Molecular dynamics, stress, and nudged elastic band method

- Molecular dynamics
- Car-Parrinello MD
- Meta-dynamics
- QM/MM
- Nudged Elastic Band (NEB)
- Stress tensor
- Variable cell optimization
- Outlook

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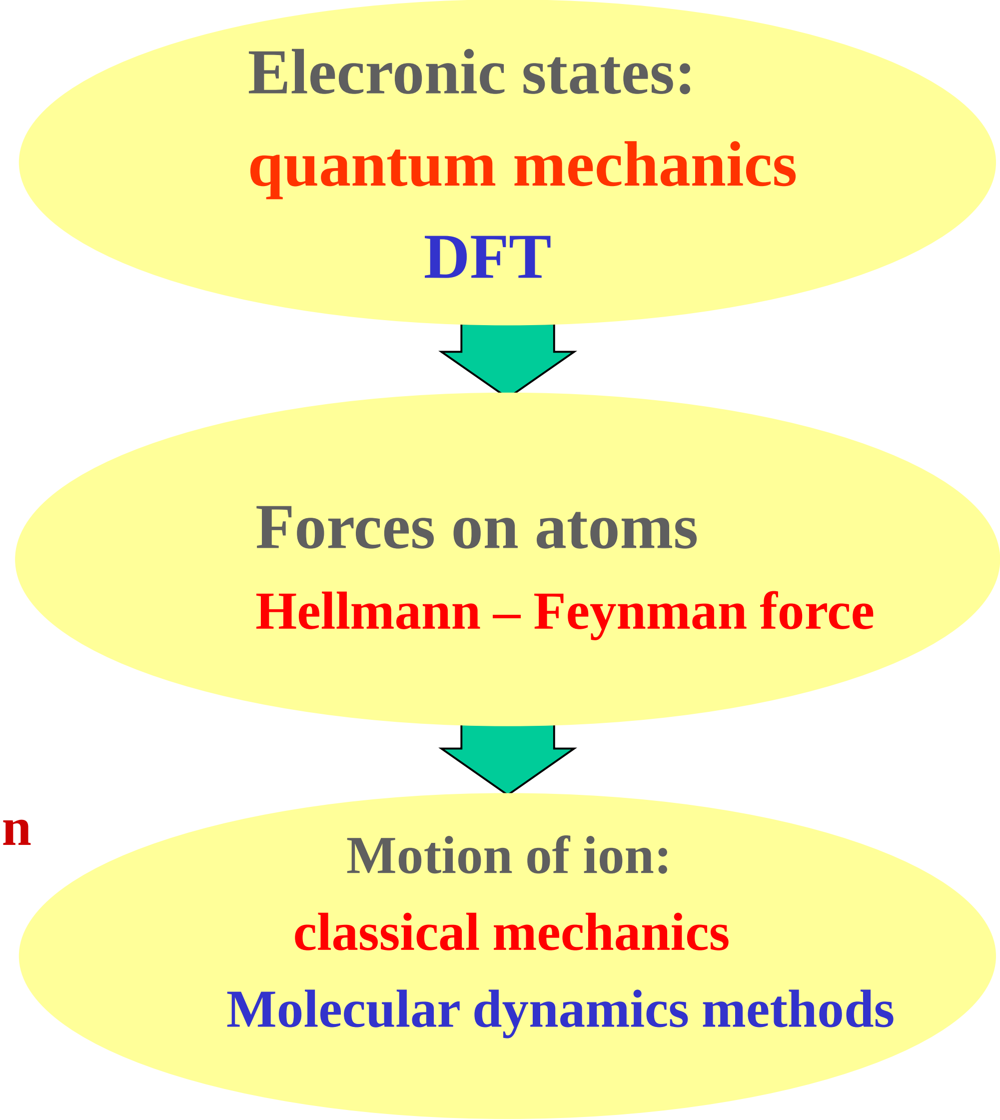
The Summer School on DFT: Theories and Practical Aspects, July 2-6, 2018, ISSP

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.



Elecronic states:

quantum mechanics

DFT

Forces on atoms

Hellmann – Feynman force

Motion of ion:

classical mechanics

Molecular dynamics methods

It enables us to treat bond formation and breaking.

Simulation of chemical reactions

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

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

Time evolution of Newton eq. by the Verlet method

Taylor expansion of the coordinate *R* at time *t*

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

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 $v_I(t) = \frac{dR_I(t)}{dt} \qquad a_I(t) = \frac{d^2R_I(t)}{dt^2}$

Velocity at t and R at t+Δt are given by

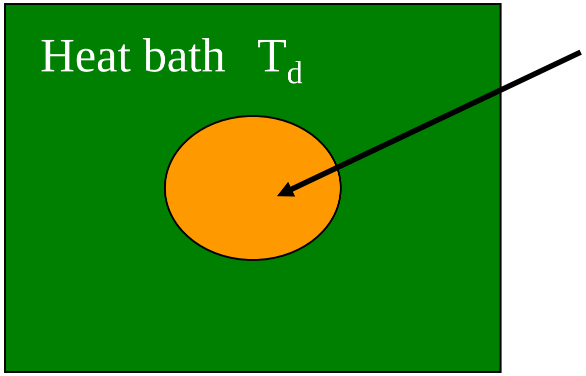
$$v_I(t) = \frac{1}{2\Delta t}\left[R_I(t+\Delta t) - R_I(t-\Delta t)\right]$$

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

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

Temperature control by the Nose-Hoover method

Micro-canonical ensemble



Let the part of system be a canonical ensemble.

$$T = \frac{2\,\Sigma_i^N \frac{\mathbf{p}_i^2}{2m_i}}{3Nk_\mathrm{B}}$$

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

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

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

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

Conserved quantity

$$H = U_\mathrm{tot} + U_\mathrm{kin} + \frac{Q}{2}\zeta^2 + 3Nk_BT_d \ln s$$

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

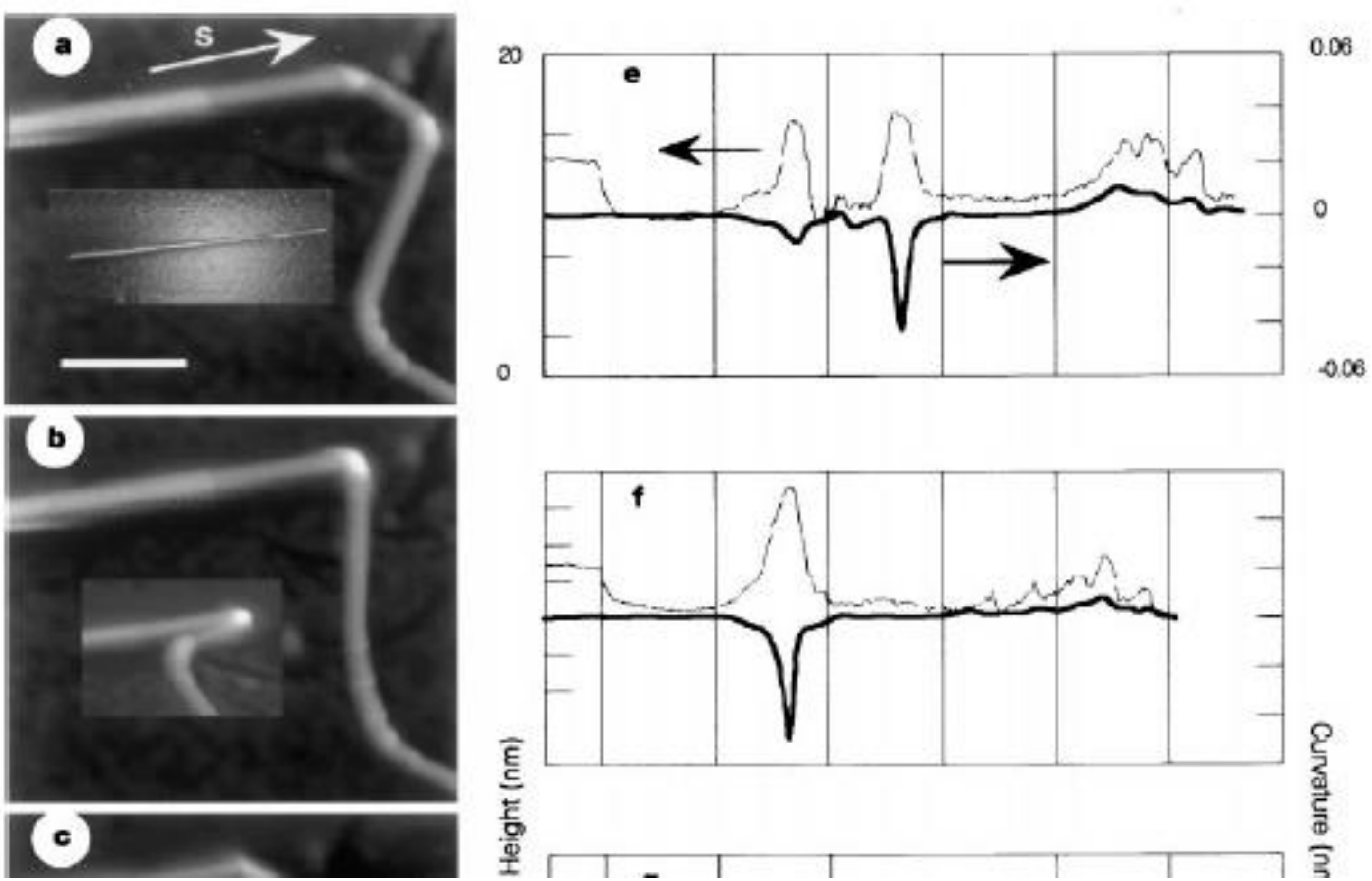
In case of $T_d < T$: ➡ ζ becomes larger → decelerating

