

Geometry optimization, NEB calculations, and molecular dynamics

- Optimization of geometry
- Force calculation in OpenMX
- Stress tensor
- Steepest decent and Newton-type methods
- Variable cell optimization
- Enthalpy optimization
- Nudged Elastic Band (NEB) method
- Molecular dynamics simulations

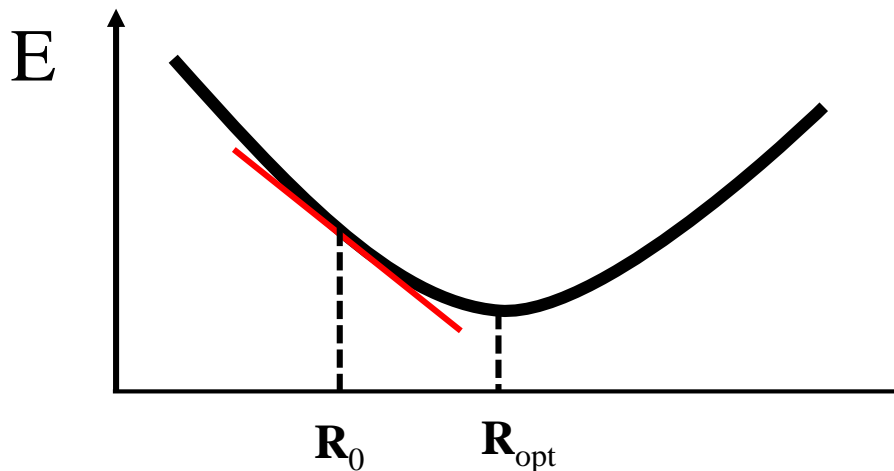
Taisuke Ozaki (ISSP, Univ. of Tokyo)

Institute for Materials Research (IMR), Tohoku University, Feb. 14, 2020.

Optimization of geometry

For a given geometrical structure, OpenMX calculates the total energy, forces on atoms, and stress tensor. By using these quantities, one can perform the following calculations:

- Optimization of molecular structures
- Optimization of lattice parameters starting from the experimental structure
- Optimization of internal coordinates while keeping the lattice vectors
- Simultaneous optimization of internal coordinates and the lattice vectors
- Relative stability of absorption sites
- Reaction coordinates, and so on.



Using the gradient at R_0 , we estimate R_{opt} .

Hellmann-Feynman theorem

$$\hat{H}\Psi = E\Psi$$

The derivative of energy consists of only the derivative of potential.

$$\begin{aligned}\frac{\partial E}{\partial R_I} &= \frac{\partial}{\partial R_I} \left(\int \Psi^* H \Psi d\tau \right) \\ &= \int \frac{\partial \Psi^*}{\partial R_I} H \Psi d\tau + \int \Psi^* \frac{\partial H}{\partial R_I} \Psi d\tau + \int \Psi^* H \frac{\partial \Psi}{\partial R_I} d\tau \\ &= \int \Psi^* \frac{\partial H}{\partial R_I} \Psi d\tau + E \int \left(\frac{\partial \Psi^*}{\partial R_I} \Psi + \Psi^* \frac{\partial \Psi}{\partial R_I} \right) d\tau \\ &= \int \Psi^* \frac{\partial H}{\partial R_I} \Psi d\tau \\ &= \int \Psi^* \frac{\partial V}{\partial R_I} \Psi d\tau\end{aligned}$$

In general, Pulay's correction is needed due to the incompleteness of basis functions

$$\frac{\partial E}{\partial R_I} = \text{Hellmann-Feynman force} + \text{Pulay's correction}$$

Calculation of forces in OpenMX

$$\mathbf{F}_i = -\frac{\partial E_{\text{tot}}}{\partial \mathbf{R}_i}$$

$$= -\boxed{\frac{\partial E_{\text{kin}}}{\partial \mathbf{R}_i}} - \boxed{\frac{\partial E_{\text{na}}}{\partial \mathbf{R}_i}} - \boxed{\frac{\partial E_{\text{scc}}}{\partial \mathbf{R}_i}} - \boxed{\frac{\partial E_{\delta\text{ee}}}{\partial \mathbf{R}_i}} - \boxed{\frac{\partial E_{\text{xc}}}{\partial \mathbf{R}_i}} - \boxed{\frac{\partial E_{\text{cc}}}{\partial \mathbf{R}_i}}$$

$$\frac{\partial E_{\delta\text{ee}}}{\partial \mathbf{R}_k} = \sum_{\mathbf{p}} \frac{\partial n(\mathbf{r}_{\mathbf{p}})}{\partial \mathbf{R}_k} \frac{\partial E_{\delta\text{ee}}}{\partial n(\mathbf{r}_{\mathbf{p}})} + \sum_{\mathbf{p}} \frac{\partial n^{\text{a}}(\mathbf{r}_{\mathbf{p}})}{\partial \mathbf{R}_k} \frac{\partial E_{\delta\text{ee}}}{\partial n^{\text{a}}(\mathbf{r}_{\mathbf{p}})}.$$

$$\begin{aligned} \frac{\partial E_{\delta\text{ee}}}{\partial n(\mathbf{r}_{\mathbf{p}})} &= \frac{1}{2} \Delta V \{ \delta V_{\text{H}}(\mathbf{r}_{\mathbf{p}}) + \sum_{\mathbf{q}} \delta n(\mathbf{r}_{\mathbf{q}}) \frac{\partial \delta V_{\text{H}}(\mathbf{r}_{\mathbf{q}})}{\partial n(\mathbf{r}_{\mathbf{p}})} \}, \\ &= \frac{1}{2} \Delta V \{ \delta V_{\text{H}}(\mathbf{r}_{\mathbf{p}}) + \frac{4\pi}{N_{\text{rsg}}} \sum_{\mathbf{G}} \frac{1}{|\mathbf{G}|^2} \sum_{\mathbf{q}} \delta n(\mathbf{r}_{\mathbf{q}}) e^{i\mathbf{G} \cdot (\mathbf{r}_{\mathbf{q}} - \mathbf{r}_{\mathbf{p}})} \}, \\ &= \Delta V \delta V_{\text{H}}(\mathbf{r}_{\mathbf{p}}). \end{aligned}$$



Easy calc.



See the left

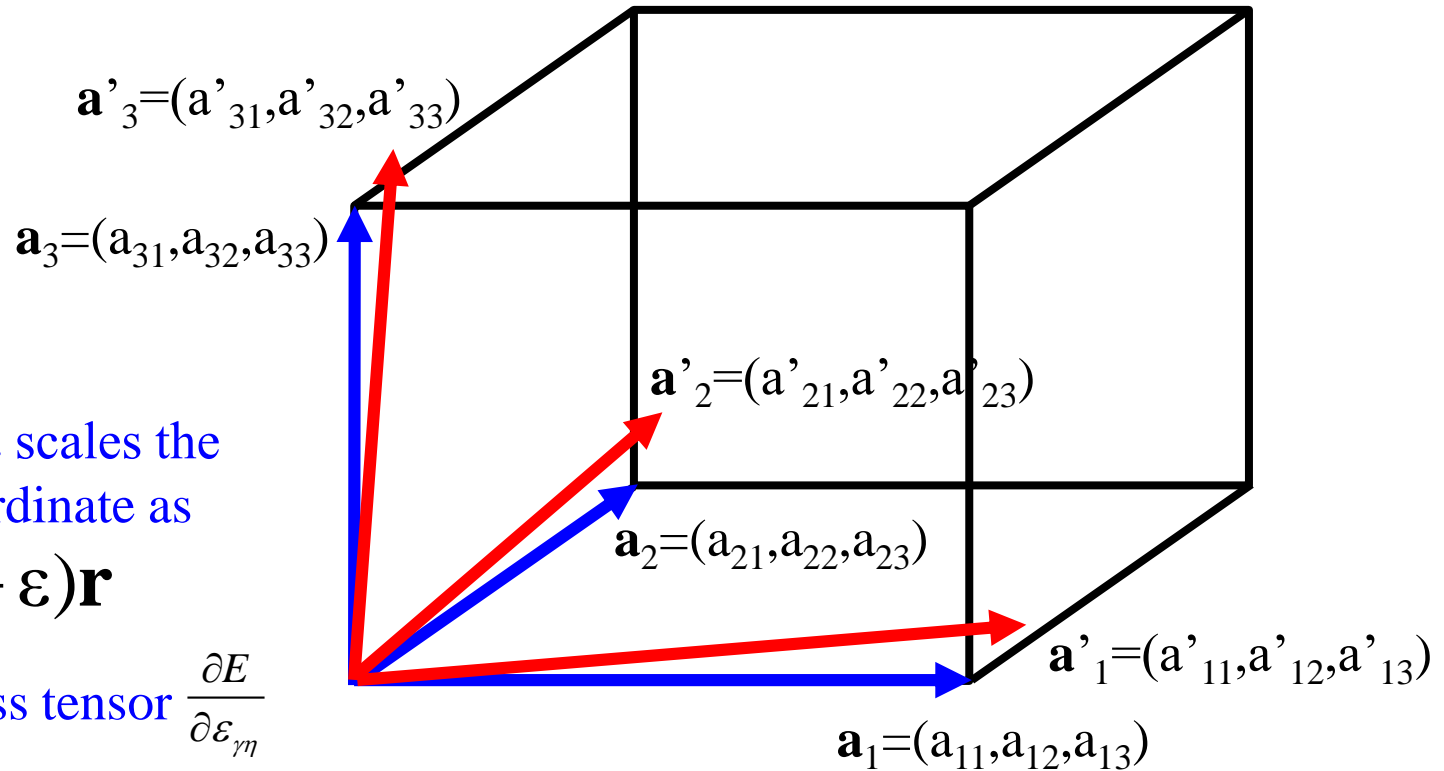
$$\begin{aligned} \frac{\partial E_{\delta\text{ee}}}{\partial n^{\text{a}}(\mathbf{r}_{\mathbf{p}})} &= -\frac{1}{2} \Delta V \{ \delta V_{\text{H}}(\mathbf{r}_{\mathbf{p}}) - \sum_{\mathbf{q}} \delta n(\mathbf{r}_{\mathbf{q}}) \frac{\partial \delta V_{\text{H}}(\mathbf{r}_{\mathbf{q}})}{\partial n^{\text{a}}(\mathbf{r}_{\mathbf{p}})} \}, \\ &= -\frac{1}{2} \Delta V \{ \delta V_{\text{H}}(\mathbf{r}_{\mathbf{p}}) + \frac{4\pi}{N_{\text{rsg}}} \sum_{\mathbf{G}} \frac{1}{|\mathbf{G}|^2} \sum_{\mathbf{q}} \delta n(\mathbf{r}_{\mathbf{q}}) e^{i\mathbf{G} \cdot (\mathbf{r}_{\mathbf{q}} - \mathbf{r}_{\mathbf{p}})} \}, \\ &= -\Delta V \delta V_{\text{H}}(\mathbf{r}_{\mathbf{p}}). \end{aligned}$$

