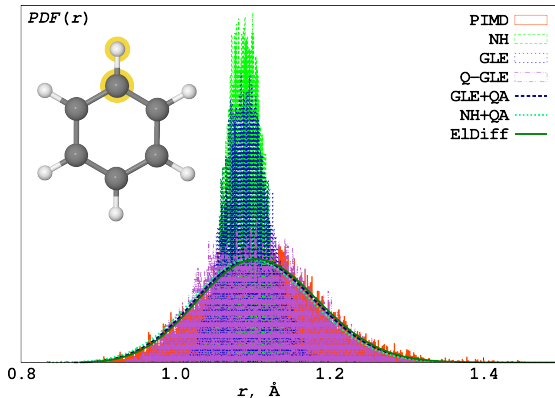
<https://sourceforge.net/projects/edsoftware/files/Qassandra/>

How does QA work?



QA test #0

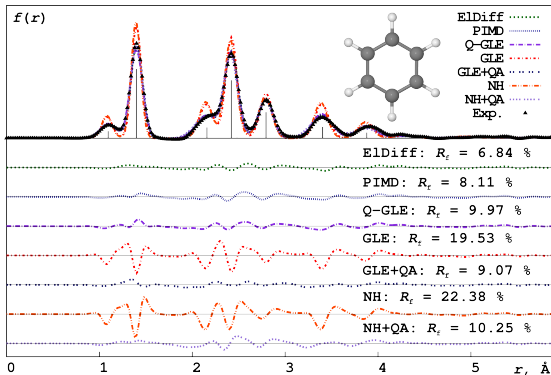
Benzene @ 300 K (BLYP/TZVP)



Tikhonov D. et al. // Accepted to PCCP, (2016)

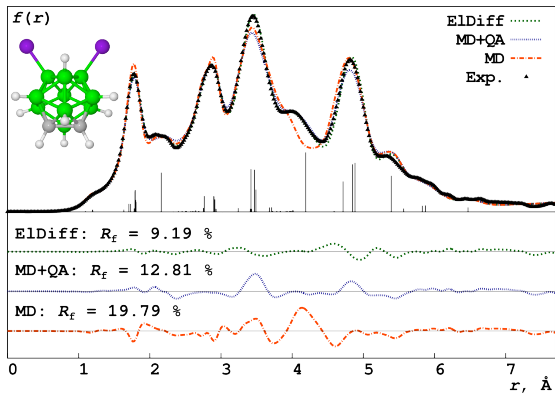
QA test #1

Benzene @ 300 K



$[r_e @ \text{CCSD(T)/cc-pVTZ}] + [I, (r_e - r_a) \kappa @ \text{BLYP/TZVP}]$

QA test #2

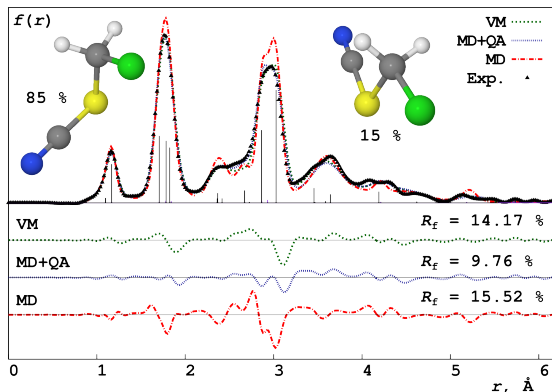
9,12-I₂-1,2-C₂B₁₀H₁₀ @ 480 K

Vishnevskiy Yu. et al.
 // *Inorg. Chem.*, **54**,
 pp. 11868–11874 (2015)

[r_e @ MP2/SDB-cc-pVTZ] + [$I, (r_e - r_a) \kappa$ @ PBE0/def2-SV(P)]

QA test #3: large-amplitude motions

CMTC @ 337 K

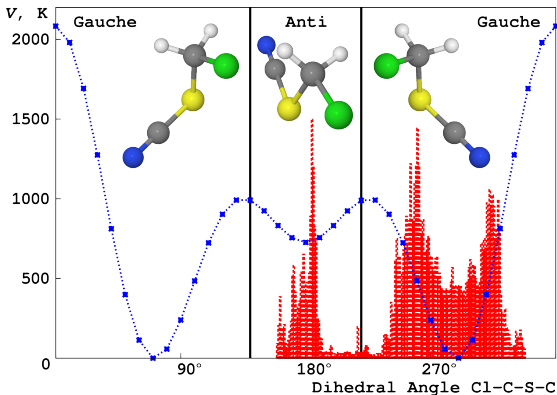


Martinez B. et al. //
PCCP, 17,
pp. 15805–15812 (2015)