In case of $T_d > T$: ➡ ζ becomes smaller → accelerating

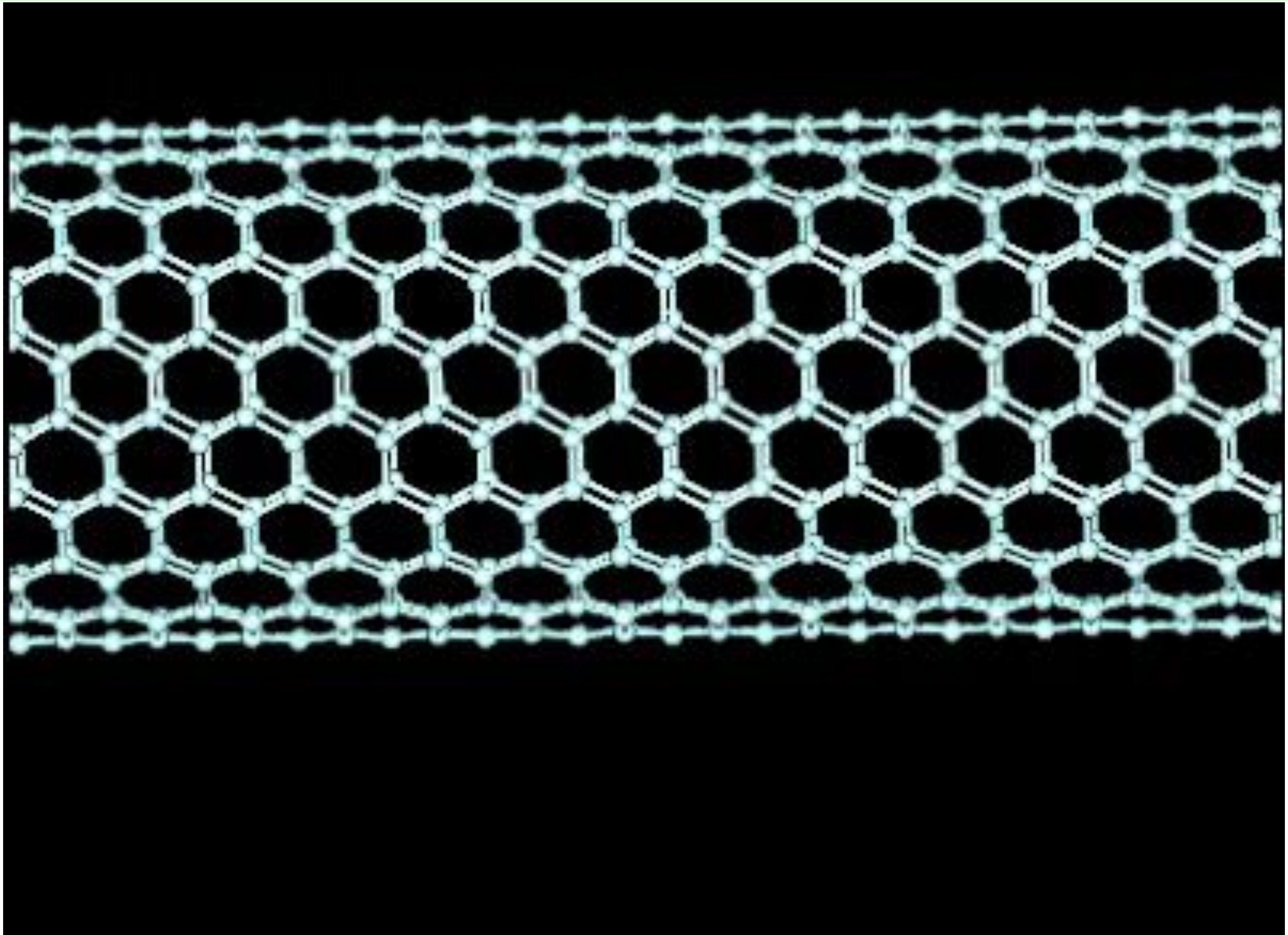
Finite temperature molecular dynamics simulation of carbon-nanotubes

Observation of buckling of CNT by AFM and STM

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

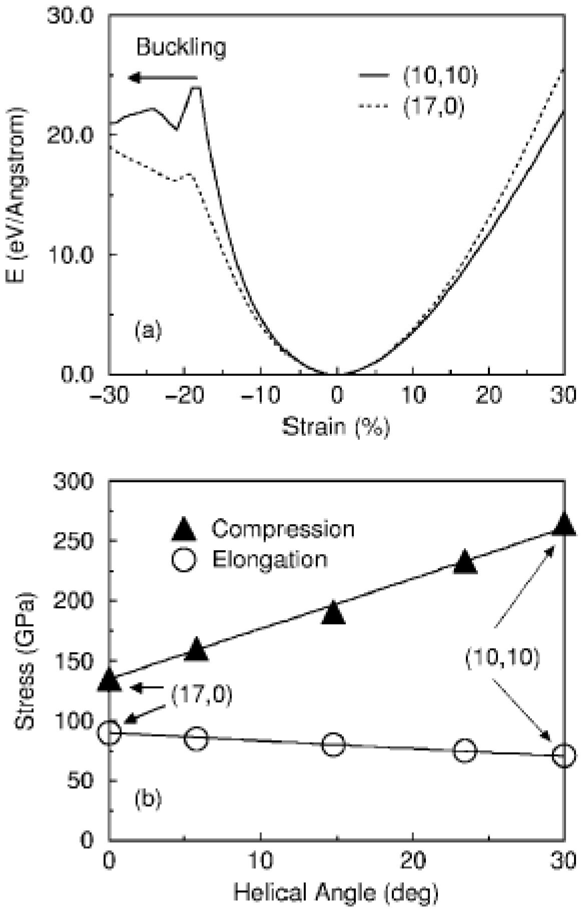


Finite temperature molecular dynamics simulation of carbon-nanotubes



Deformation of CNT under finite temperature

Energy curve and stress at 15 % compression



Temperature dependence of buckling

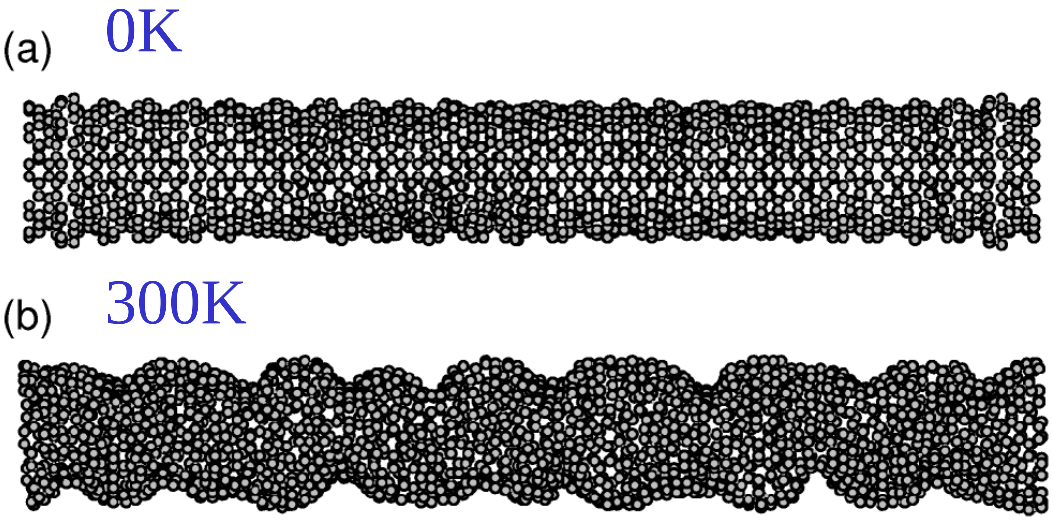


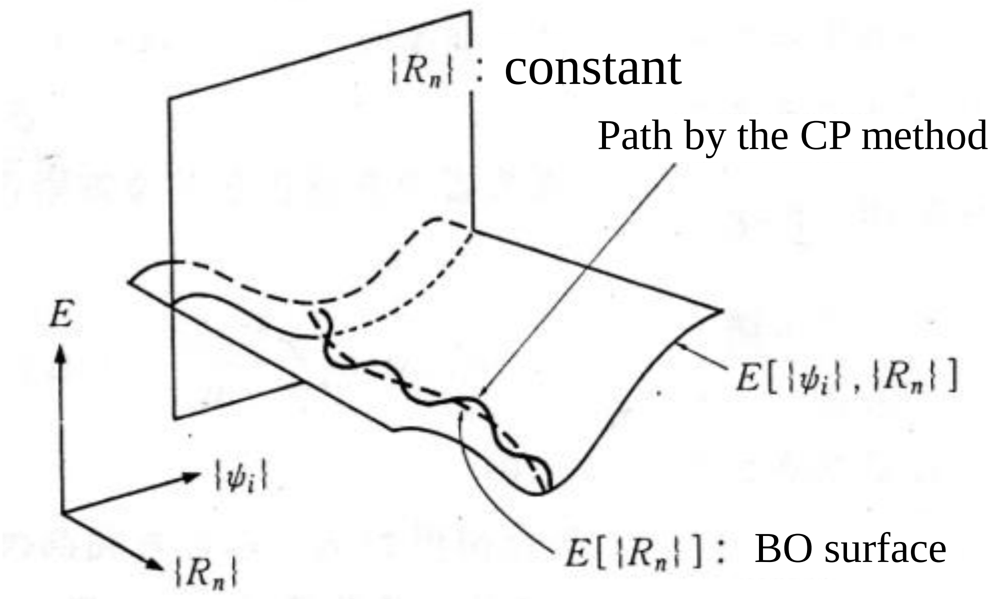
FIG. 1. Buckling of (10, 10) nanotubes, which include 2280 carbon atoms, under axial compression at (a) 0 and (b) 300 K obtained by $O(N)$ TBMD simulations. These snapshots are at 80% of the initial length (140 Å).