$$\begin{aligned} \frac{\partial n(\mathbf{r}_{\mathbf{p}})}{\partial \mathbf{R}_k} &= \sum_{i\alpha,j\beta} \sum_{\nu} \{ \frac{\partial c_{i\alpha,\nu}^*}{\partial \mathbf{R}_k} c_{j\beta,\nu} \chi_{i\alpha}(\mathbf{r}) \chi_{j\beta}(\mathbf{r}) + c_{i\alpha,\nu}^* \frac{\partial c_{j\beta,\nu}}{\partial \mathbf{R}_k} \chi_{i\alpha}(\mathbf{r}_{\mathbf{p}}) \chi_{j\beta}(\mathbf{r}_{\mathbf{p}}) \} \\ &\quad + 2 \sum_{\alpha,j\beta} \rho_{k\alpha,j\beta} \frac{\partial \chi_{k\alpha}(\mathbf{r}_{\mathbf{p}})}{\partial \mathbf{R}_k} \chi_{j\beta}(\mathbf{r}_{\mathbf{p}}). \end{aligned}$$

$$\begin{aligned} \frac{\partial E_{\text{xc}}}{\partial \mathbf{R}_k} &= \sum_{\mathbf{p}} \frac{\partial n(\mathbf{r}_{\mathbf{p}})}{\partial \mathbf{R}_k} \frac{\partial E_{\text{xc}}}{\partial n(\mathbf{r}_{\mathbf{p}})}, \\ &= \Delta V \sum_{\mathbf{p}} \frac{\partial n(\mathbf{r}_{\mathbf{p}})}{\partial \mathbf{R}_k} v_{\text{xc}}(n(\mathbf{r}_{\mathbf{p}})). \end{aligned}$$

Forces are always analytic at any grid fineness and at zero temperature, even if numerical basis functions and numerical grids.

Stress tensor



Strain tensor ε scales the Cartesian coordinate as

$$\mathbf{r}' = (\mathbf{I} + \varepsilon)\mathbf{r}$$

Then, the stress tensor $\frac{\partial E}{\partial \varepsilon_{\gamma\eta}}$

can be related the energy derivative w.r.t. cell vectors $\frac{\partial E}{\partial a_{ij}}$ by

$$\frac{\partial E}{\partial a_{ij}} = \sum_{\gamma\eta} \frac{\partial \varepsilon_{\gamma\eta}}{\partial a_{ij}} \frac{\partial E}{\partial \varepsilon_{\gamma\eta}} = \sum_{\gamma} b_{\gamma i} \frac{\partial E}{\partial \varepsilon_{\gamma j}}$$

where

$$b = a^{-1}$$

Stress tensor in OpenMX

In OpenMX, the total energy is defined by

$$E_{\text{tot}} = E_{\text{kin}} + E_{\text{na}} + E_{\text{ec}}^{(\text{NL})} + E_{\delta\text{ee}} + E_{\text{XC}} + E_{\text{scc}}$$

Thus, at least there are six contributions to stress tensor.

$$\frac{\partial E_{\text{tot}}}{\partial \varepsilon_{\gamma\eta}} = \boxed{\frac{\partial E_{\text{kin}}}{\partial \varepsilon_{\gamma\eta}}} + \boxed{\frac{\partial E_{\text{na}}}{\partial \varepsilon_{\gamma\eta}}} + \boxed{\frac{\partial E_{\text{ec}}^{(\text{NL})}}{\partial \varepsilon_{\gamma\eta}}} + \boxed{\frac{\partial E_{\delta\text{ee}}}{\partial \varepsilon_{\gamma\eta}}} + \boxed{\frac{\partial E_{\text{XC}}}{\partial \varepsilon_{\gamma\eta}}} + \boxed{\frac{\partial E_{\text{scc}}}{\partial \varepsilon_{\gamma\eta}}}$$

- **The terms** are decomposed to derivatives of matrix elements and overlap stress, leading to rather straightforward analytic calculations.
- **The term** is analytically evaluated in reciprocal space.
- **The term** is analytically evaluated in real space with a carefully derived formula.

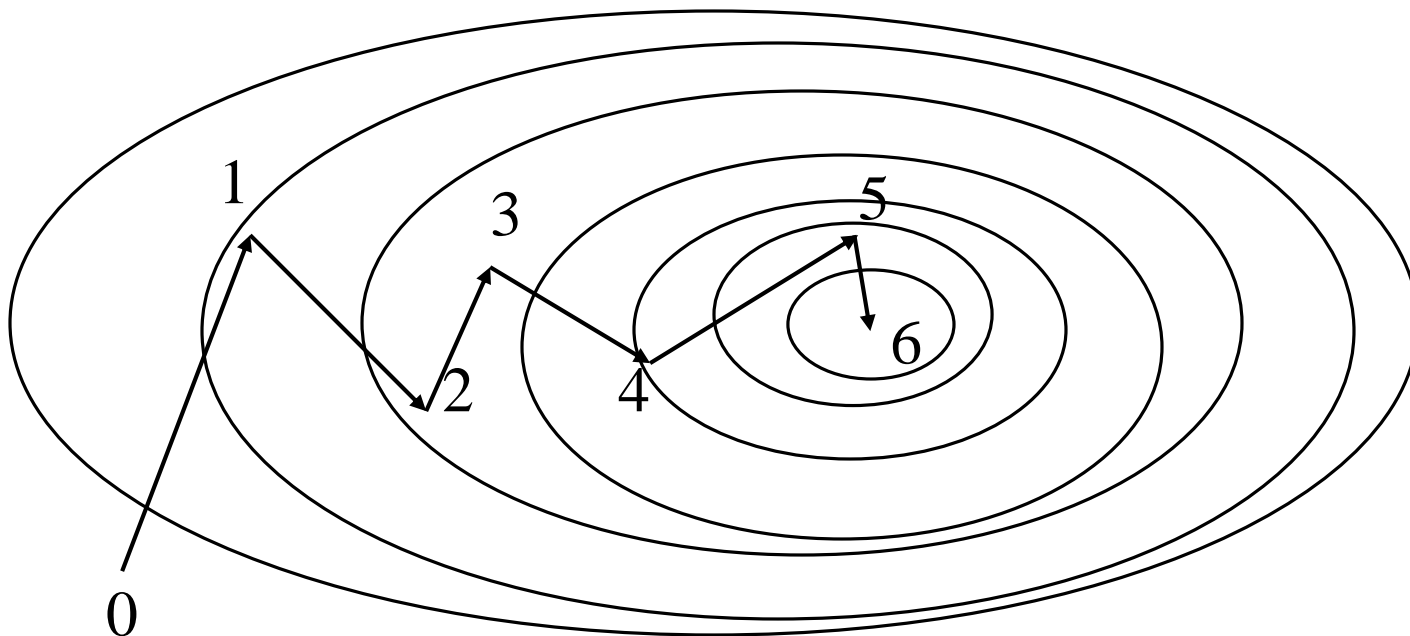
The computational time is almost the same as that for the force calculation.

Geometry optimization

To quantitatively investigate structural, physical, and chemical properties of molecules and solids, it would be important to obtain optimized structures.

Steepest decent (SD) method

The structure is changed along the steepest decent step by step.



It may not be so efficient.

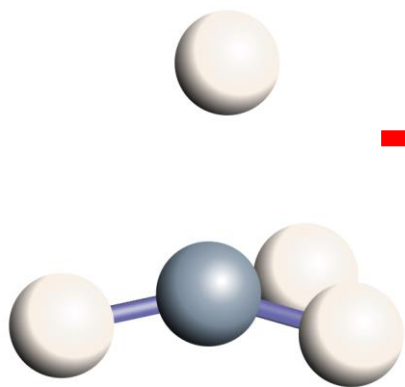
Geometry optimization by the SD method

Let us change the x -coordinate of carbon atom in a methane molecule to 0.3 Å as

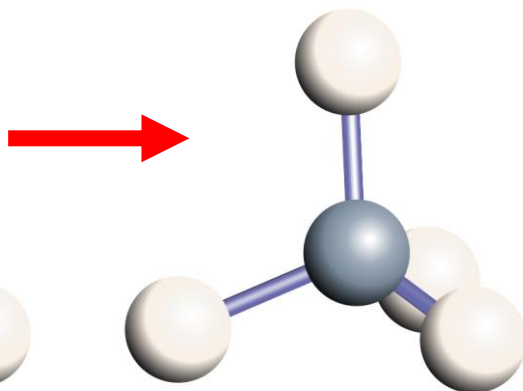
```
<Atoms.SpeciesAndCoordinates  
 1  C   0.300000  0.000000  0.000000  2.0  2.0  
 2  H   -0.889981 -0.629312  0.000000  0.5  0.5  
 3  H    0.000000  0.629312 -0.889981  0.5  0.5  
 4  H    0.000000  0.629312  0.889981  0.5  0.5  
 5  H    0.889981 -0.629312  0.000000  0.5  0.5  
Atoms.SpeciesAndCoordinates>
```

Using “Methane2.dat” in the directory
“work”, you can trace the calculation.