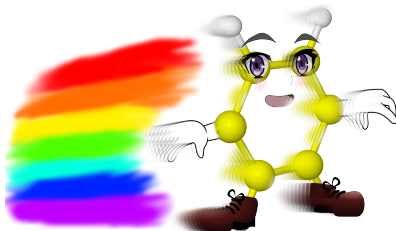
$[r_e @ \text{CCSD(T)}/\text{cc-pVTZ}] + [I, (r_e - r_a) \kappa @ \text{PBE0}/\text{def2-SVP}]$

QA test #3: large-amplitude motions

CMTC @ 337 K

(CClH₂)SCN (CMTC) @ PBE0/def2-SVP

Application of MD simulations in VSp



Obtaining VSp from MD

Conventional recommendations:

1. Get several NVE trajectories → compute spectra
→ average these spectra
2. Use small time steps

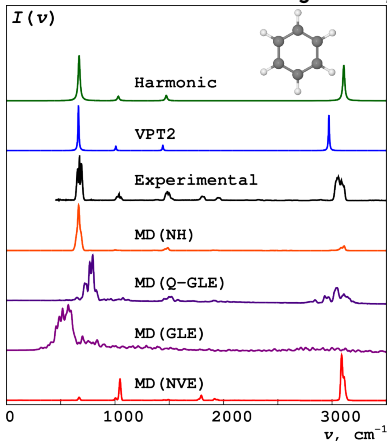
Horníček J. et al. // *J. Chem. Phys.*, **127**, p. 084502 (2007)

Fischer S. et al. // *J. Phys. Chem. B*, **120**, pp. 1429–1436 (2016)

Can we overcome them?

Overcoming Recommendation #1

How about one NVT trajectory?



NH Chains

Can be used.

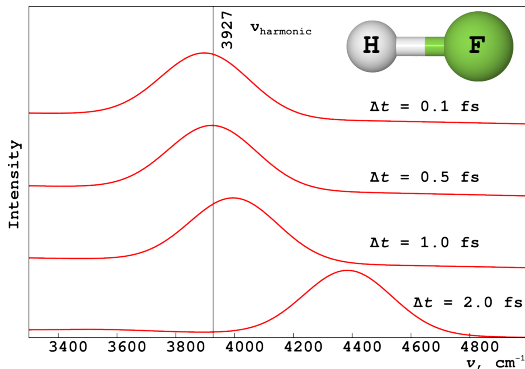
But watch for the
"flying ice cube"
effect

(Q-)CN-GLE

Is too noisy $\Rightarrow$
cannot be used

Recommendation #2

What's wrong with large time steps?



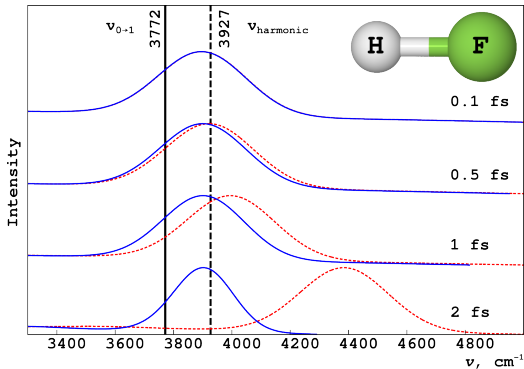
PBE0/def2-SVP

NVE MD

$t_{\text{total}} = 1 \text{ ps}$

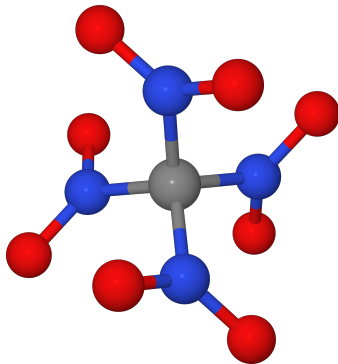
Overcoming Recommendation #2

Can we correct this behavior? **Yes we can!**



$$\nu_{\text{corr}} = \frac{\sqrt{1 - \cos(2\pi \cdot \Delta t \cdot \nu_{\text{ini}})}}{\sqrt{2\pi \cdot \Delta t}}$$