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

Car-Parrinello (CP) method for FPMD

By introducing a fictitious mass for wave functions and fictitious kinetic energy of wave functions, the following Lagrangian can be defined:

$$L = \sum_i \mu_i \int |\dot{\psi}_i|^2 d\mathbf{r} + \frac{1}{2} \sum_n M_n \dot{\mathbf{R}}_n^2 - E[\{\psi_i\}, \{\mathbf{R}_n\}] + \sum_{ij} \lambda_{ij} \left(\int \psi_i^* \psi_j d\mathbf{r} - \delta_{ij} \right)$$

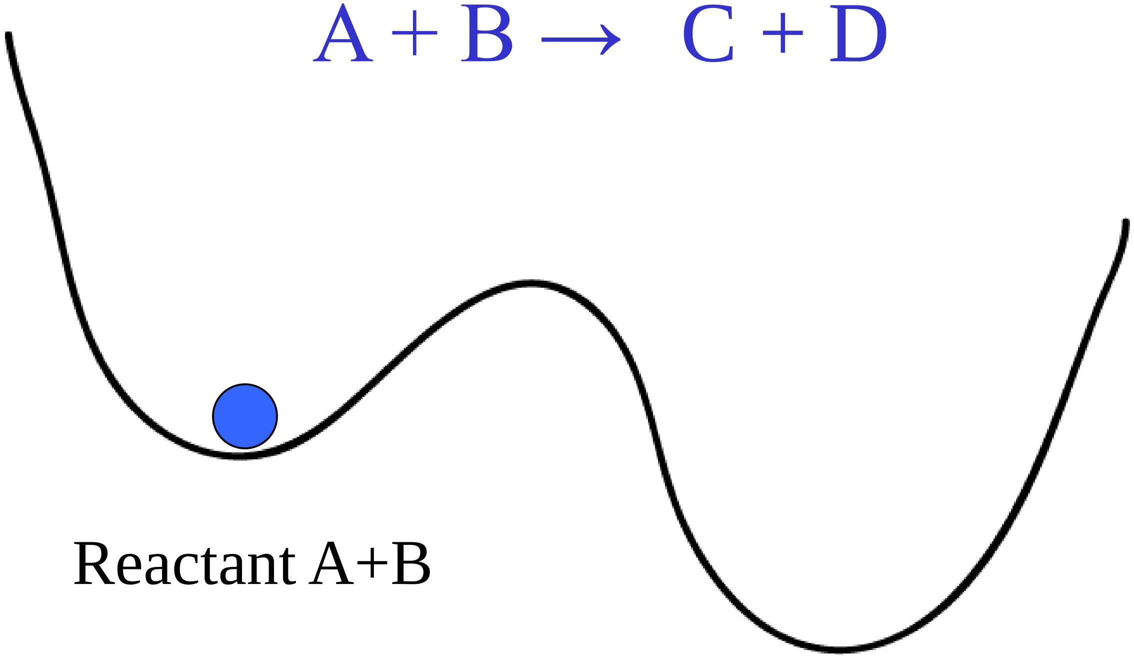


R. Car and M. Parrinello,
PRL 55, 2471 (1985).

The dynamics by the CP method proceeds while vibrating near the Born-Oppenheimer surface, while the conventional dynamics corresponds to dashed line.

Meta-dynamics for accelerating rare events

$$A + B \rightarrow C + D$$



Reactant A+B

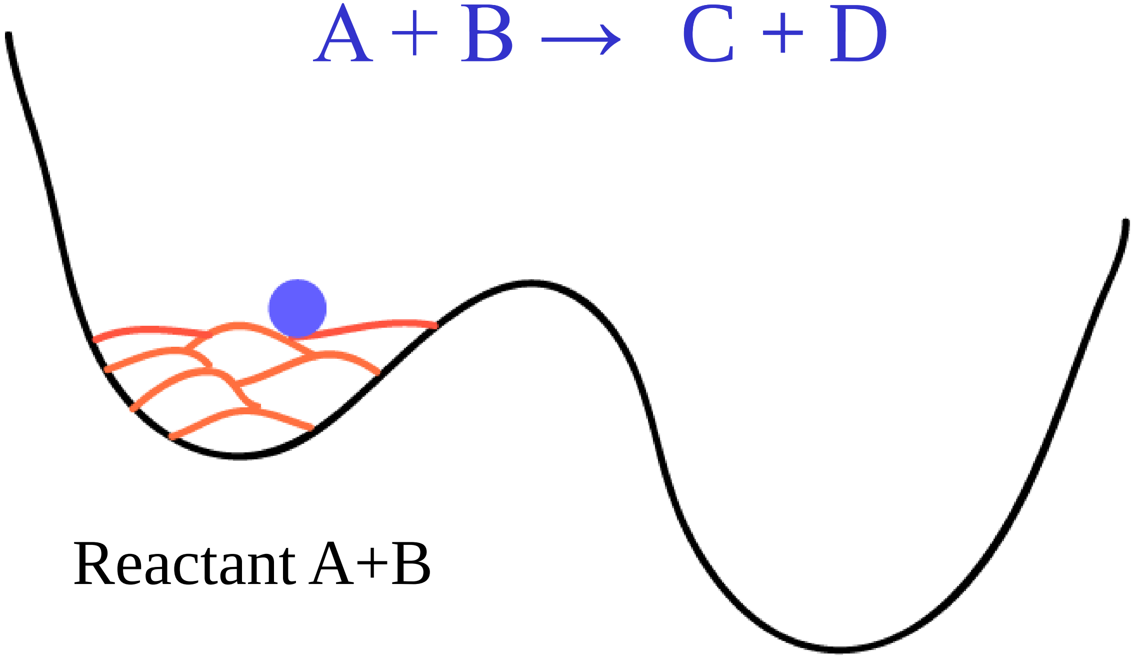
Product C+D

Although the CP-MD method is quite efficient, actual reactions will require a long time simulation.

A. Laio and M. Parrinello,
PNAS 99, 12562 (2002).

Meta-dynamics for accelerating rare events

$$A + B \rightarrow C + D$$



Reactant A+B

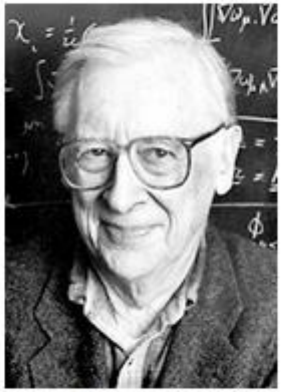
Product C+D

After exploring certain phase space, a penalty is given by adding gaussian functions to there to avoid exploring the same phase space again. This treatment can significantly accelerate exploring of phase space.

Nobel Prizes

The Nobel Prize in Chemistry 1998

Walter Kohn



John A. Pople

The Nobel Prize in Chemistry 1998 was divided equally between Walter Kohn ***"for his development of the density-functional theory"*** **and John A. Pople** ***"for his development of computational methods in quantum chemistry"*****.**