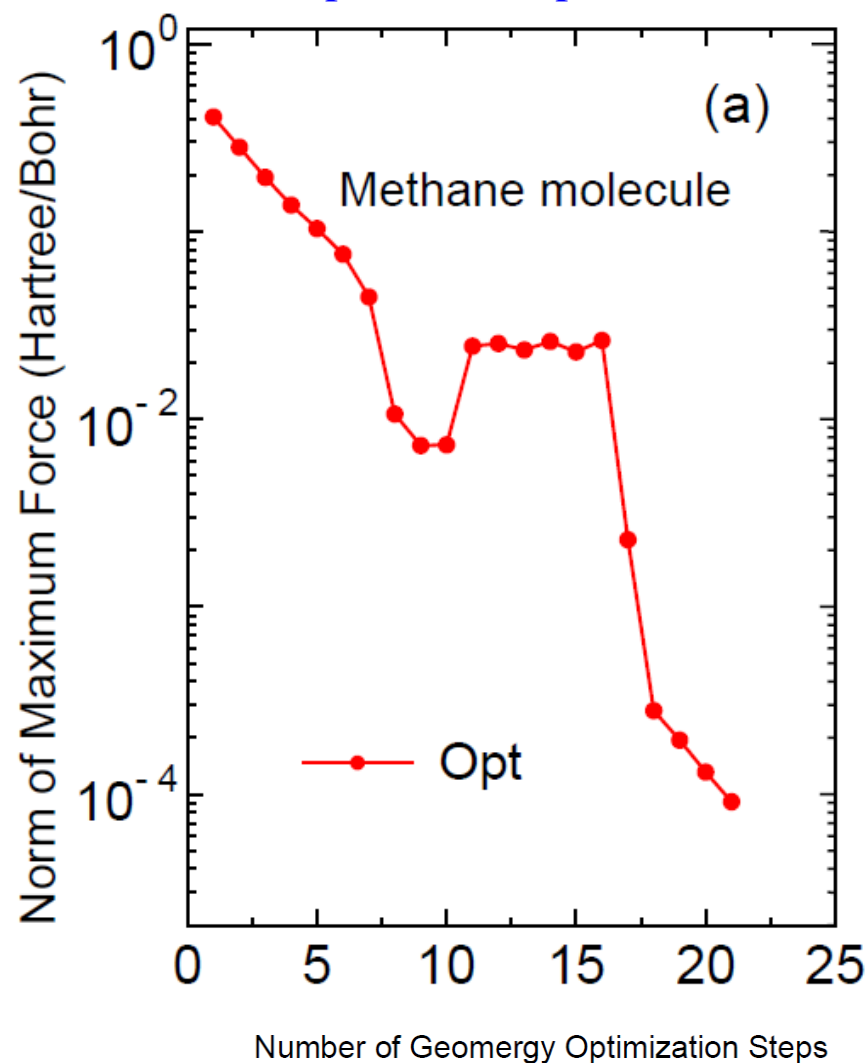
Initial structure



Final structure



Optimization process



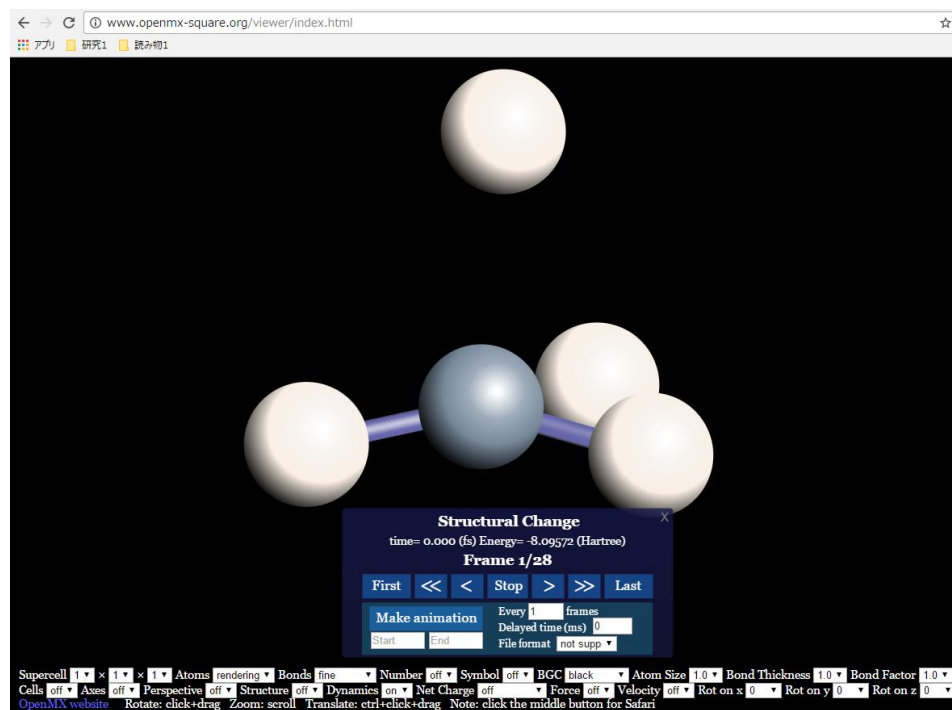
Relevant output files for the geometry optimization

In [met2.out](#), the history of optimization can be confirmed.

```
*****
*****
***** History of geometry optimization *****
*****
```

MD_iter	SD_scaling	Maximum force (Hartree/Bohr)	Maximum step (Ang)	Utot (Hartree)
1	1.25981733	0.40873710	0.10583545	-8.09571722
2	1.25981733	0.12000148	0.08000099	-8.16523842
3	1.25981733	0.06115237	0.04076824	-8.18400222
4	1.25981733	0.01811189	0.01207460	-8.18831175
5	3.14954331	0.01076505	0.01794175	-8.18898468
6	3.14954331	0.00576811	0.00961351	-8.18980390
7	3.14954331	0.00355034	0.00591724	-8.19010991
8	3.14954331	0.00255760	0.00426266	-8.19022887
9	7.87385828	0.00218904	0.00912099	-8.19027446
10	7.87385828	0.00863395	0.03597478	-8.19023586
11	1.57477166	0.04692594	0.03910495	-8.18816953
12	1.57477166	0.01357319	0.01131099	-8.19012703
13	3.93692914	0.00406864	0.00847634	-8.19029047
14	3.93692914	0.00915707	0.01907723	-8.19022710
15	0.78738583	0.02067017	0.00861257	-8.18990108
16	0.78738583	0.00721609	0.00300671	-8.19025699
17	1.96846457	0.00255359	0.00265999	-8.19030094
18	1.96846457	0.00163789	0.00170613	-8.19030460
19	1.96846457	0.00105501	0.00109897	-8.19030613
20	1.96846457	0.00068667	0.00071528	-8.19030671
21	4.92116143	0.00044434	0.00115713	-8.19030697
22	4.92116143	0.00138402	0.00360421	-8.19030537
23	0.98423229	0.00427346	0.00222576	-8.19028994
24	0.98423229	0.00078570	0.00040922	-8.19030656
25	2.46058071	0.00013628	0.00017745	-8.19030709
26	2.46058071	0.00014411	0.00018765	-8.19030714
27	0.49211614	0.00015118	0.00003937	-8.19030709
28	0.49211614	0.00008899	0.00002317	-8.19030713

By dragging and dropping [met2.md](#) to [OpenMX Viewer](#), the optimization process can be easily visualized.



Geometry optimization by Newton-type methods

By Taylor-expanding, we have

$$E = E_0 + \sum_i^{3N} \left(\frac{\partial E}{\partial x_i} \right)_0 (x_i - x_i^{(0)}) + \frac{1}{2} \sum_{i,j}^{3N} \left(\frac{\partial^2 E}{\partial x_i \partial x_j} \right)_0 (x_i - x_i^{(0)}) (x_j - x_j^{(0)}) + \dots,$$

The derivative of the total energy w.r.t. coordinates leads to

$$\frac{\partial E}{\partial x_k} = \left(\frac{\partial E}{\partial x_k} \right)_0 + \sum_i^{3N} \left(\frac{\partial^2 E}{\partial x_k \partial x_i} \right)_0 (x_i - x_i^{(0)}).$$

$$\frac{\partial E}{\partial x_k} = 0 \quad \longrightarrow \quad \begin{pmatrix} \left(\frac{\partial^2 E}{\partial x_1 \partial x_1} \right)_0 & \left(\frac{\partial^2 E}{\partial x_1 \partial x_2} \right)_0 & \cdots \\ \left(\frac{\partial^2 E}{\partial x_2 \partial x_1} \right)_0 & \left(\frac{\partial^2 E}{\partial x_2 \partial x_2} \right)_0 & \cdots \\ \cdots & \cdots & \cdots \end{pmatrix} \begin{pmatrix} (x_1 - x_1^{(0)}) \\ (x_2 - x_2^{(0)}) \\ \cdots \end{pmatrix} = - \begin{pmatrix} \left(\frac{\partial E}{\partial x_1} \right)_0 \\ \left(\frac{\partial E}{\partial x_2} \right)_0 \\ \cdots \end{pmatrix}.$$

$$H \Delta \mathbf{x} = -\mathbf{g},$$

By solving the Eq. for $\Delta \mathbf{x}$, we have

$$\mathbf{x}^{(n+1)} = \mathbf{x}^{(n)} - (H^{(n)})^{-1} \mathbf{g}^{(n)}.$$

If the Hessian matrix H can be computed, the method is efficient.
However, it may be difficult to evaluate H in general.

Geometry optimization by Newton-type methods

The geometry optimization in OpenMX is based on quasi Newton methods. In Ver. 3.9, the following four methods are available.

$$\mathbf{r}_{\text{new}} = \mathbf{r}_{\text{DIIS}} + \Delta\mathbf{r} \qquad \Delta\mathbf{r} = -H^{-1}\mathbf{g}_{\text{DIIS}}$$

Methods of calculating approximate Hessian matrix H

DIIS	BFGS	RF(rational function)	EF(eigenvector following)
H=I	BFGS	BFGS+RF	BFGS plus monitoring of eigenvalues of H

Broyden-Fletcher-Goldfarb-Shanno (BFGS) method

$$H_k = H_{k-1} + \frac{|\Delta\mathbf{g}_k\rangle\langle\Delta\mathbf{g}_k|}{\langle\Delta\mathbf{g}_k|\Delta\mathbf{r}_k\rangle} - \frac{|H_k\Delta\mathbf{r}_k\rangle\langle\Delta\mathbf{r}_kH_k|}{\langle\Delta\mathbf{r}_k|H_k|\Delta\mathbf{r}_k\rangle}$$

If the inner product in the red box is positive, the positive definiteness of H is guaranteed.

Approximate initial Hessian by Schlegel

Schlegel proposed a way of constructing an approximate Hessian. A force constant for every pair of elements is fitted to the following formula, where dataset were constructed by B3LYP calculations.

$$F = \frac{A}{(r - B)^3}$$

H.B. Schlegel, Theoret. Chim. Acta (Berl.) 66, 333 (1984); J.M. Wittbrodt and H.B. Schlegel, J. Mol. Struc. (Theochem) 398-399, 55 (1997).