Tetranitromethane (TNM)



4 internal rotations of NO_2 groups

- Stosick A., et al. // *JACS*, **61**, pp. 1127–1130 (1939)
 Sadova N., et al. // *J. Struct. Chem.*, **15**, pp. 593–595 (1974)
 Sadova N., et al. // *J. Mol. Struct.*, **31**, pp. 399–402 (1976)

Dynamic models in GED

$\nu_{LAM} \ll \nu_{SAM}$, therefore:

$$\rho_{vib}(\mathbf{q}_{LAM}, \mathbf{q}_{SAM}) \approx \rho_{LAM}(\mathbf{q}_{LAM}) \cdot \rho_{SAM}(\mathbf{q}_{SAM} | \mathbf{q}_{LAM})$$

(adiabatic separation of LAM and SAM)

Usually

$$\theta_{D,LAM}^{max} = \frac{h\nu_{LAM}^{max}}{k} \ll T_{exp}$$

therefore:

$$\rho_{LAM}(\mathbf{q}_{LAM}) \propto \exp\left(-\frac{V(\mathbf{q}_{LAM})}{kT}\right)$$

The Curse of Dimensionality

1D dynamic models:



casual and boring... since 1950-s

2D dynamic models:

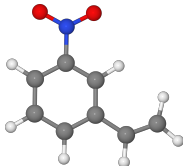


less then dosen since 2000

3D dynamic models:

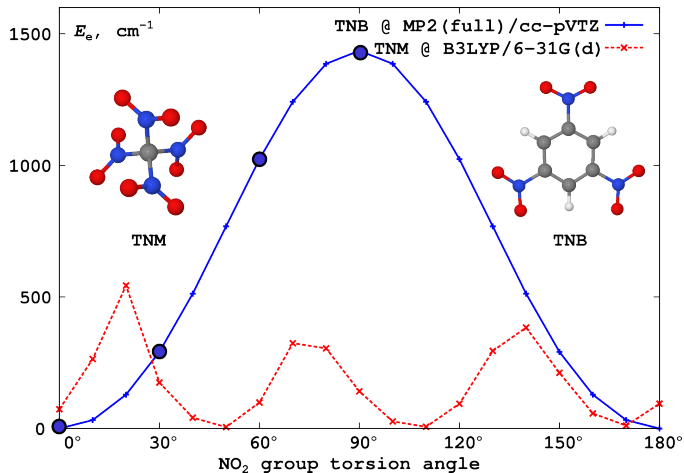


so far only one & very symmetrical

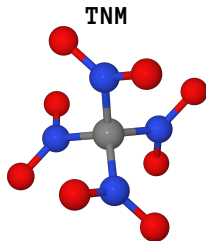
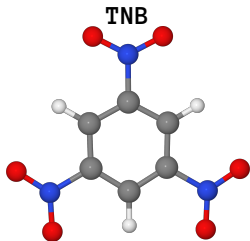


- Morino Y. et al. // *J. Chem. Phys.*, **28**, 185-197 (1958)
Tsuji T. et al. // *J. Mol. Struct.*, **554**, 203-210 (2000)
Kovtun M. et al. // *J. Phys. Chem. A*, **119**, 1657-1665 (2015)
Khaikin L. et al. // *Struct. Chem.*, **26**, 1651-1687 (2015)