The Nobel Prize in Chemistry 2013

© Harvard University

Martin Karplus

Photo: © S. Fisch

Michael Levitt

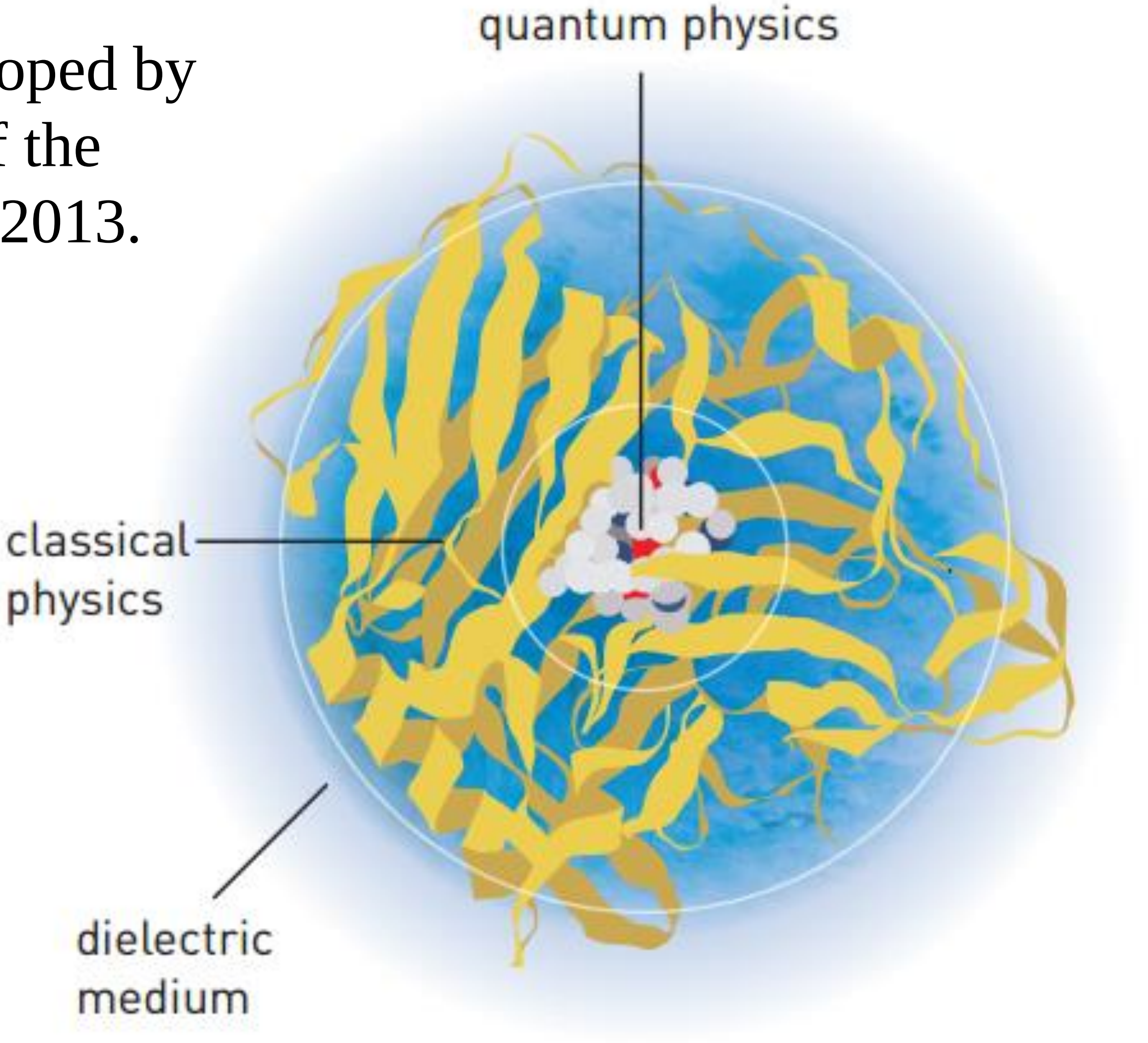
Photo: Wikimedia Commons

Arieh Warshel

The Nobel Prize in Chemistry 2013 was awarded jointly to Martin Karplus, Michael Levitt and Arieh Warshel ***"for the development of multiscale models for complex chemical systems"*****.**

QM/MM method

The idea developed by the laureates of the Nobel prize in 2013.



An application of CPMD

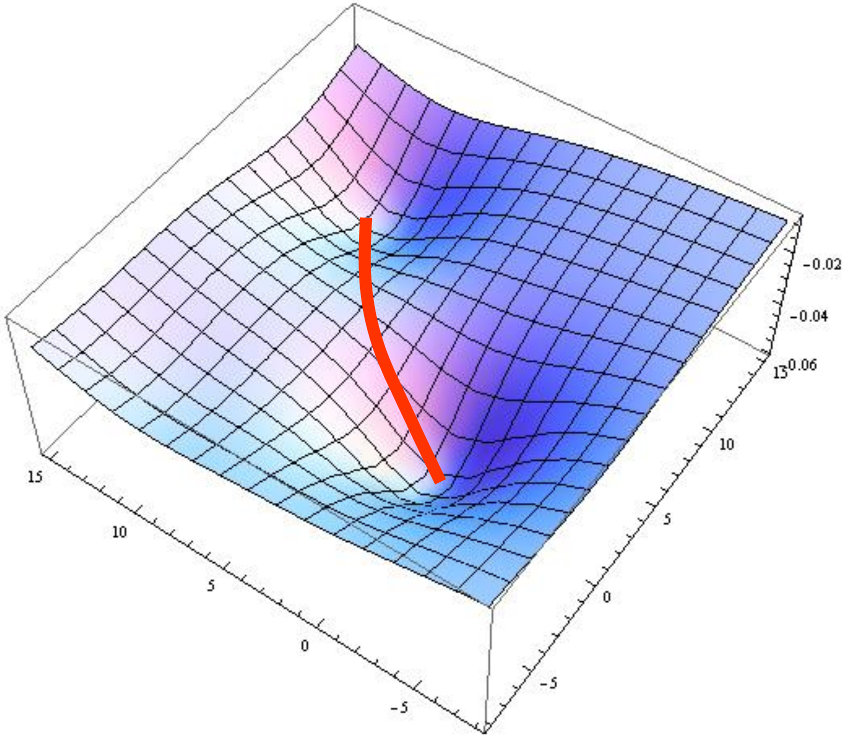
A First Principles Molecular Dynamics insight to ATPase (ATP Synthase)

- Prof. M. Boero (Univ. of Strasbourg)
- Dr. T. Ikeda (Genken),
- Prof. E. Itoh(Tokushima Bunri Univ.),
- Prof. K. Terakura (NIMS)

JACS 128 (51), 16798 (2006).

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.



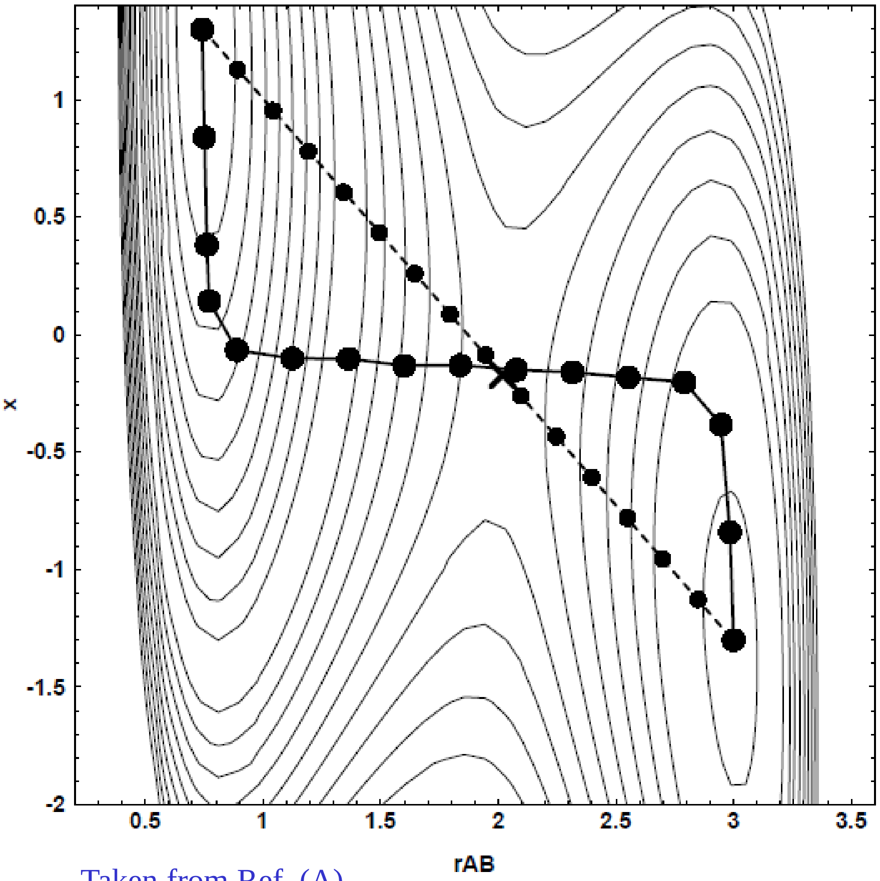
(A) H. Jonsson, G. Mills, and K. W. Jacobsen, in *Classical and Quantum Dynamics in Condensed Phase Simulations*, edited by B. J. Berne, G. Ciccotti, and D. F. Coker (World Scientific, Singapore, 1998), p. 385.

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

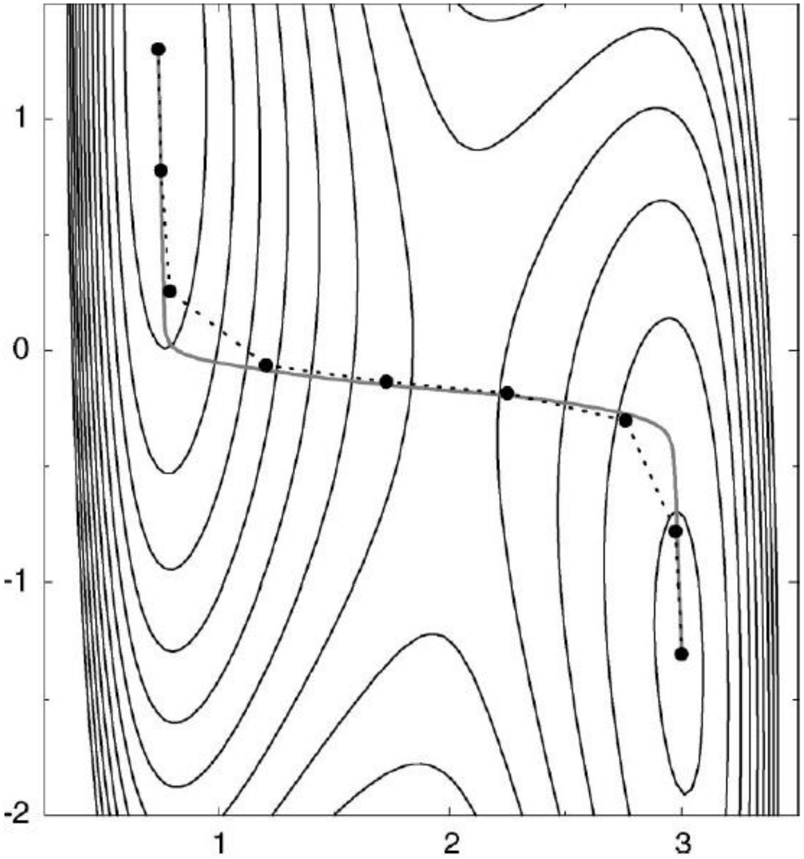
In later slides, they are referred as Refs. (A) and (B).

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.