Parameter *B* for Badger's rule computed at the B3LYP level of theory

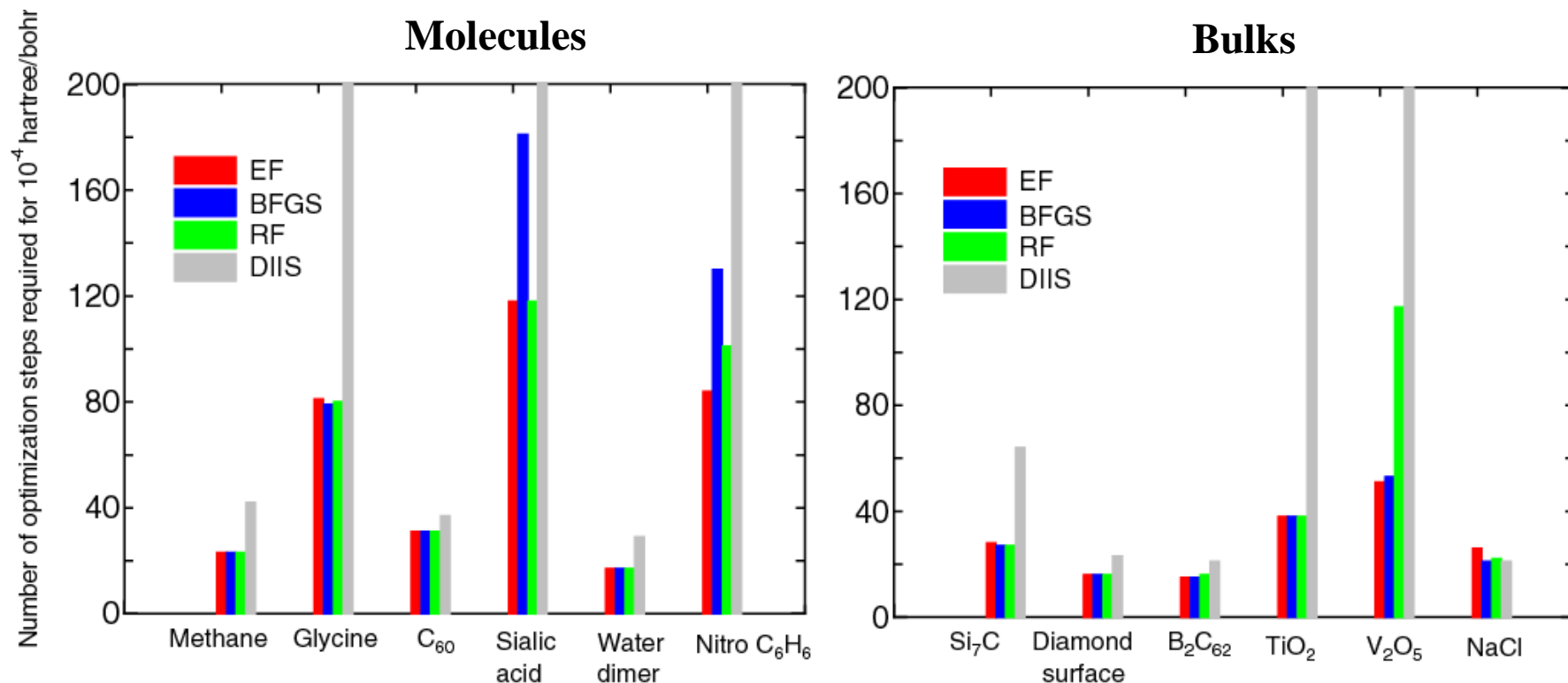
Period	1 H	2 Li-F	3 Na-Cl	4 K-Br	5 Rb-I	6 Cs-At
1	- 0.2573	0.3401	0.6937	0.7126	0.8335	0.9491
2		0.9652	1.2843	1.4725	1.6549	1.7190
3			1.6925	1.8238	2.1164	2.3185
4				2.0203	2.2137	2.5206
5					2.3718	2.5110

Suppose the total energy is given by the sum of pairwise potentials. Then, the derivatives lead to the following relation:

$$V_2 = \frac{1}{2} \sum_i \left(\sum_{Rn} \sum_j f(|r_i + R_n - r_j|) \right) \quad H = BF$$

where B is the B-matrix of Wilson, H is the approximate Hessian in Cartesian coordinate.

Comparison of four methods



- The benchmark calculations imply that the EF and RF work well.
- Large molecules with structural large freedom are hard to get convergence.

The input file and output files for the benchmark calculations are available in `openmx3.9/work/geoopt_example`.

Keywords relevant to geometry optimization

MD.Type	EF	# Opt DIIS BFGS RF EF
MD.Opt.DIIS.History	3	# default=3
MD.Opt.StartDIIS	5	# default=5
MD.Opt.EveryDIIS	200	# default=200
MD.maxIter	100	# default=1
MD.Opt.criterion	1.0e-4	# default=0.0003 (Hartree/Bohr)

The behavior of the quasi Newton methods can be controlled by the following two keywords:

MD.Opt.DIIS.History	3 # default=3
MD.Opt.StartDIIS	5 # default=5

The keyword 'MD.Opt.DIIS.History' gives the number of previous steps to estimate the optimized structure used in the geometry optimization by 'DIIS', 'EF', and 'RF'. The default value is 3.

The geometry optimization step at which 'DIIS', 'EF', or 'RF' starts is specified by the keyword 'MD.Opt.StartDIIS'. The geometry optimization steps before starting the DIIS-type method is performed by the steepest decent method. The default value is 5.

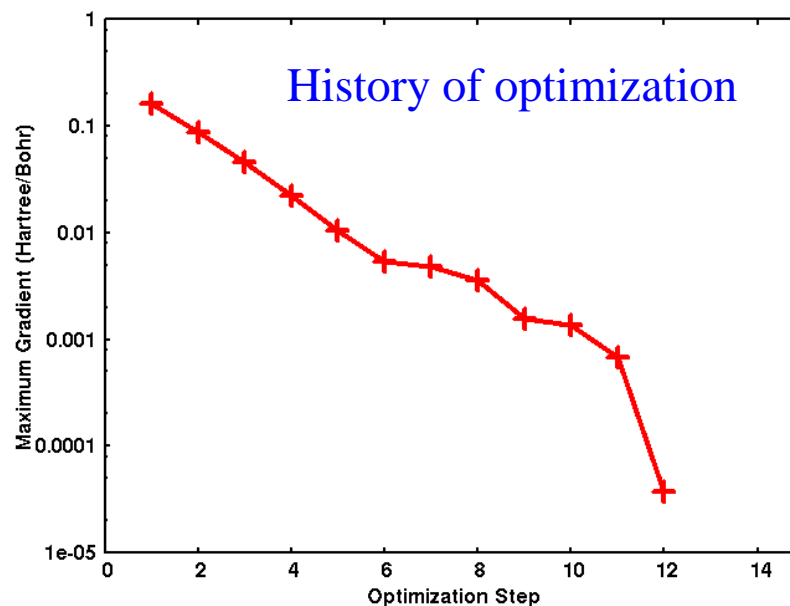
Variable cell optimization

Let us start optimization of diamond lattice with a displacement as

```
Atoms.Number      2
Atoms.SpeciesAndCoordinates.Unit  frac # Ang|AU
<Atoms.SpeciesAndCoordinates
  1  C  0.10000000000000  0.00000000000000  -0.05000000000000  2.0  2.0
  2  C  0.25000000000000  0.25000000000000  0.25000000000000  2.0  2.0
Atoms.SpeciesAndCoordinates>
Atoms.UnitVectors.Unit      Ang # Ang|AU
<Atoms.UnitVectors
  1.6400  1.6400  0.0000
  1.6400  0.0000  1.6400
  0.0000  1.6400  1.6400
Atoms.UnitVectors>
```

Relevant keywords:

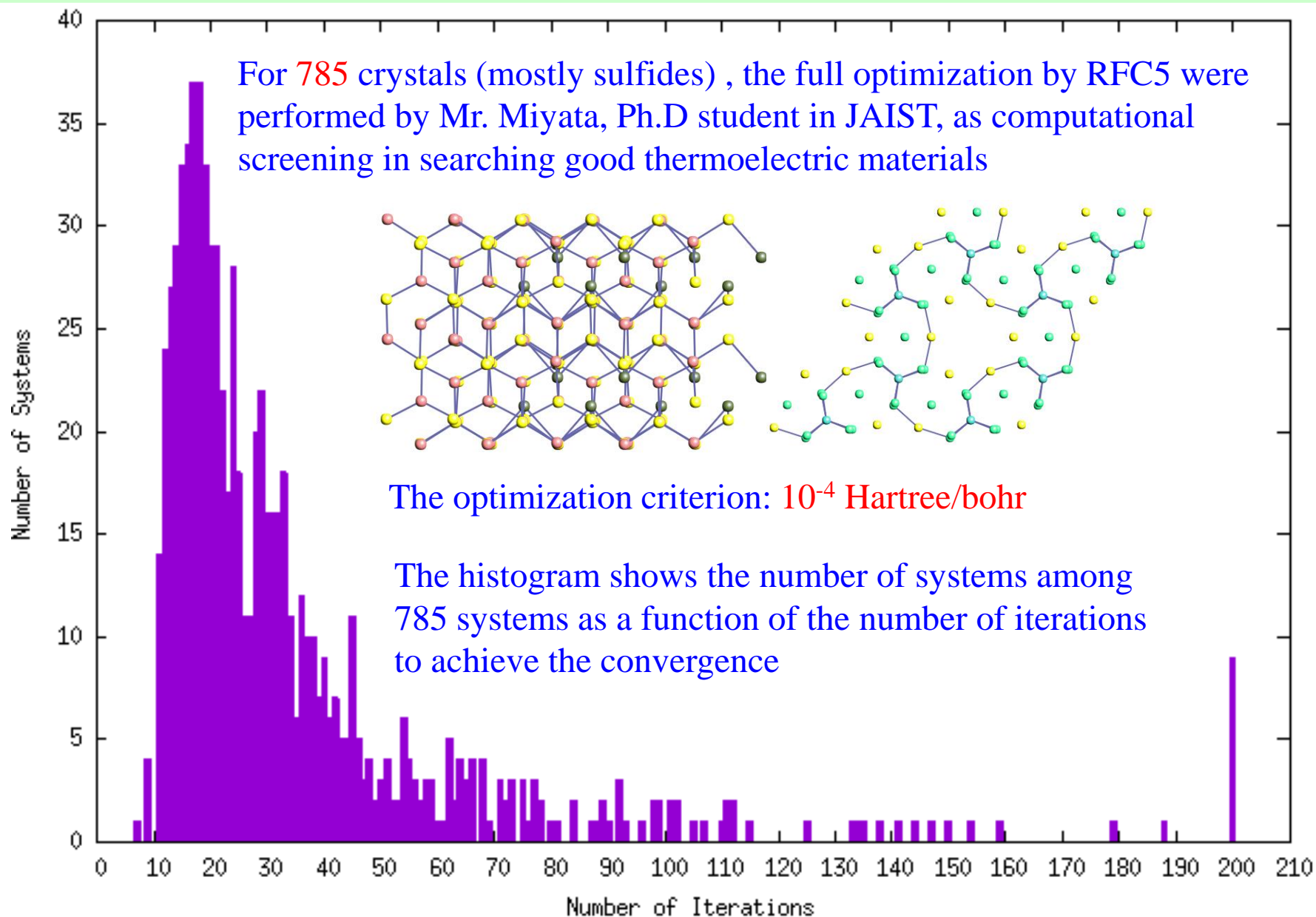
```
MD.Type      RFC5
MD.Opt.DIIS.History  3
MD.Opt.StartDIIS    7
MD.Opt.EveryDIIS    100000
MD.maxIter      100
MD.TimeStep     1.0
MD.Opt.criterion  0.0003
```



The calculation can be traced by “Cdia-RF5.dat” in work/cellopt_example.

Please see also the page 74 in the manual.