TNB vs. TNM



TNB vs. TNM

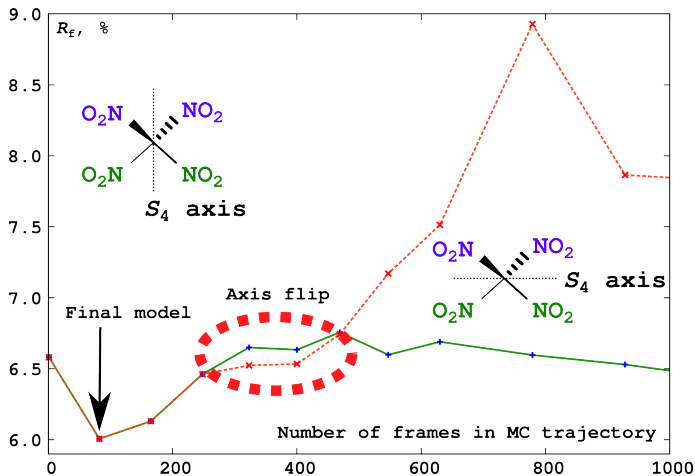


Torsion angle scan step = 10°

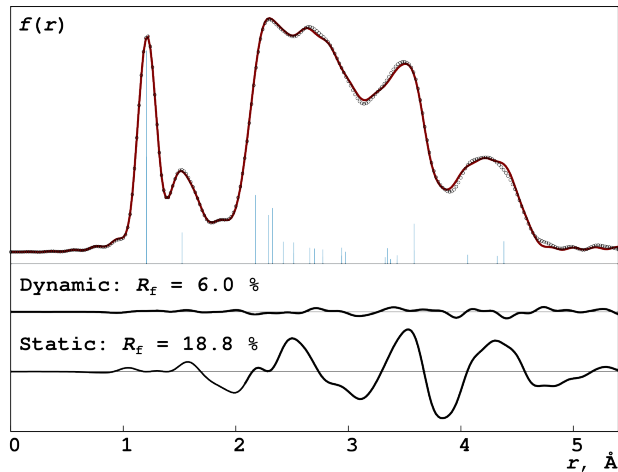
$$N_{\text{unique}} \geq \frac{36^3}{|G_{96}|} \approx 5 \cdot 10^2$$

$$N_{\text{unique}} \geq \frac{36^4}{|G_{384}|} \approx 4 \cdot 10^3$$

MCMC for 4D dynamic model of TNM



4D dynamic model vs. static



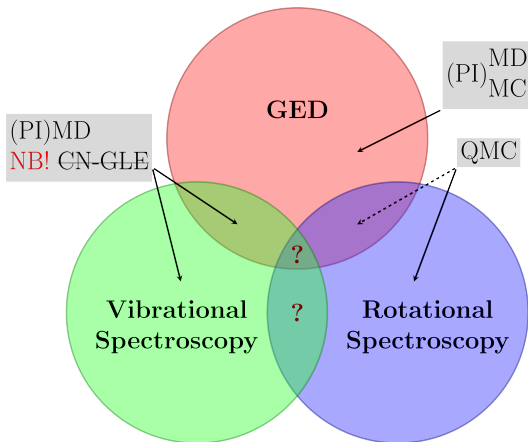
Results

What novel things did we do:

- ★ Qassandra
- ★ Benchmarks for usage of MD simulations in GED
- ★ Frequency correction for VSp from MD
- ★ 4D dynamic model for TNM using MCMC

Conclusion

Applicability of MD and MC:



Acknolegements

- ★ Dr. Yu. Vishnevskiy
- ★ Dr. V. Rybkin
- ★ Dr. A. Rykov
- ★ Dr. C. Reuter
- ★ J. Schwabedissen
- ★ Prof. N. Vogt

Thank You for the Attention!