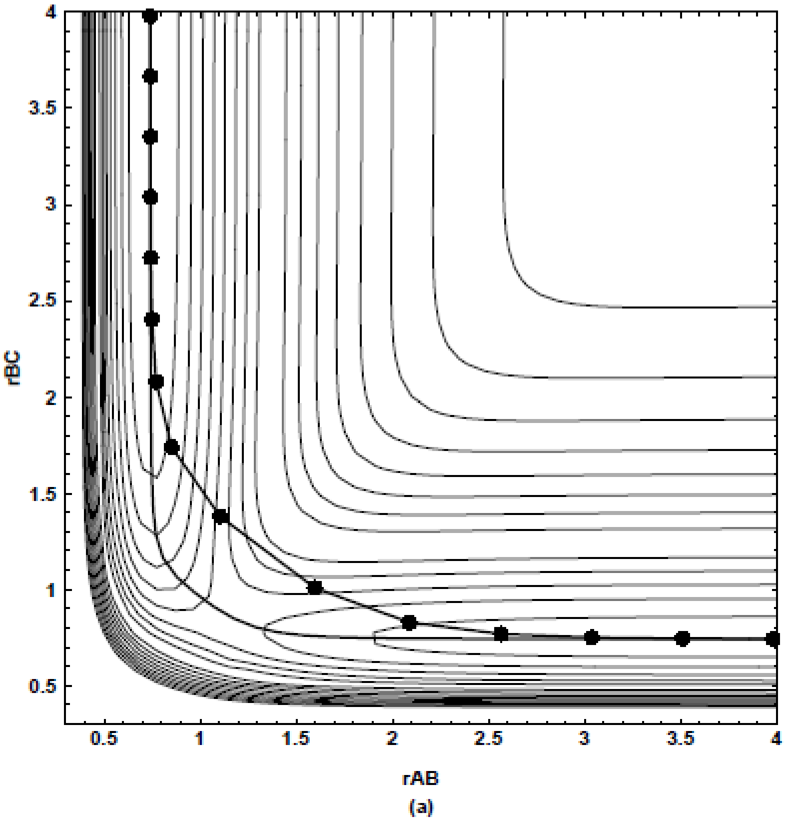
Taken from Ref. (A).



Taken from Ref. (B).

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).

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

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

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.

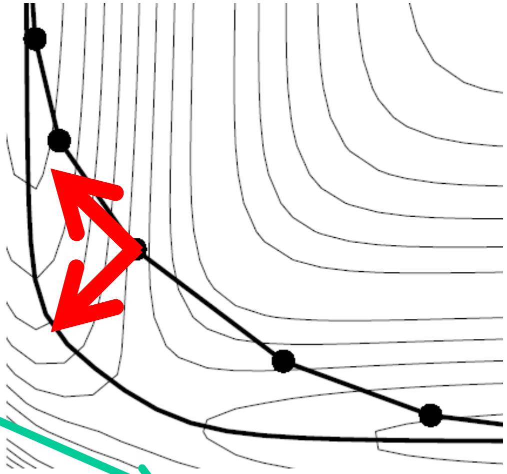
One should consider another way to avoid the drift of the energy pathway.

Nudged Elastic Band (NEB) method

The force can be divided to two contributions:

Parallel force

Perpendicular force



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

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.

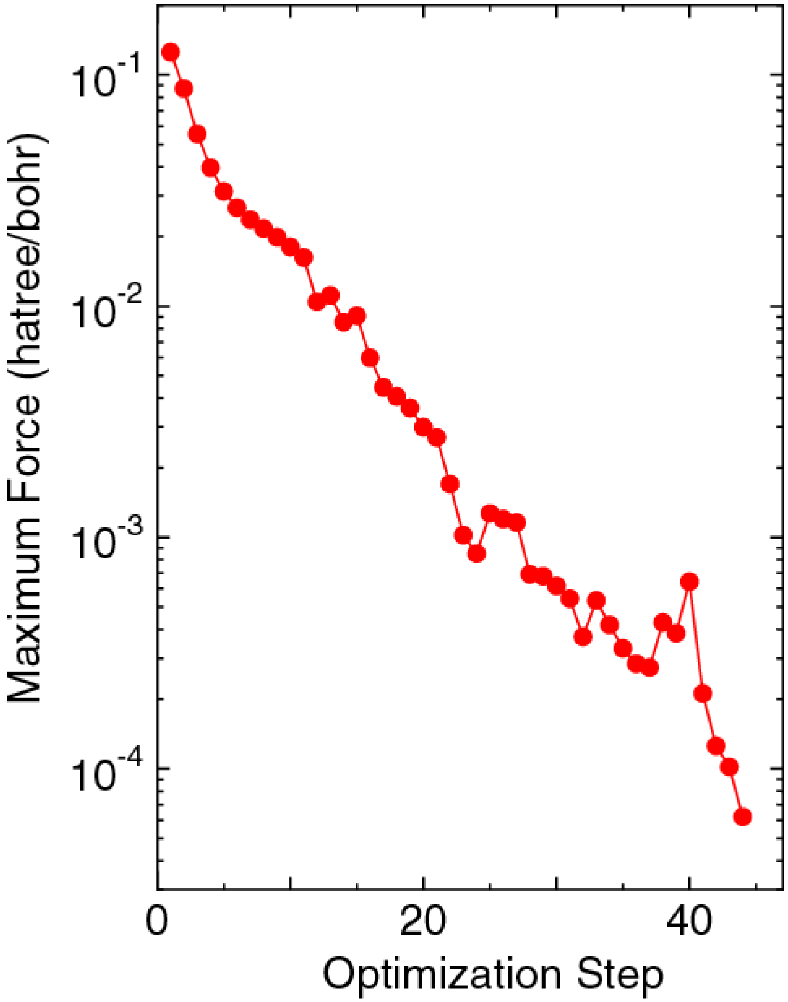
To calculate the force, only two terms are taken into account among four contributions.

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

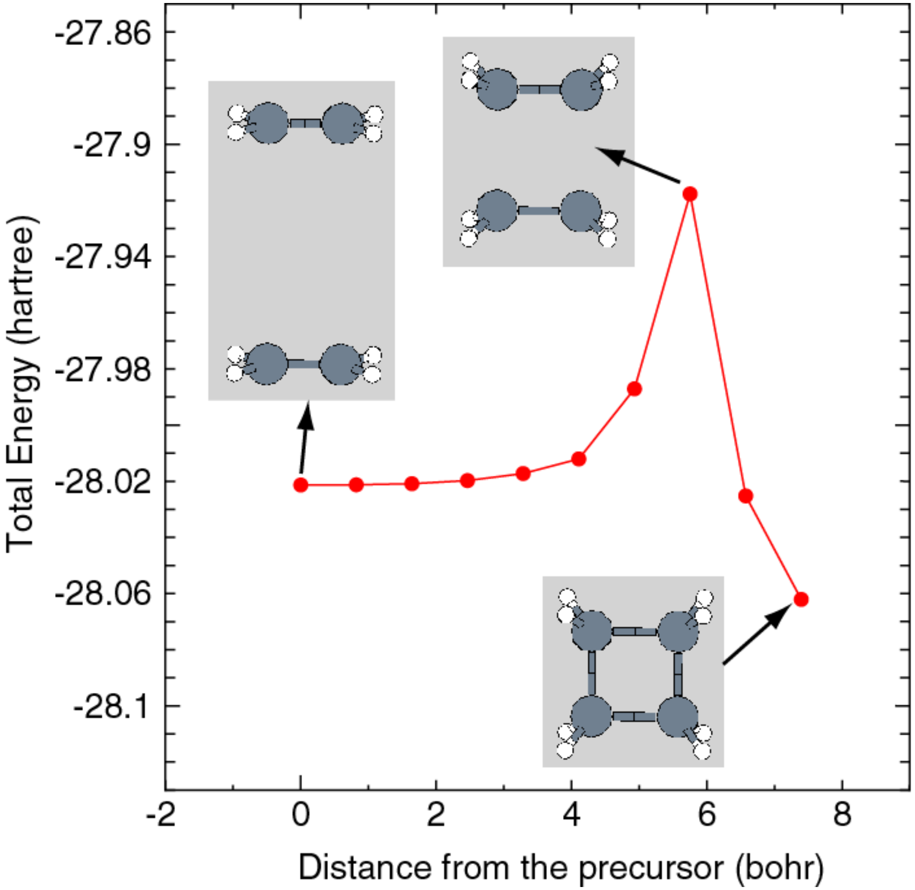
The treatment allows us to avoid the drift of energy pathway, while the physical meaning of the object function is not clear anymore.