Benchmark calculations of RFC5



Optimization of the enthalpy

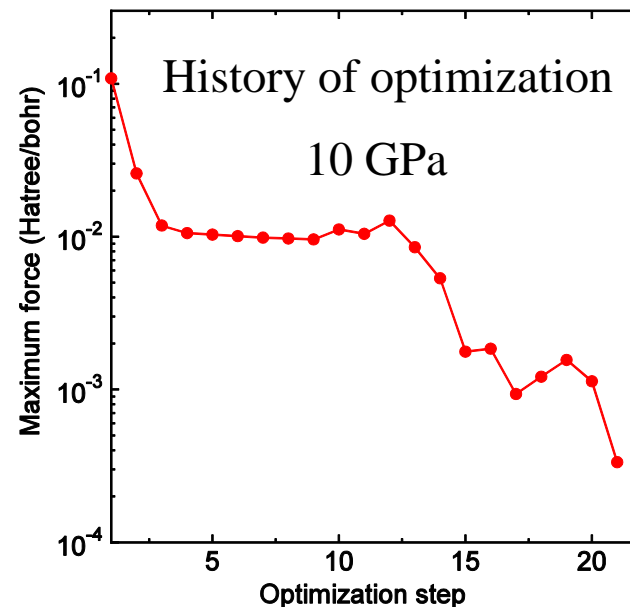
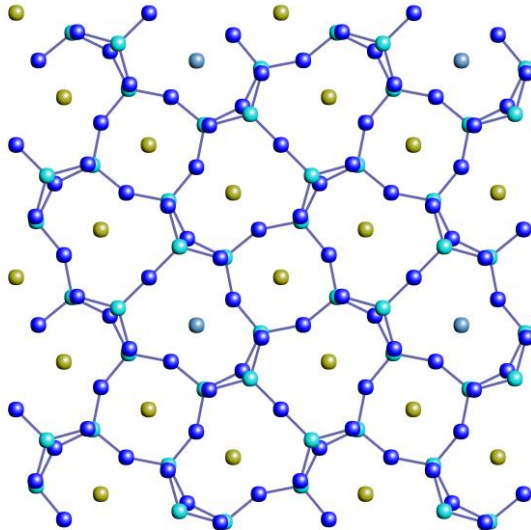
Under an external pressure p , the structural optimization can be performed by minimizing the enthalpy defined with

$$H = E + pV$$

The stress tensor is easily calculated by

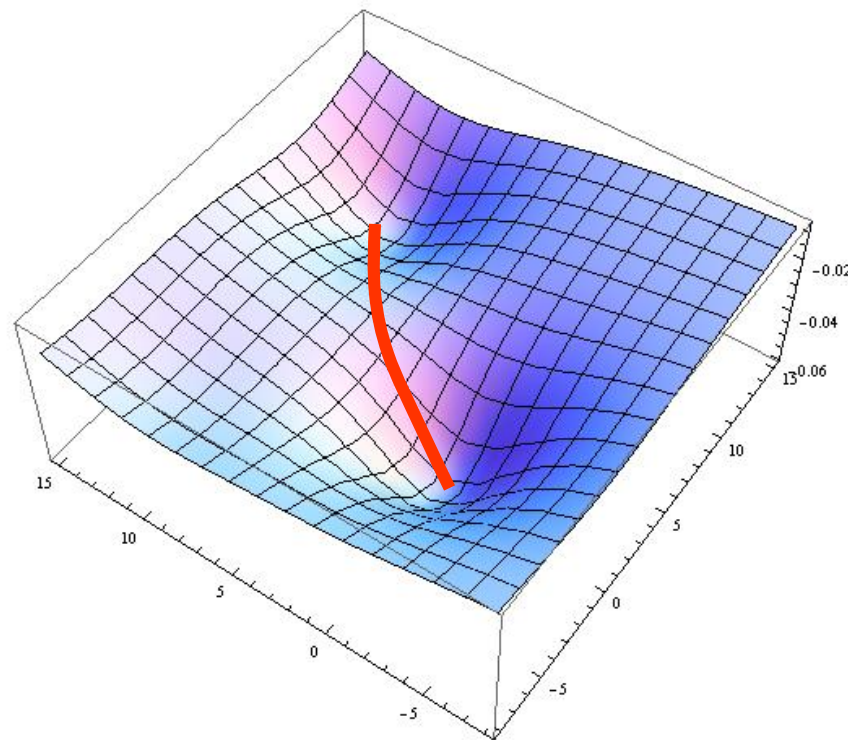
$$\frac{\partial H}{\partial \varepsilon_{\gamma\eta}} = \frac{\partial E}{\partial \varepsilon_{\gamma\eta}} + p \frac{\partial V}{\partial \varepsilon_{\gamma\eta}} = \frac{\partial E}{\partial \varepsilon_{\gamma\eta}} + pV \delta_{\gamma\eta}$$

$\text{La}_3\text{Si}_6\text{N}_{11}:\text{Ce}_{2c}$



Finding reaction coordinates: Nudged Elastic Band (NEB) method

The total energy of a system is a function in a hyperspace of $(3N-3)$ dimensions. The reaction coordinate is defined by a minimum energy pathway connecting two local minima in the hyperspace. The nudged elastic band (NEB) method is a very efficient tool to find the minimum energy pathway.



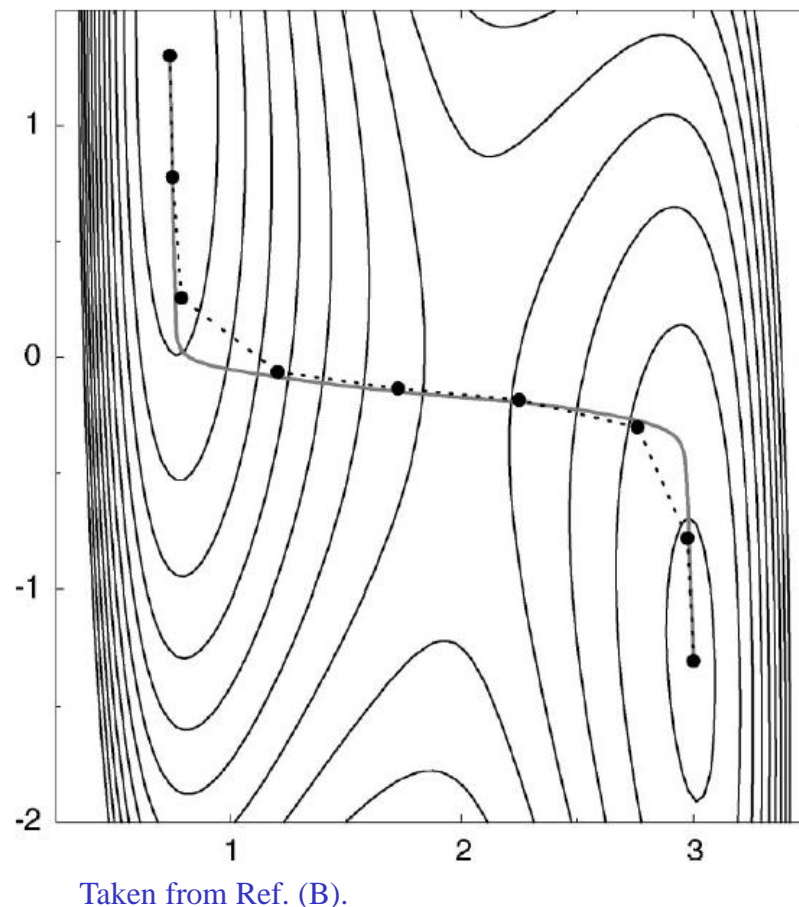
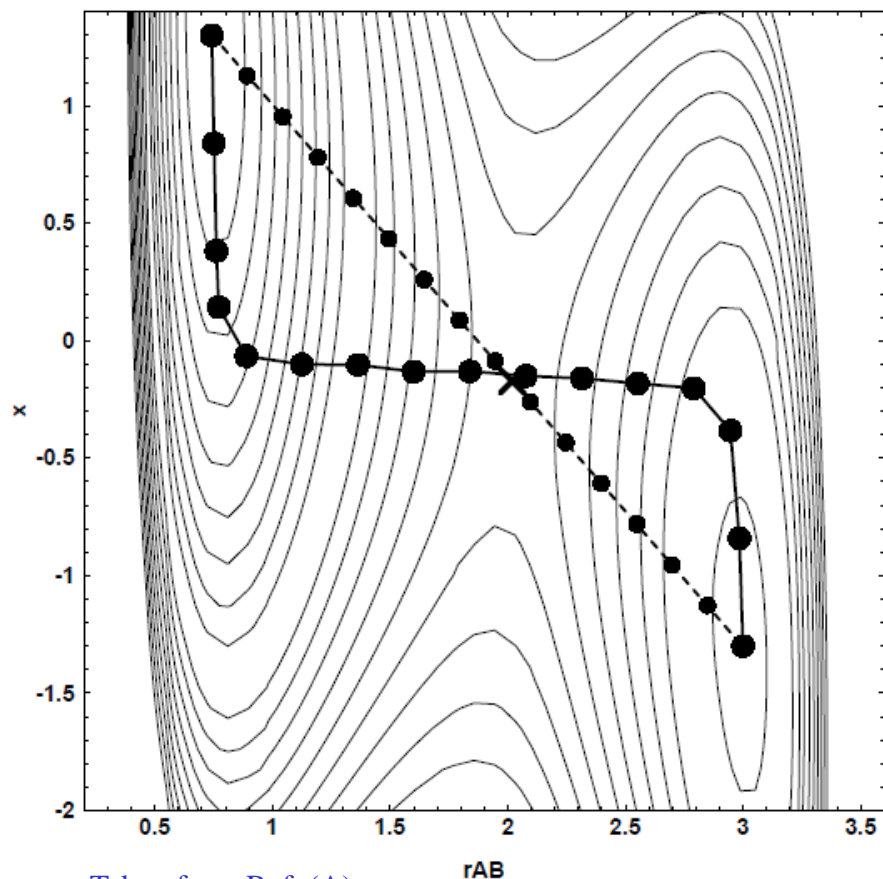
(A) H. Jonsson, G. Mills, and K. W. Jacobsen, in *Classical and Quantum Dynamics in Condensed Phase Simulations*, edited by B. J. Berne, G. Ciccotti, and D. F. Coker (World Scientific, Singapore, 1998), p. 385.

(B) G. Henkelman and H. Jonsson, JCP 113, 9978 (2000).

In later slides, they are referred as Refs. (A) and (B).