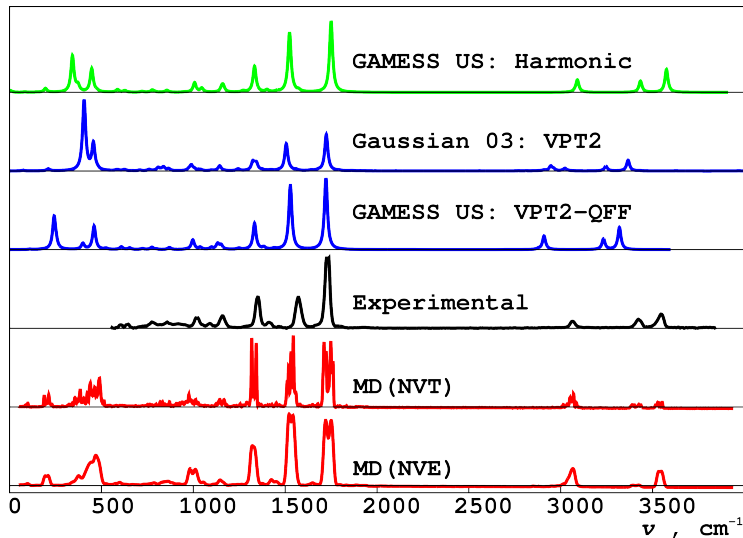
Application of classical MC for GED

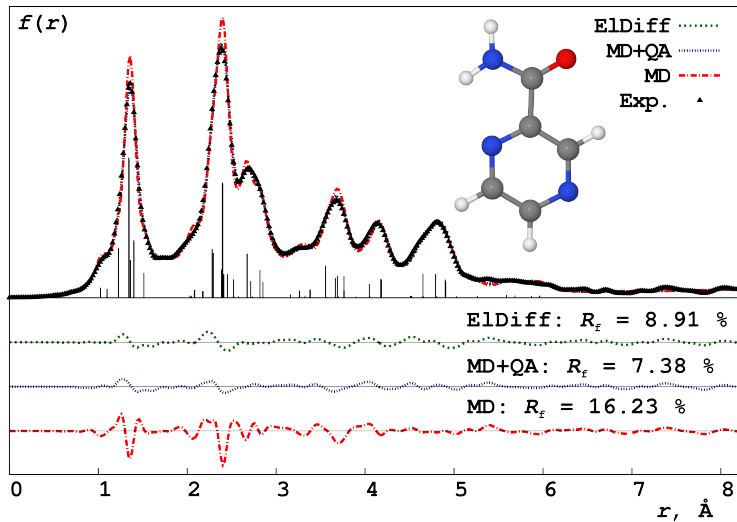
CS₂ @ 288 K

	Exp. (GED)	ElDiff	MC+QA	MC
$r_g(\text{C-S}), \text{Å}$	1.559(2)	1.565	1.567	1.564
$l(\text{C-S}), \text{Å}$	0.036(4)	0.039	0.040	0.024
$r_g(\text{S}\cdots\text{S}), \text{Å}$	3.113(4)	3.123	3.121	3.119
$l(\text{S}\cdots\text{S}), \text{Å}$	0.045(4)	0.042	0.042	0.032
$\angle_g(\text{SCS}), ^\circ$	173	172	170	172

$[r_e @ \text{CCSD(T)/cc-pQ TZ}] + [l, (r_e - r_a) \kappa @ \text{BP86/6-31G}]$

Morino Y. et al. // *Bull. Chem. Soc. of Japan*, **35**, 1661-1667 (1962)





Estimation of number of unique pseudoconformers

Let $\mathbf{S}_i \subseteq \mathbf{G}_{MS}$, $|\mathbf{S}_1| \leq |\mathbf{S}_2| \leq \dots \leq |\mathbf{S}_M|$,

$$N_{total} = \sum_{i=1}^M n_i \cdot \frac{|\mathbf{G}_{MS}|}{|\mathbf{S}_i|} \leq \frac{|\mathbf{G}_{MS}|}{|\mathbf{S}_1|} \sum_{i=1}^M n_i$$

Note, that $N_{uniq} = \sum_{i=1}^M n_i$, therefore:

$$N_{uniq} \geq N_{total} \frac{|\mathbf{S}_1|}{|\mathbf{G}_{MS}|}$$

Notations:

$\mathbf{G}_{MS}$ – molecular symmetry group for LAM, $\mathbf{S}_i$ – point symmetry group for pseudoconformers, n_i – number of unique pseudoconformers with symmetry $\mathbf{S}_i$, M – number of possible symmetries, N_{total} – total size of the grid of pseudoconformers for LAM, N_{uniq} – number of unique pseudoconformers.

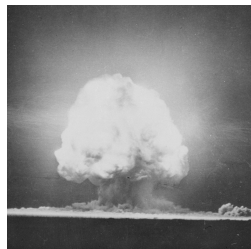
Metropolis sampling

- On the i -th step a new trial configuration is chosen.
- The trial configuration becomes $(i+1)$ -th in the MCMC trajectory if

$$p = \min \left\{ 1, \exp \left(-\frac{(E_{\text{trial}} - E_i)}{kT} \right) \right\} \geq a ,$$

where $a \in [0,1]$ – is a random number chosen from the uniform distribution.

If not, $(i+1)$ -th configuration is equal to i -th.