2+2 reaction of ethylene molecules

Optimization history

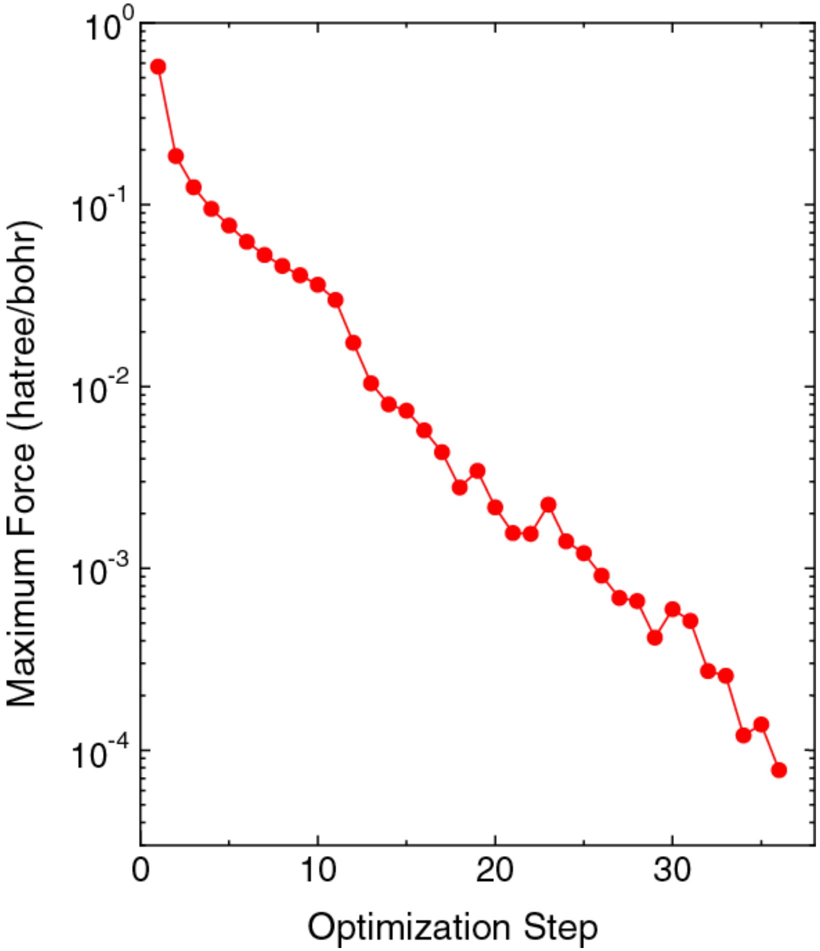


Minimum energy path way and corresponding structures

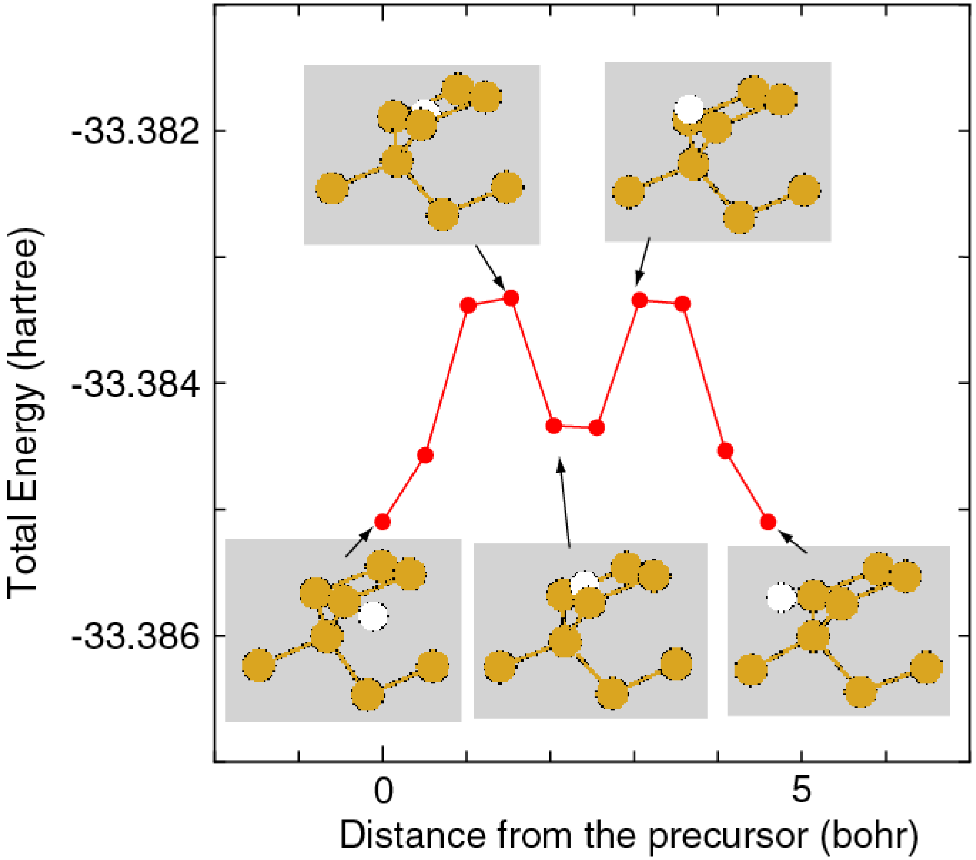


Diffusion of H atom in bulk Si

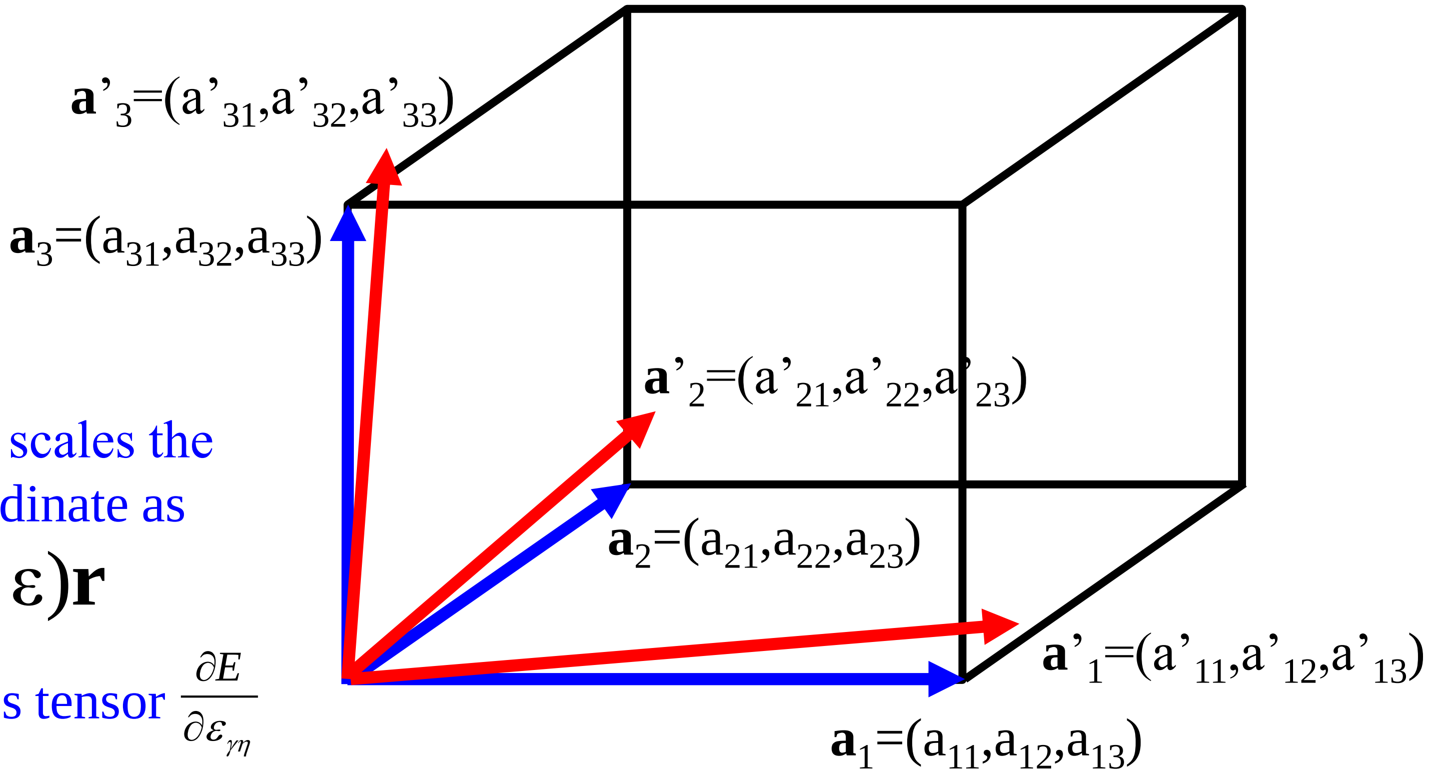
Optimization history



Minimum energy path way and corresponding structures



Stress tensor



Strain tensor ε scales the Cartesian coordinate as

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

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

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

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

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

- **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.

Stress tensor for $\mathrm{E}_{\mathrm{kin}}$, E_{na}, and E_{ec}

The derivative of $\mathrm{E}_{\mathrm{kin}}$ is given by

$$\frac{\partial E_{\mathrm{kin}}}{\partial \varepsilon_{\gamma\eta}} = \sum_{\sigma}\sum_{n}\sum_{i\alpha j\beta} \frac{\partial \rho^{(\mathbf{R}_n)}_{\sigma,i\alpha j\beta}}{\partial \varepsilon_{\gamma\eta}} \left\langle \chi_{i\alpha}(\mathbf{r}-\mathbf{t}_i) \middle| \hat{T} \middle| \chi_{j\beta}(\mathbf{r}-\mathbf{t}_i-\mathbf{R}_n) \right\rangle$$

$$+\sum_{\sigma}\sum_{n}\sum_{i\alpha j\beta} \rho^{(\mathbf{R}_n)}_{\sigma,i\alpha j\beta} \frac{\partial}{\partial \varepsilon_{\gamma\eta}} \left\langle \chi_{i\alpha}(\mathbf{r}-\mathbf{t}_i) \middle| \hat{T} \middle| \chi_{j\beta}(\mathbf{r}-\mathbf{t}_i-\mathbf{R}_n) \right\rangle$$

The latter derivatives can be transformed to the derivatives w.r.t. Cartesian coordinates:

$$\frac{\partial}{\partial \varepsilon_{\gamma\eta}} \left\langle \chi_{i\alpha}(\mathbf{r}-\mathbf{t}_i) \middle| \hat{T} \middle| \chi_{j\beta}(\mathbf{r}-\mathbf{t}_i-\mathbf{R}_n) \right\rangle = \left(\frac{\partial}{\partial t_i^{\gamma}} \left\langle \chi_{i\alpha}(\mathbf{r}-\mathbf{t}_i) \middle| \hat{T} \middle| \chi_{j\beta}(\mathbf{r}-\mathbf{t}_i-\mathbf{R}_n) \right\rangle \right) t^{\eta}_{ij,n}$$

where

$$\mathbf{t}_{ij,n} = \mathbf{t}_i - \mathbf{t}_j - \mathbf{R}_n$$

The former derivatives can be transformed to the overlap stress tensor:

$$\sum_{\sigma}\sum_{n}\sum_{i\alpha j\beta} \frac{\partial \rho^{(\mathbf{R}_n)}_{\sigma,i\alpha j\beta}}{\partial \varepsilon_{\gamma\eta}} \left\langle \chi_{i\alpha}(\mathbf{r}-\mathbf{t}_i) \middle| \hat{T} \middle| \chi_{j\beta}(\mathbf{r}-\mathbf{t}_i-\mathbf{R}_n) \right\rangle$$

$$= -\sum_{\sigma}\sum_{n}\sum_{i\alpha j\beta} E^{(\mathbf{R}_n)}_{\sigma,i\alpha j\beta} \frac{\partial S^{(\mathbf{R}_n)}_{i\alpha j\beta}}{\partial t_i^{\gamma}} t^{\eta}_{ij,n}$$

The energy terms, E_{na} and E_{ec}, can also be evaluated in a similar way.