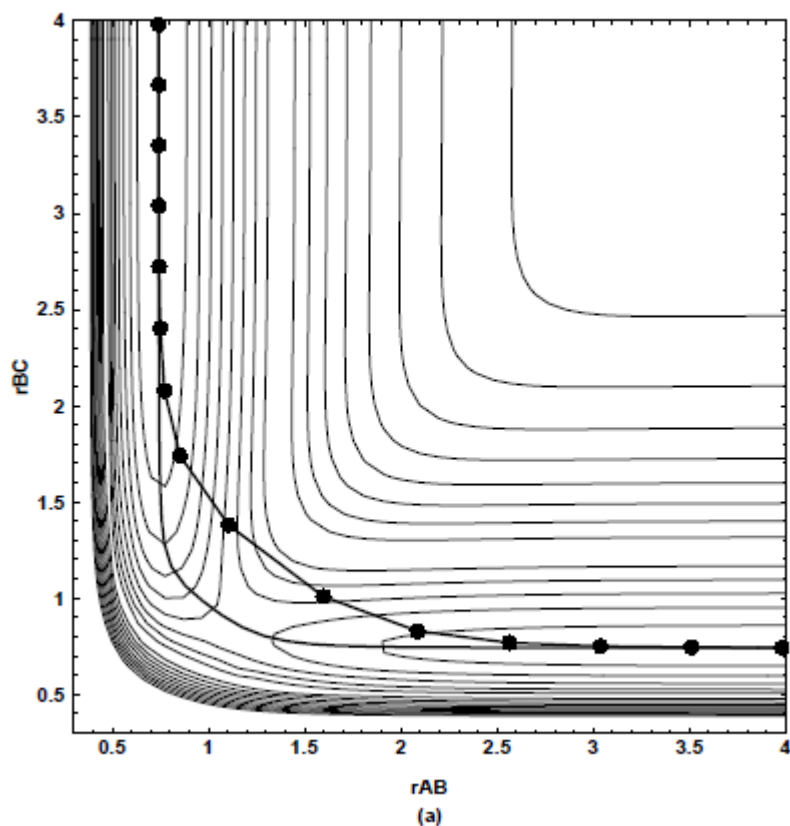
Nudged Elastic Band (NEB) method

The NEB method provides a way to find a minimum energy pathway (MEP) connecting two local minima by introducing images interacting each other located on a trial pathway.



Plain Elastic Band (PEB) method

A simple idea to find a MEP is to introduce an interaction between neighboring images by a spring. The optimization of the object function S tries to shorten the length of MEP.



Taken from Ref. (A).

$$S(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_{P-1}) = \sum_{i=0}^P E(\mathbf{R}_i) + \sum_{i=1}^P \frac{Pk}{2} (\mathbf{R}_i - \mathbf{R}_{i-1})^2$$

$$\frac{\partial S(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_{P-1})}{\partial \mathbf{R}_k} \rightarrow 0$$

The idea is called a plain elastic band (PEB) method. However, the PEB method tends to cause a drift of energy pathway as shown in the left figure.

One should consider another way to avoid the drift of the energy pathway.

Nudged Elastic Band (NEB) method

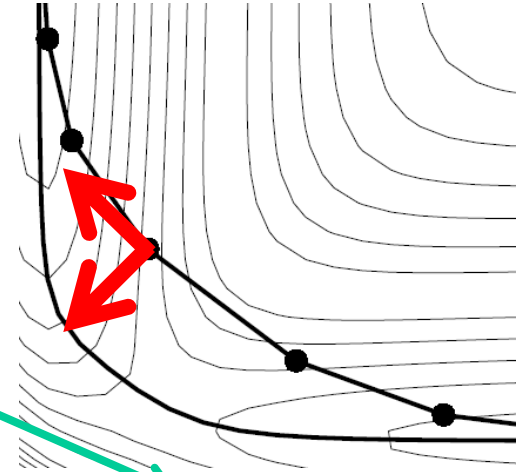
The force can be divided to two contributions:

Parallel force

Perpendicular force

$$S(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_{P-1}) = \sum_{i=0}^P E(\mathbf{R}_i) + \sum_{i=1}^P \frac{Pk}{2} (\mathbf{R}_i - \mathbf{R}_{i-1})^2$$

causing non-equidistance
distribution of images along
the energy pathway.



$$\left(\frac{\partial E(\mathbf{R}_k)}{\partial \mathbf{R}_k} \right)_{\parallel} \quad \left(\frac{\partial E(\mathbf{R}_k)}{\partial \mathbf{R}_k} \right)_{\perp} \quad \left(\frac{\partial E_{\text{spring}}}{\partial \mathbf{R}_k} \right)_{\parallel} \quad \left(\frac{\partial E_{\text{spring}}}{\partial \mathbf{R}_k} \right)_{\perp}$$

causing the drift of energy pathway
upward along the perpendicular
direction.

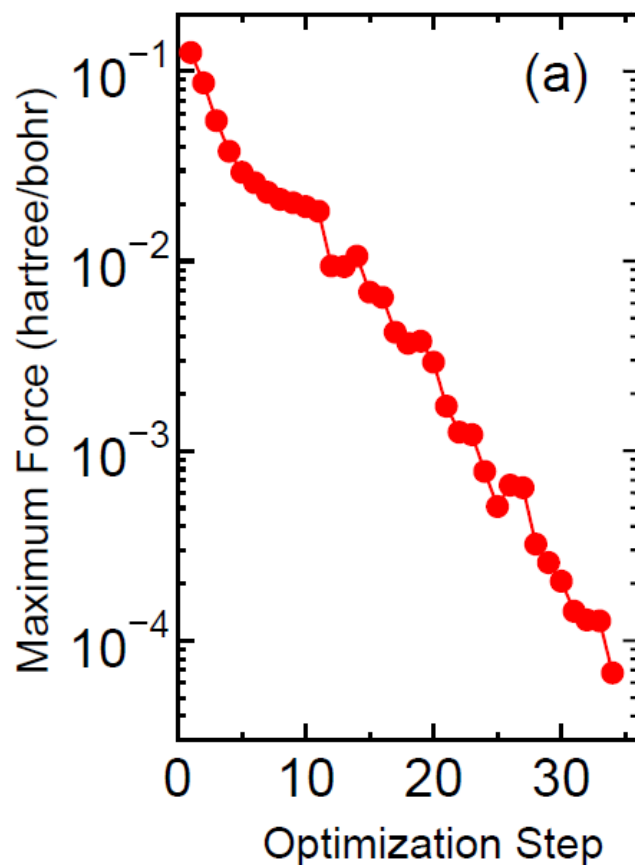
To calculate the
force, only two
terms are taken into
account among
four contributions.

$$\mathbf{F}_k = - \left(\frac{\partial E(\mathbf{R}_k)}{\partial \mathbf{R}_k} \right)_{\perp} - \left(\frac{\partial E_{\text{spring}}}{\partial \mathbf{R}_k} \right)_{\parallel}$$

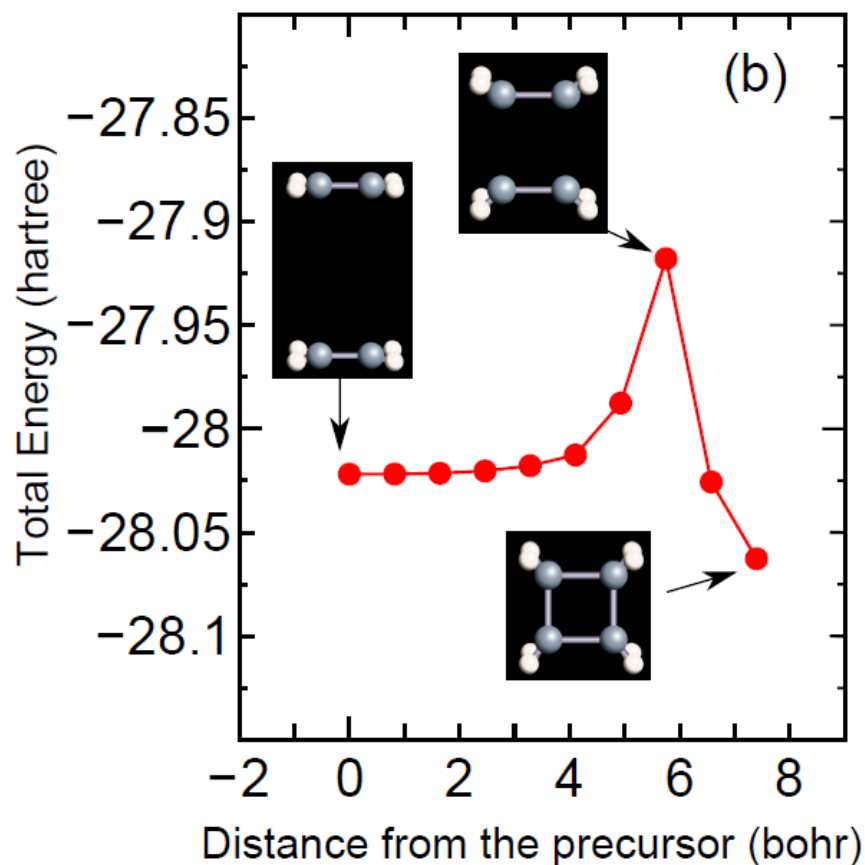
The treatment allows
us to avoid the drift of
energy pathway, while
the physical meaning
of the object function is
not clear anymore.