Qassandra formulas

$$P_{class}(\xi) \propto \exp\left(-\frac{\xi^2}{2\langle\xi^2\rangle}\right) (1 + c_1\xi + c_3\xi^3 + \dots)$$

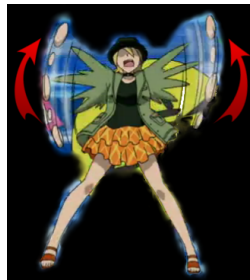
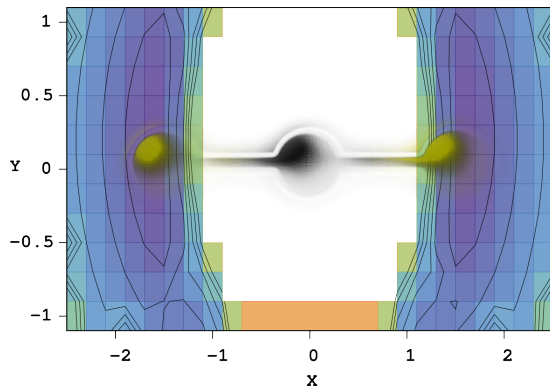
$$\langle\xi^2\rangle_{quant} = \frac{\hbar}{2\mu\omega} \coth\left(\frac{\hbar\omega}{2kT}\right)$$

$$\langle\xi\rangle_{quant} - \langle\xi\rangle_{class} = 3c_3\langle\xi^2\rangle_{MD} (\langle\xi^2\rangle_{quant} - \langle\xi^2\rangle_{MD})$$

$$\kappa_{quant} = 3c_3\langle\xi^2\rangle_{MD} \frac{\hbar^2}{4\mu^2\omega^2} \left(\frac{1}{3} + \frac{1}{\sinh^2\left(\frac{\hbar\omega}{2kT}\right)} \right)$$

$$\xi = r - r_e \quad , \quad \omega^2 = \frac{\langle v^2 \rangle_{MD}}{\langle \xi^2 \rangle_{MD}} \quad , \quad \mu = \frac{m_1 m_2}{m_1 + m_2}$$

Anharmonicity in GED



Vibrational parameters:

$$r_g = \langle r \rangle$$

$$I^2 = \langle r^2 \rangle - \langle r \rangle^2$$

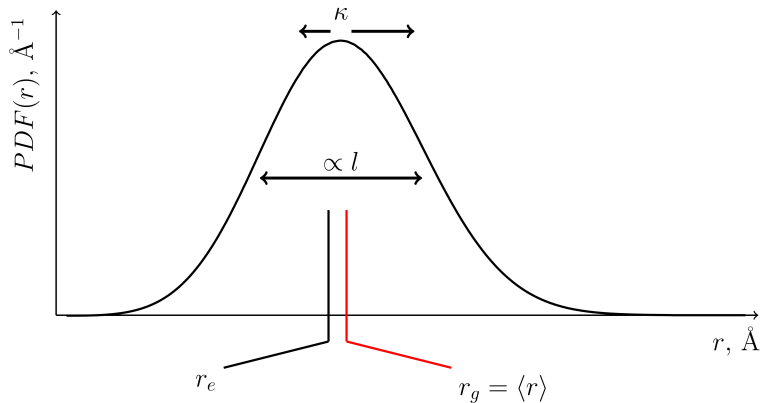
$$\kappa = \frac{1}{6} (\langle r^3 \rangle - 3\langle r \rangle \langle r^2 \rangle + 2\langle r \rangle^3)$$

$$r_a = \langle 1/r \rangle^{-1} \approx r_g - \frac{I^2}{r_e}$$

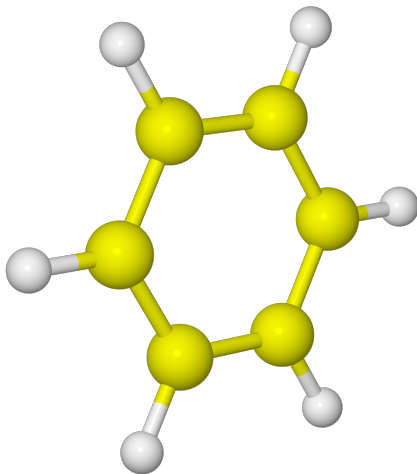
Discrepancy between experiment and model:

$$R_f = \sqrt{\frac{\sum_k (sM(s)_k^{\text{exp}} - sM(s)_k^{\text{theor}})^2}{\sum_k (sM(s)_k^{\text{exp}})^2}} \cdot 100\%$$