Stress tensor for $E_{\delta\mathrm{ee}}$

The derivative of $E_{\delta\mathrm{ee}}$ is given by

$$\frac{\partial E_{\delta\mathrm{ee}}}{\partial \varepsilon_{\gamma\eta}} = \delta_{\gamma\eta}\int \delta n(\mathbf{r})\delta V_{\mathrm{H}}(\mathbf{r})d\mathbf{r} + \frac{1}{2}\int \frac{\partial \delta n(\mathbf{r})}{\partial \varepsilon_{\gamma\eta}}\delta V_{\mathrm{H}}(\mathbf{r})d\mathbf{r} + \frac{1}{2}\int \delta n(\mathbf{r})\frac{\partial \delta V_{\mathrm{H}}(\mathbf{r})}{\partial \varepsilon_{\gamma\eta}}d\mathbf{r}$$

The second term is given by

$$\begin{aligned}\frac{1}{2}\int \frac{\partial \delta n(\mathbf{r})}{\partial \varepsilon_{\gamma\eta}}\delta V_{\mathrm{H}}(\mathbf{r})d\mathbf{r} &= \frac{1}{2}\int_{\Omega}\delta V_{\mathrm{H}}\sum_{\sigma}\sum_{n}^{N}\sum_{i\alpha,j\beta}\left[\frac{\delta\rho_{\sigma,i\alpha j\beta}^{(\mathbf{R}_n)}}{\delta\varepsilon_{\gamma\eta}}\phi_{i\alpha}(\mathbf{r}-\mathbf{t}_i)\phi_{j\beta}(\mathbf{r}-\mathbf{t}_j-\mathbf{R}_n)\right. \\ &+\rho_{\sigma,i\alpha j\beta}^{(\mathbf{R}_n)}\left\{\nabla_{\gamma}\phi_{i\alpha}(\mathbf{r}-\mathbf{t}_i)(r^{\eta}-t_i^{\eta})\right\}\phi_{j\beta}(\mathbf{r}-\mathbf{t}_j-\mathbf{R}_n) \\ &\left.+\rho_{\sigma,i\alpha j\beta}^{(\mathbf{R}_n)}\phi_{i\alpha}(\mathbf{r}-\mathbf{t}_i)\left\{\nabla_{\gamma}\phi_{i\alpha}(\mathbf{r}-\mathbf{t}_i-\mathbf{R}_n)(r^{\eta}-t_i^{\eta}-R_n^{\eta})\right\}\right]\mathrm{d}\mathbf{r} \\ &-\frac{1}{2}\int_{\Omega}\delta V_{\mathrm{H}}\left\{\sum_{I}\nabla_{\gamma}n_I^{(a)}(\mathbf{r}-\mathbf{t}_I)(r^{\eta}-t_I^{\eta})\right\}\mathrm{d}\mathbf{r}\end{aligned}$$

The third term is given by

$$\frac{1}{2}\int \delta n(\mathbf{r})\frac{\partial \delta V_{\mathrm{H}}(\mathbf{r})}{\partial \varepsilon_{\gamma\eta}}d\mathbf{r} = 4\pi\int_{\Omega}\delta n(\mathbf{r})\sum_{\mathbf{G}}\delta n(\mathbf{G})\frac{G_{\gamma}G_{\eta}}{|\mathbf{G}|^4}\exp(\mathrm{i}\mathbf{G}\cdot\mathbf{r})\mathrm{d}\mathbf{r}$$

Stress tensor for $\mathbf{E}_{\mathbf{xc}}$

The derivative of E_{xc} is given by

$$\frac{\partial E_{\mathrm{XC}}}{\partial \varepsilon_{\gamma\eta}} = \delta_{\gamma\eta} E_{\mathrm{xc}} + \Delta V \sum_{\sigma} \sum_{p} \frac{\partial f_{\mathrm{xc}}}{\partial n_p^{(\sigma)}} \frac{\partial n_p^{(\sigma)}}{\partial \varepsilon_{\gamma\eta}} + \Delta V \sum_{\sigma} \sum_{p} \frac{\partial f_{\mathrm{xc}}}{\partial |n_p^{(\sigma)}|} \frac{\partial |n_p^{(\sigma)}|}{\partial \nabla n_p^{(\sigma)}} \cdot \frac{\partial \nabla n_p^{(\sigma)}}{\partial \varepsilon_{\gamma\eta}} + \mathrm{PCC\ term}$$

The second term contributes the overlap stress tensor, and third term can be evaluated as

$$\Delta V \sum_{\sigma} \sum_{p} \frac{\partial f_{\mathrm{xc}}}{\partial |n_p^{(\sigma)}|} \frac{\partial |n_p^{(\sigma)}|}{\partial \nabla n_p^{(\sigma)}} \cdot \frac{\partial \nabla n_p^{(\sigma)}}{\partial \varepsilon_{\gamma\eta}} = -\Delta V \sum_{\sigma} \sum_{p} \nabla \cdot A_p^{\sigma} \frac{\partial n_p^{\sigma}}{\partial \varepsilon_{\gamma\eta}} - \Delta V \sum_{\sigma} \sum_{p} \frac{\partial n_p^{\sigma}}{\partial x_{\gamma}} A_{p,\eta}^{\sigma}$$

where $$A_p^{\sigma} = \frac{\partial f_{\mathrm{xc}}}{\partial |n_p^{(\sigma)}|} \frac{\partial |n_p^{(\sigma)}|}{\partial \nabla n_p^{(\sigma)}}$$

The last term is given by

$$\mathrm{PCC\ term} = \Delta V \sum_{\sigma} \sum_{p} v_{\mathrm{xc}}^{\sigma} \frac{\partial \underline{n}_p^{(\sigma)}}{\partial \varepsilon_{\gamma\eta}} - \Delta V \sum_{\sigma} \sum_{p} \frac{\partial \underline{n}_p^{(\sigma)}}{\partial x_{\gamma}} A_{p,\eta}^{\sigma}$$

Variable cell optimization

Initial Hessian:	Schlegel's method
Preconditioning:	RMM-DIIS
Hessian update:	BFGS
Update of positions:	Rational function (RF)

RF method

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

It is very important to construct the initial Hessian including internal coordinates, cell vectors, and the cross term for fast and stable convergence.

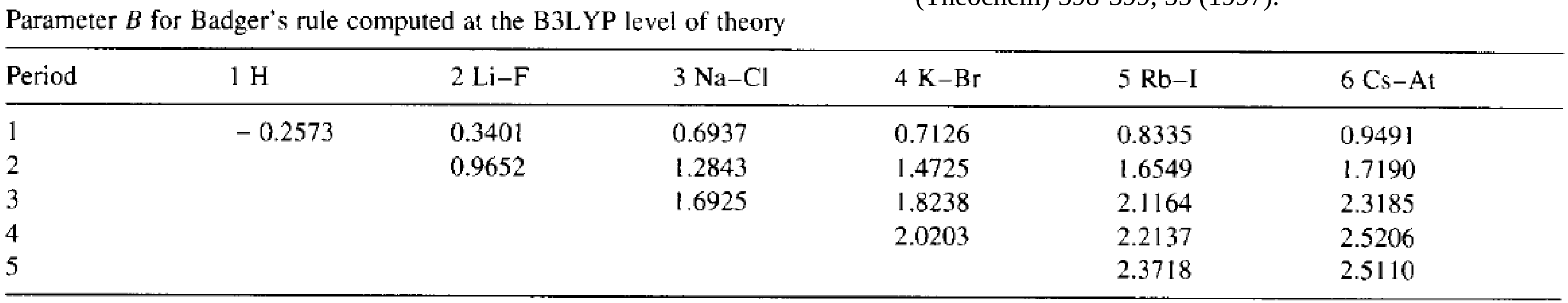
$$H = BF = \begin{pmatrix} Int & \boxed{Int - Cell} \\ \boxed{Cell - Int} & Cell \end{pmatrix}$$