2+2 reaction of ethylene molecules

Optimization history

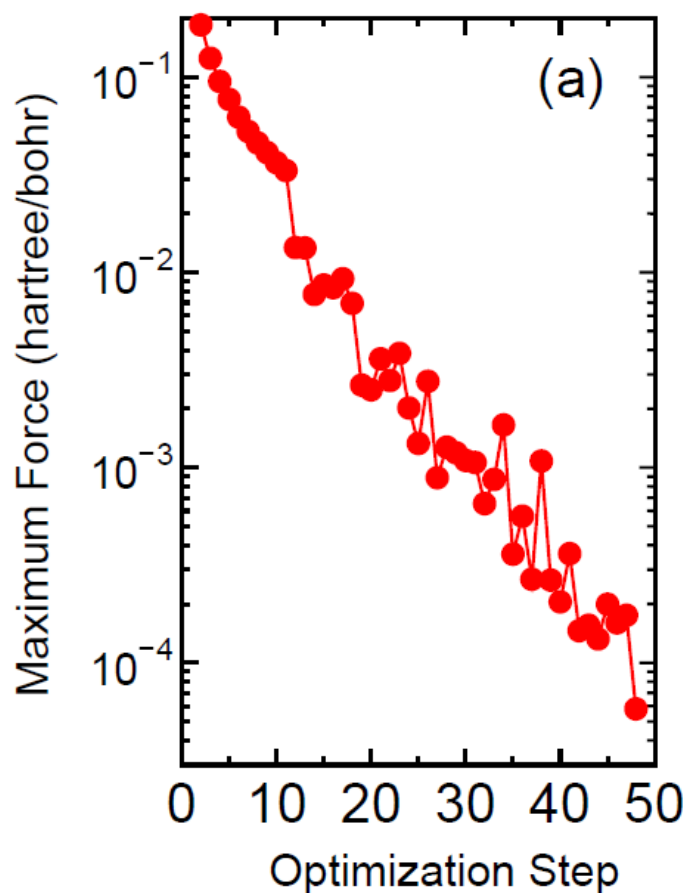


Minimum energy path way and corresponding structures

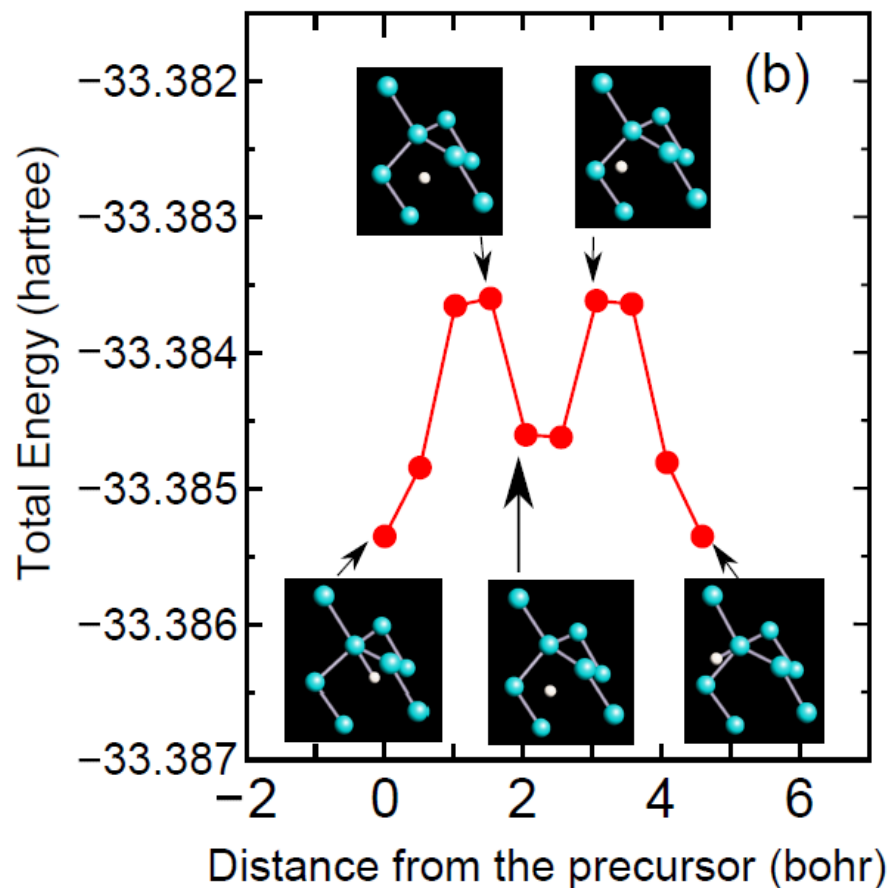


Diffusion of H atom in bulk Si

Optimization history



Minimum energy path way
and corresponding structures

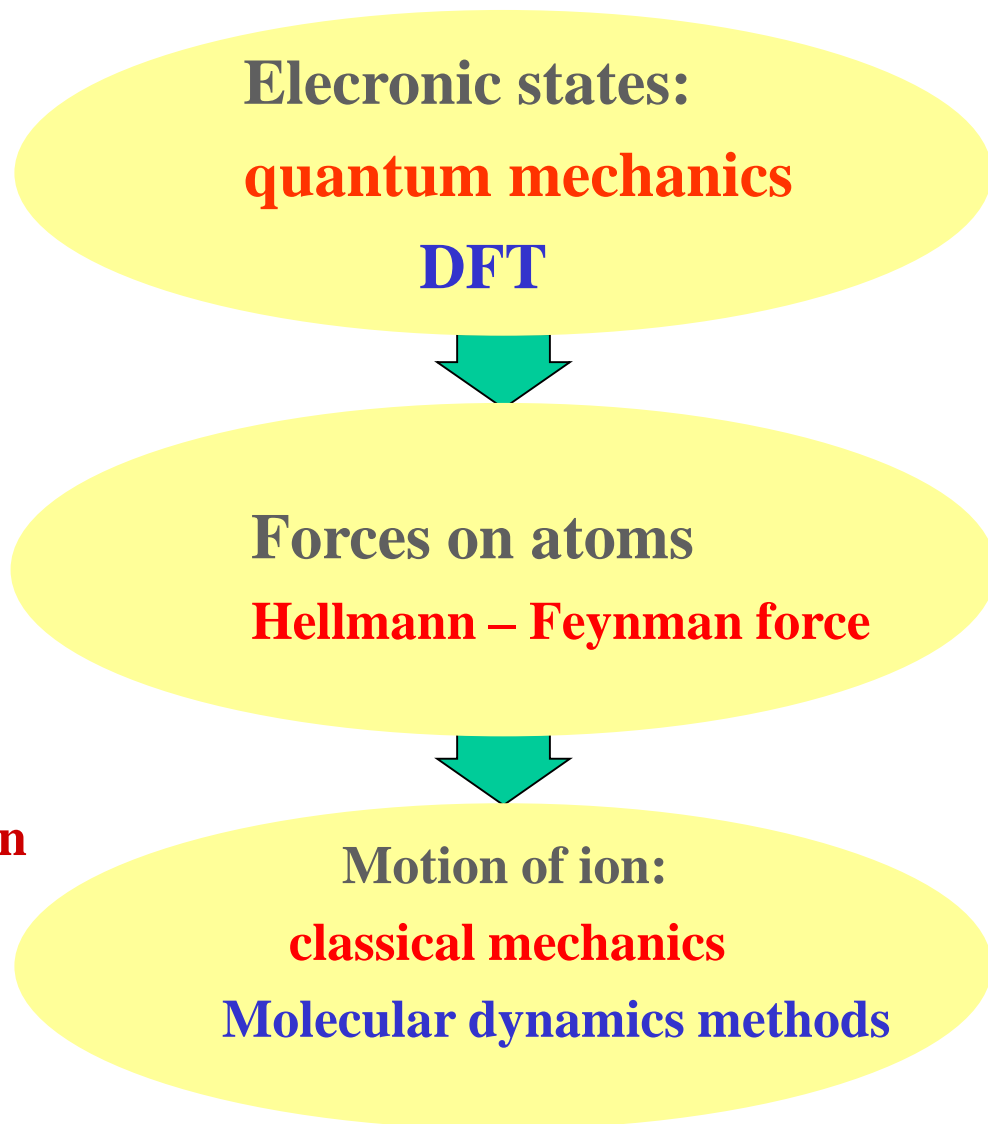


What is FPMD ?

In usual molecular dynamics simulations, the total energy is expressed by classical model potentials. On the other hand, in the FPMD the total energy and forces on atoms are evaluated based on quantum mechanics.

It enables us to treat bond formation and breaking.

Simulation of chemical reactions



Time evolution of Newton eq. by the Verlet method

Taylor expansion of the coordinate R at time t

$$R_I(t \pm \Delta t) = R_I(t) \pm \frac{dR_I(t)}{dt}\Delta t + \frac{1}{2}\frac{d^2R_I(t)}{dt^2}(\Delta t)^2 \quad \dots (1)$$

Sum of (1) $R_I(t + \Delta t) + R_I(t - \Delta t) = 2R_I(t) + \frac{d^2R_I(t)}{dt^2}(\Delta t)^2$

Diff of (1) $R_I(t + \Delta t) - R_I(t - \Delta t) = 2\frac{dR_I(t)}{dt}\Delta t$

Definition of velocity and acceleration $v_I(t) = \frac{dR_I(t)}{dt} \quad a_I(t) = \frac{d^2R_I(t)}{dt^2}$

Velocity at t and R at $t+\Delta t$ are given by

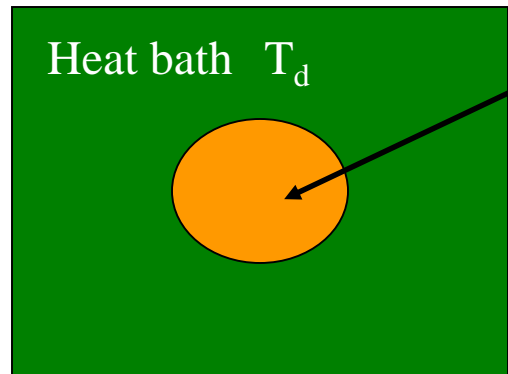
$$v_I(t) = \frac{1}{2\Delta t} [R_I(t + \Delta t) - R_I(t - \Delta t)]$$

$$R_I(t + \Delta t) = 2R_I(t) - R_I(t - \Delta t) + a_I(t)(\Delta t)^2$$

$$a_I(t) = -\frac{\nabla_I E}{m_I}$$

Temperature control by the Nose-Hoover method

Micro-canonical ensemble



Let the part of system be a canonical ensemble.

$$T = \frac{2 \sum_i^N \frac{\mathbf{p}_i^2}{2m_i}}{3Nk_B}$$

$$t_v = \frac{1}{Q} \left(2 \sum_i^N \frac{\mathbf{p}_i^2}{2m_i} - 3Nk_B T_d \right)$$

Conserved quantity

$$H = U_{\text{tot}} + U_{\text{kin}} + \frac{Q}{2} \zeta^2 + 3Nk_B T_d \ln s$$

$$\frac{d\mathbf{q}_i}{dt} = \frac{\mathbf{p}_i}{m_i}$$

$$\frac{d\mathbf{p}_i}{dt} = -\frac{\partial U_{\text{tot}}}{\partial \mathbf{q}_i} - \zeta \mathbf{p}_i$$

$$\frac{d\zeta}{dt} = \frac{1}{Q} \left(2 \sum_i^N \frac{\mathbf{p}_i^2}{2m_i} - 3Nk_B T_d \right)$$

$$\zeta = \frac{d \ln s}{dt}$$

In case of $T_d < T$:



ζ becomes larger \rightarrow decelerating

In case of $T_d > T$:

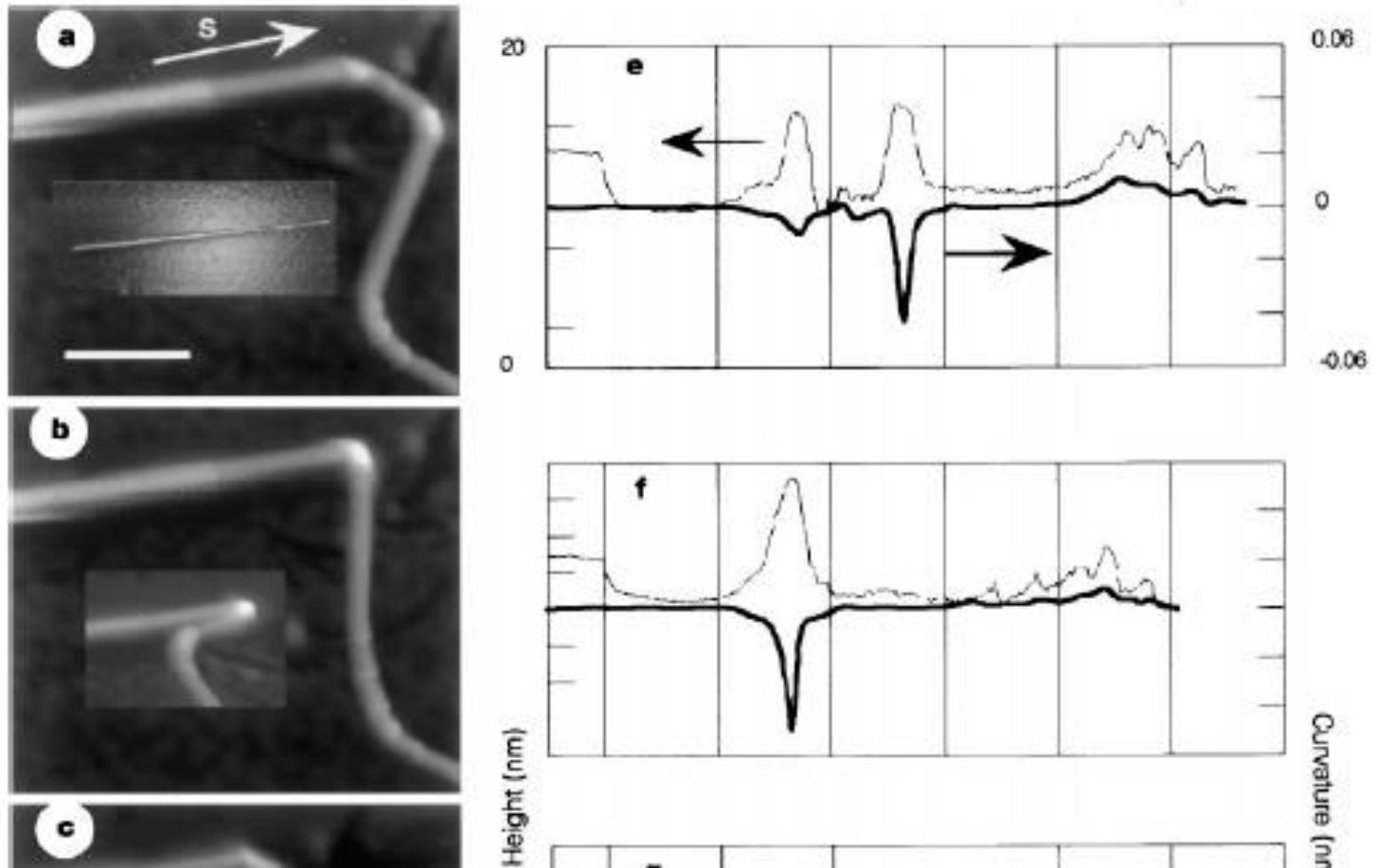


ζ becomes smaller \rightarrow accelerating

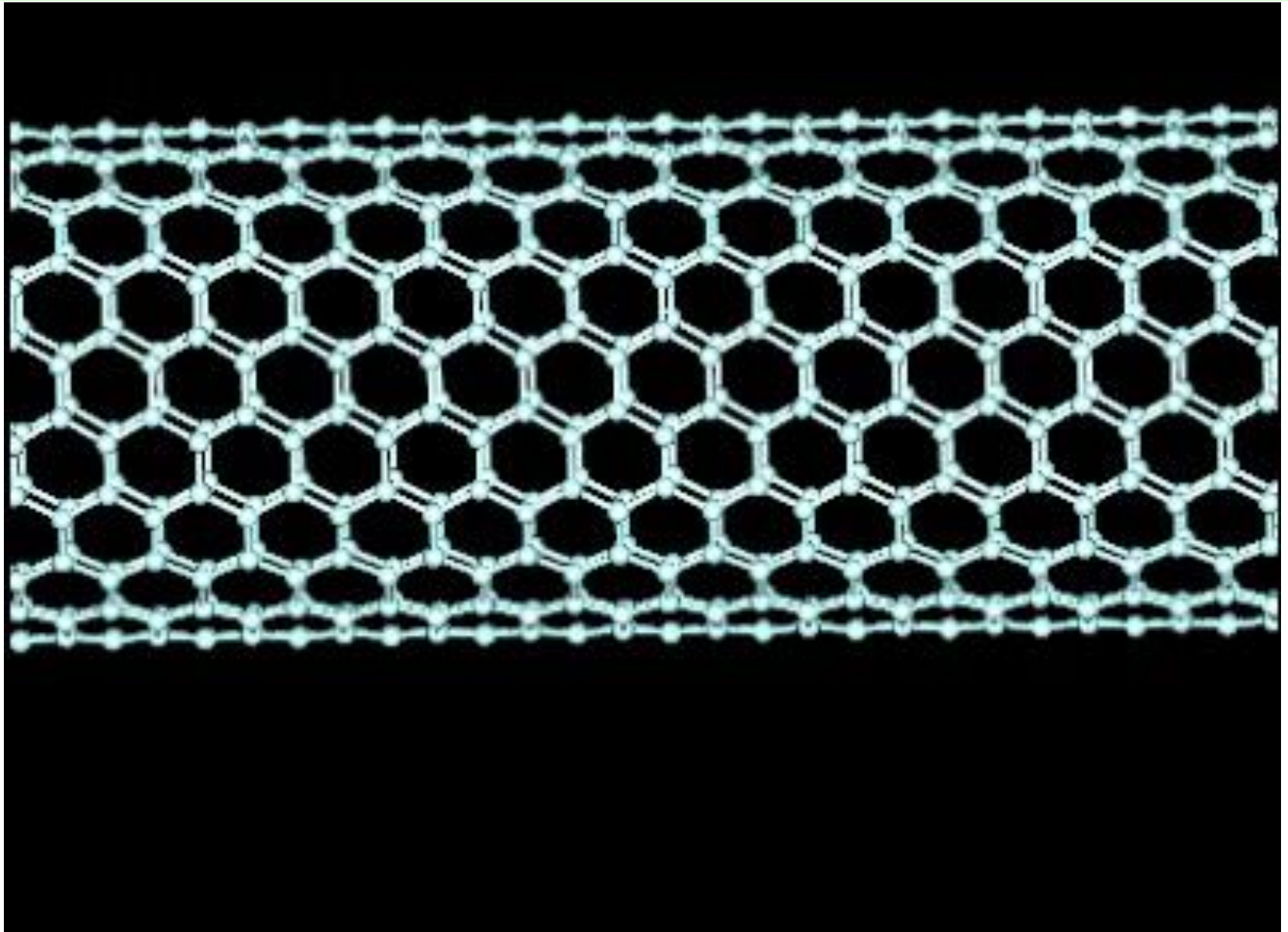
Finite temperature molecular dynamics simulation of carbon-nanotubes

Observation of buckling of CNT by AFM and STM

M.R.Falvo et al., Nature 389, 582 (1997)

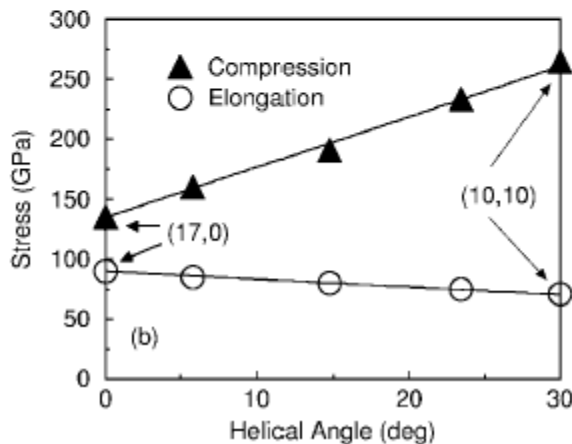
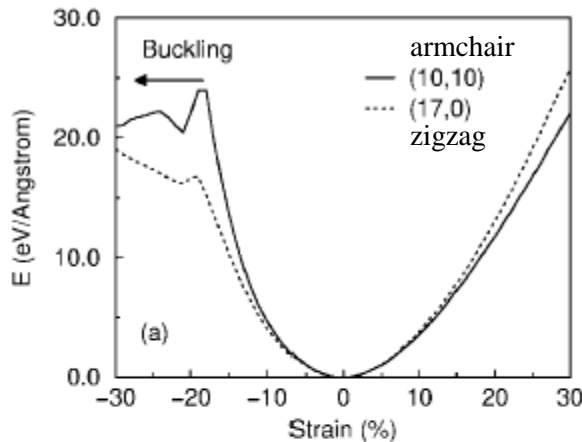


Finite temperature molecular dynamics simulation of carbon-nanotubes



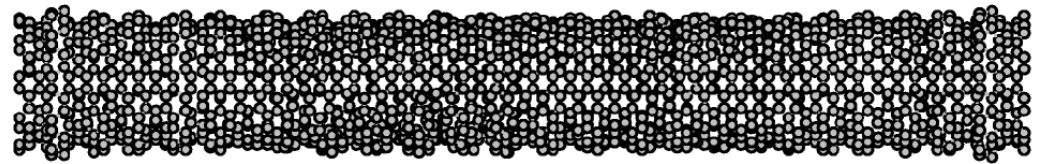
Deformation of CNT under finite temperature

Energy curve and stress at
15 % compression



Temperature dependence of buckling

(a) 0K



(b) 300K

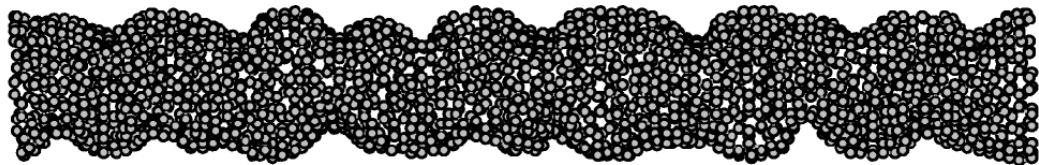


FIG. 1. Buckling of (10,10) nanotubes, which include 2280 carbon atoms, under axial compression at (a) 0 and (b) 300 K obtained by $O(N)$ TBMD simulations. These snapshots are at 80% of the initial length (140 Å).

TO, Y. Iwasa, and T. Mitani, PRL 84, 1712 (2000).

Exercises

- Perform the geometry optimization of a distorted methane molecule. Please follow the guidance in the page 69 of the manual.
- Perform the variable cell optimization of diamond. Please follow the guidance in the pages 74-76 of the manual.
- Perform the enthalpy optimization of Si bulk. Please follow the guidance in the pages 77-78 of the manual.