Pair distribution peak scheme

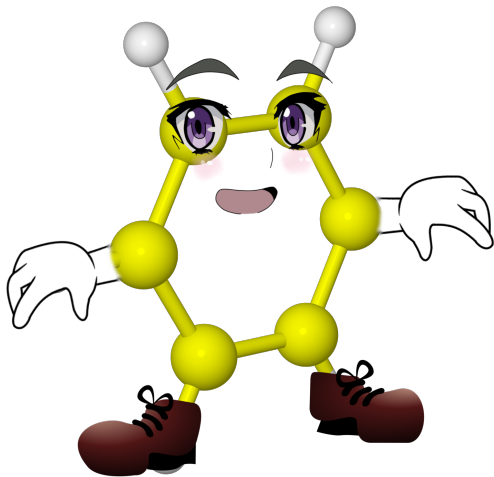


Molecular dynamics simulations (MD)



System = molecule

Molecular dynamics simulations (MD)



System = molecule



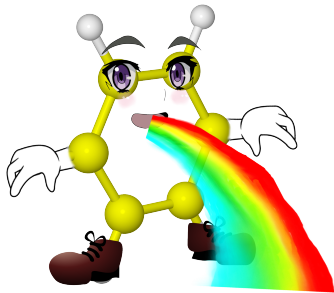
Classical motions on the PES



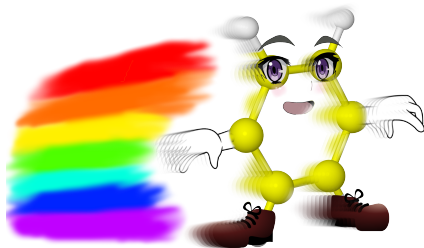
Classical motions on the PES with thermostat

NVT MD: thermostating

Energy loss ($E_{kin} \downarrow$)



Energy gain ($E_{kin} \uparrow$)



Problems in MD simulations: "Flying Ice Cube Effect"



Non-equilibrium distribution of energy for the degrees of freedom

Solution: better thermostats

Problem of the solution: limited availability

Problems in MD simulations: classical behavior



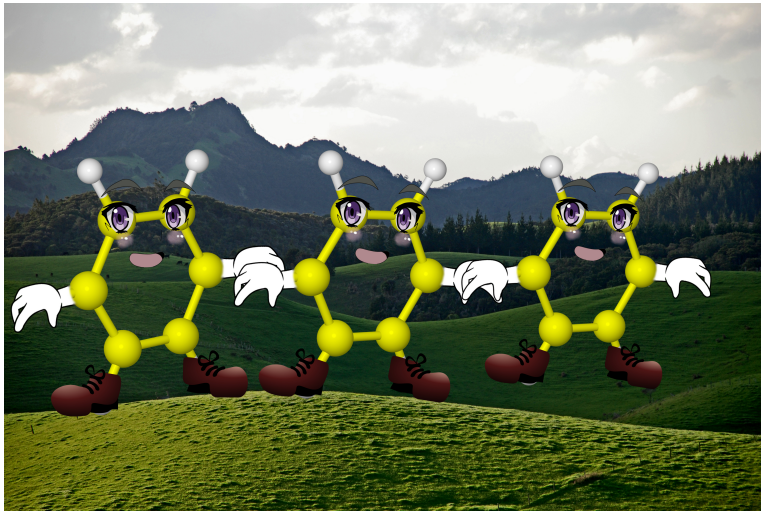
The lighter the atom – the more of quantum behavior

Solution #1: PIMD

Problems of solution #1: computational costs increase, limited availability

Solution #2: colored-noise thermostats

Problem of solution #2: limited availability



Accounting quantum motions using path-integral approach

Types of systems in thermodynamics

Isolated system = NVE



Heat exchange ... ✗

Matter exchange ... ✗

Types of systems in thermodynamics

Closed system = NVT



Heat exchange ... ✓

Matter exchange ... ✗

Types of systems in thermodynamics

Open system = μVT



Heat exchange ... ✓

Matter exchange ... ✓