Approximate 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

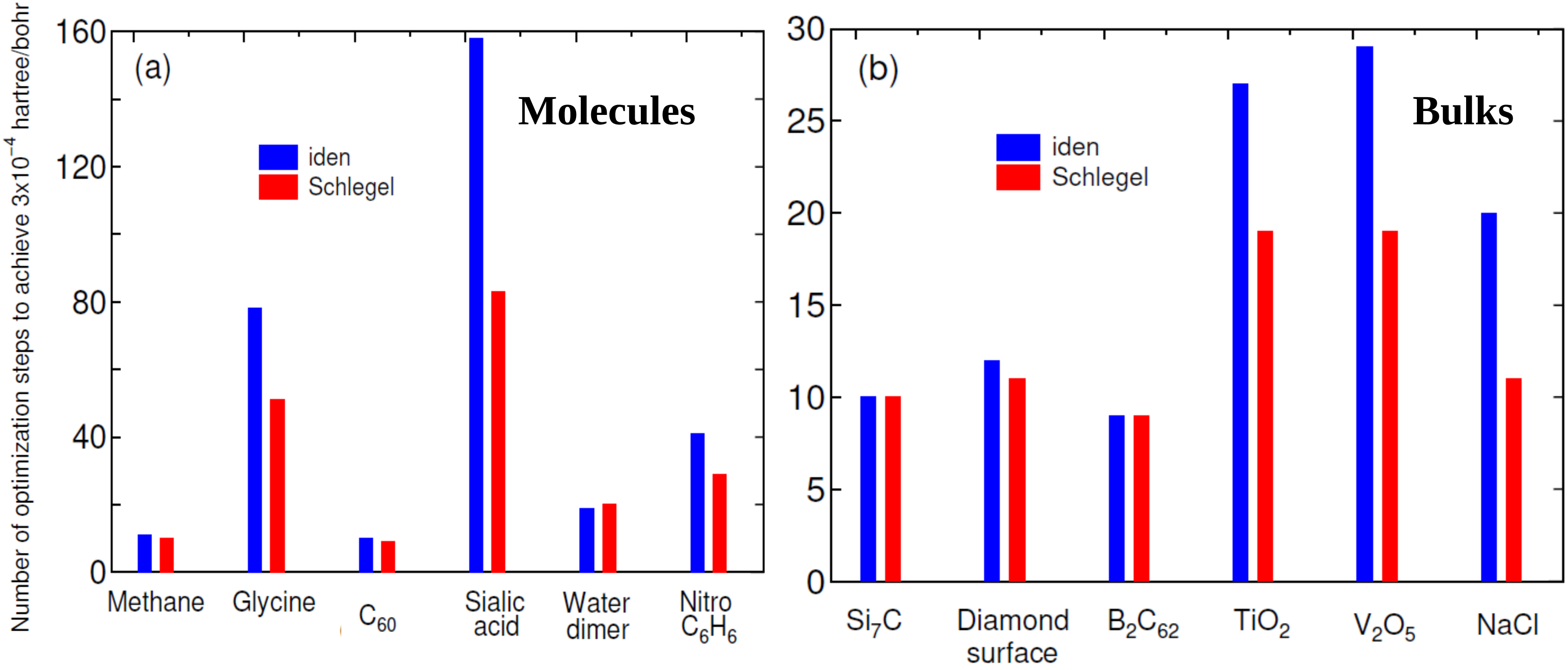
Suppose the total energy is given by the sum of pairwise potentials. Then, the derivatives lead to the following relation:

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

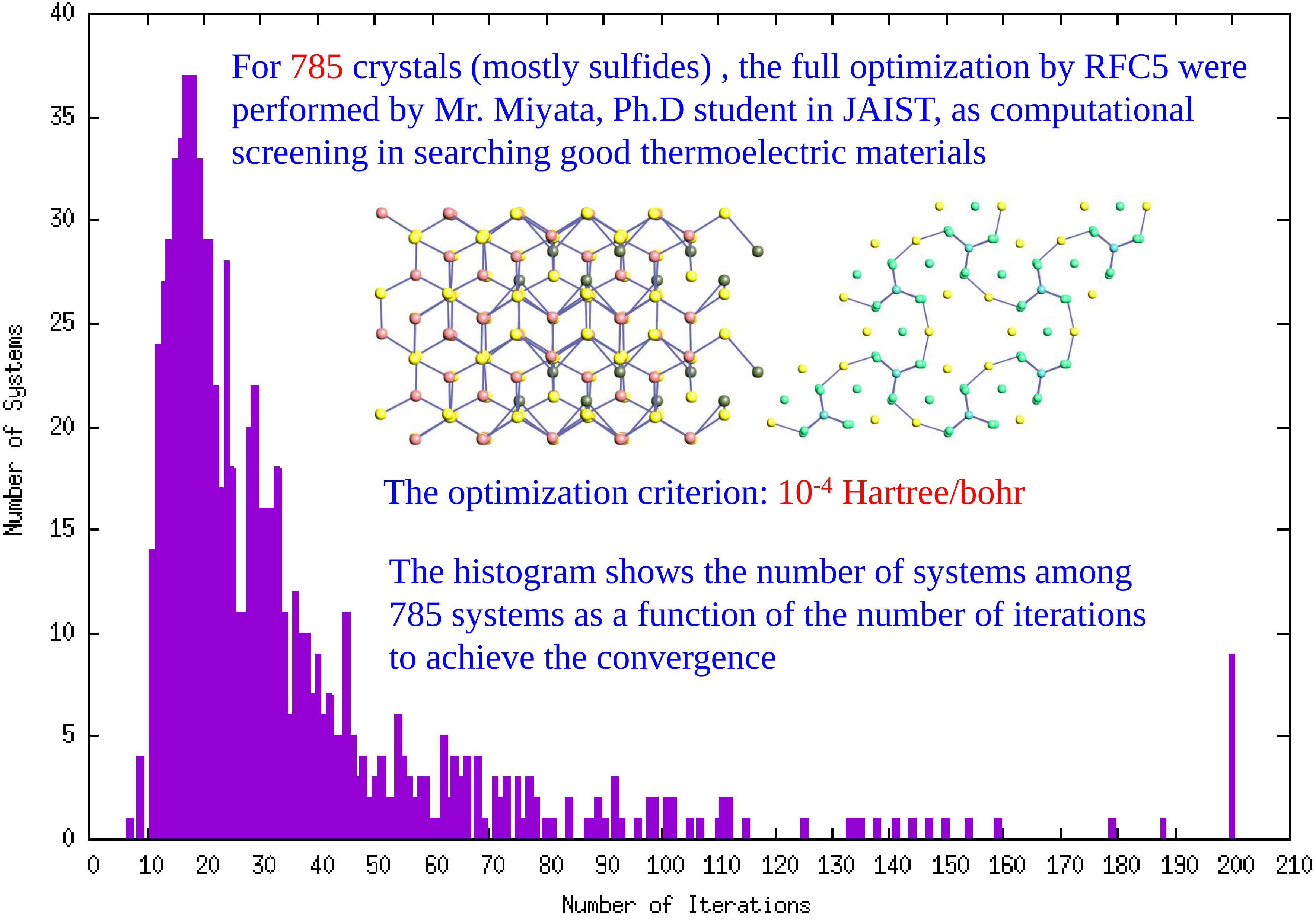
where B is the B-matrix of Wilson, H is the approximate Hessian in Cartesian coordinate.

Benchmark of the approximate Hessian in OpenMX

For both molecules and bulks, it is found that the Schlegel’s method improves the convergence substantially.



Benchmark calculations of RFC5



For 785 crystals (mostly sulfides) , the full optimization by RFC5 were performed by Mr. Miyata, Ph.D student in JAIST, as computational screening in searching good thermoelectric materials

The optimization criterion: 10^{-4} Hartree/bohr

The histogram shows the number of systems among 785 systems as a function of the number of iterations to achieve the convergence

Optimization of the enthalpy

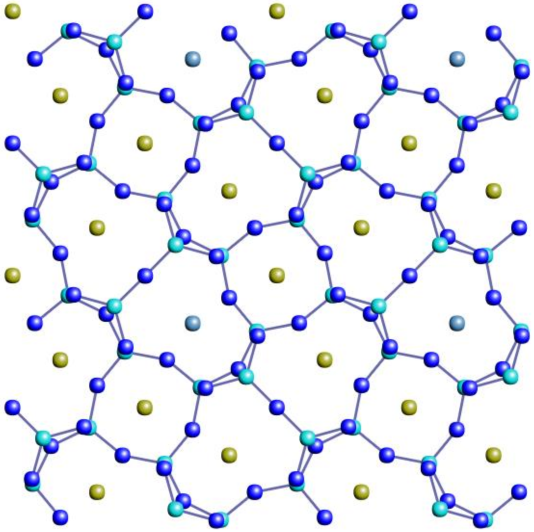
Under an external pressure p, the structural optimization can be performed by minimizing the enthalpy defined with

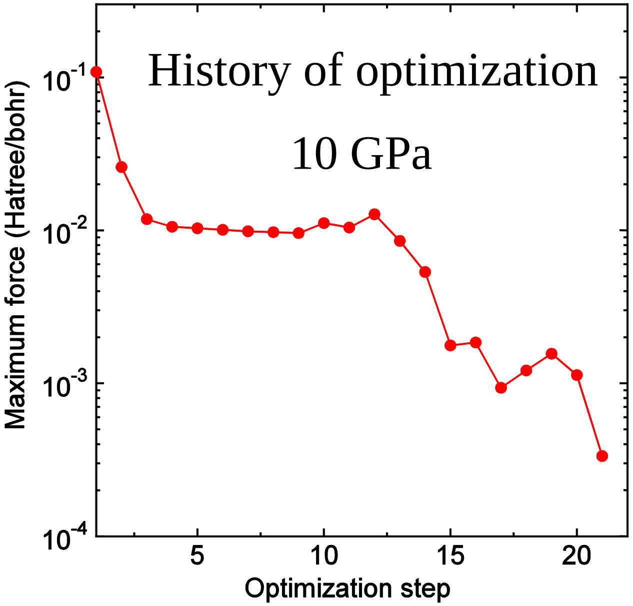
$$H = E + pV$$

The stress tensor is easily calculated by

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

$La_3Si_6N_{11}$: Ce_{2c}





Outlook

We have discussed the following topics related to dynamical behaviors and stability of materials.

- Molecular dynamics
- Car-Parrinello MD
- Meta-dynamics
- QM/MM
- Nudged Elastic Band (NEB)
- Stress tensor
- Variable cell optimization

Dynamical behaviors such as chemical reactions and diffusion processes can be addressed by first-principles molecular dynamics and the NEB methods. Variable cell optimization with stress tensor enables us to investigate stability of materials, and to explore novel crystal structures.