The 32th CMD workshop

”Practice of Esopt”

Introduction

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Let’s start the X window system

- We use machines operated by a Linux system .
- Each user is identified by “user id” & “password”.
- Your terminal might start by pushing the monitor button ⏻ .

Use the id of “cmd” for ubuntsu with pw, “c.m.dworkshop”.

Access to the PC cluster in phys.sci.

- Login the X terminal machine:
  - Account : stud** or cmd
  - Password : none or “cmdworkshop”

- Open a terminal window, and access `rl’.

```
[stud** ~]$ ssh –Y –l stud** rl.phys.sci.osaka-u.ac.jp
passwd:
…
[stud**@rl ~]$
```

Preparation for the program package

- Copy the program package.

  Type the red characters in a single line without “return” in the middle.

  [stud**@rl ~] cp /home/CMD/teac01/ESopt-CMD32-fw.tgz .

  “a space and a period” are requested.

- Unpack the package by tar command.

  [stud**@rl ~] tar zxvf ESopt-CMD32-fw.tgz

How to compile the program?

- Change the directry to the main directry of ESopt, check the header of makefile, then `make'.

```
[stud**@rl ~]$ cd ESopt-CMD32-fw
[stud**@rl ~/ESopt-CMD32-fw]$ ls
a0ene.pl            getll.f90            mkvel.f90 ….
….
[stud**@rl ~/ESopt-CMD32-fw]$ head makefile
# The makefile for ES_opt
#
DESTDIR=Si-band                <= this is the destination
#
…
[stud**@rl ~/ESopt-CMD32-fw]$ cp INPUT_DATA/CORD-Si-b
    INPUT_DATA/CORD
[stud**@rl ~/ESopt-CMD32-fw]$ make < input_make
```

Please rewrite this line!!!

Run the program

- Change the directory to the destination written in the header of the makefile

  DESTDIR=Si-band <= you may rewrite this name.

- If you have a working directory named `Si-band', you may submit a job using the queing system,

```
[stud**@rl ~/ESopt-CMD32-fw]$ cd Si-band
[stud**@rl Si-band]$ qsub qsub
[stud**@rl Si-band]$ qstat
```

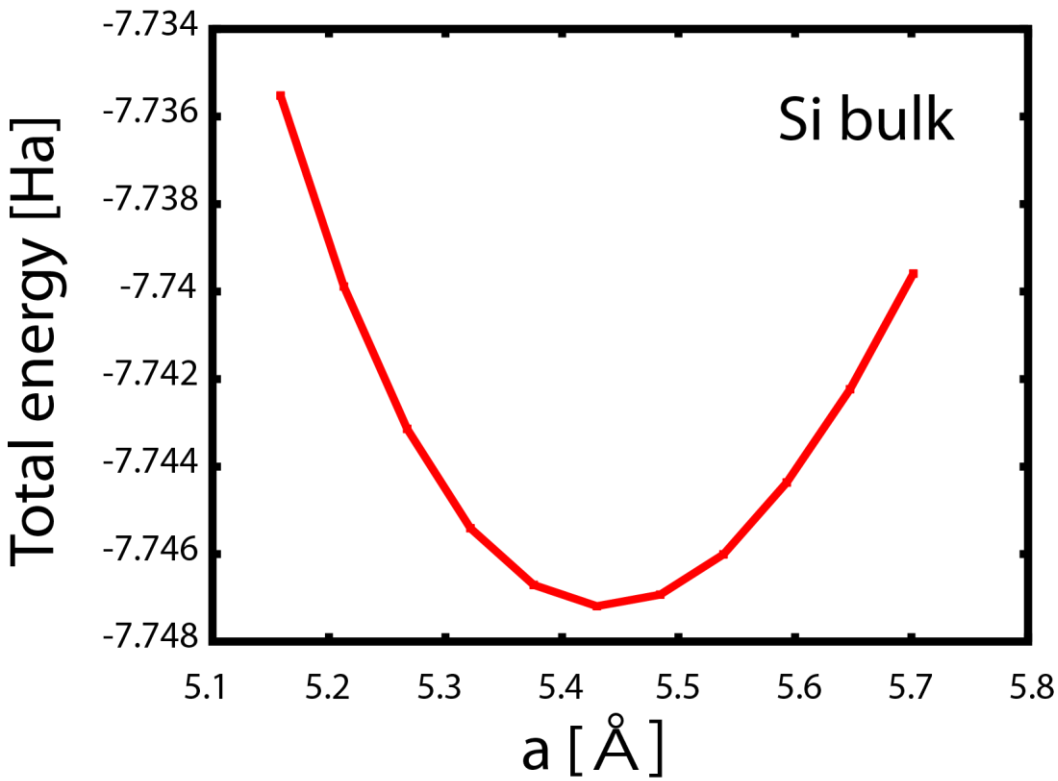
What happens, when you compile it?

- At beginning, make creates executable file, “opt”.
- Once “opt” is made, make will create a working directry for each project given in INPUT_DATA/CORD.
- The name of the working directry is given in the header of makefile.
- Some temporary data files are created in a sub directry “mknon”.

Bulk modulus: Second derivative of E(V)

Bulk modulus at T=0: $B_0 = -\frac{Vdp}{dV} = \frac{Vd^2E}{dV^2}$,

Murnaghan eq. of states: $E(V) = E_0 + \frac{B_0 V}{B_0'}\left(\frac{(V_0/V)^{B_0'}}{B_0'-1} + 1\right) - \frac{B_0 V_0}{B_0'-1}$.



calc_mode: bas
band_calc: metal

E_{cut} = 40 Ry.

"Total energy" is seen by looking at MONIT/energy.

In this calculation, "murnfit" tells that B_0=89GPa.

A non-linear fitting problem

- Murnaghan's equation of states

$$E(V) = \frac{B_0 V}{B_0'}\left(\frac{(V_0/V)^{B_0'}}{(B_0'-1)}+1\right)+C$$

$$= \alpha V^{1-B_0'} + \beta V + \gamma$$

$$= \alpha V^{\delta} + \beta V + \gamma$$

$$\alpha = \frac{B_0' V_0^{B_0'}}{B_0'(B_0'-1)}, \beta = \frac{B_0}{B_0'}, \gamma = C, \delta = 1 - B_0'$$

We let four sets of $(V, E(V))$ be (x_i, y_i) $(i=1,4)$.

$$\begin{pmatrix} y_1 \\ y_2 \\ y_3 \end{pmatrix} = \begin{pmatrix} x_1^{\delta} & x_1 & 1 \\ x_2^{\delta} & x_2 & 1 \\ x_3^{\delta} & x_3 & 1 \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \\ \gamma \end{pmatrix} \Rightarrow \alpha(\delta), \beta(\delta), \gamma(\delta)$$

$$g(\delta) = y_4 - \left(\alpha(\delta) x_4^{\delta} + \beta(\delta) x_4 + \gamma(\delta)\right)$$

Finding δ which gives $g(\delta)=0$ is important.

Trial 1: Bulk modulus of c-BN

- Change the directory to the destination in “makefile” as,

  DESTDIR=cBN <= you may rewrite this name.
- If you see utility/cBN_scripts, CORD files for the test as well as some utility scripts, chev.sh, sub.sh, and summ.sh are stored.

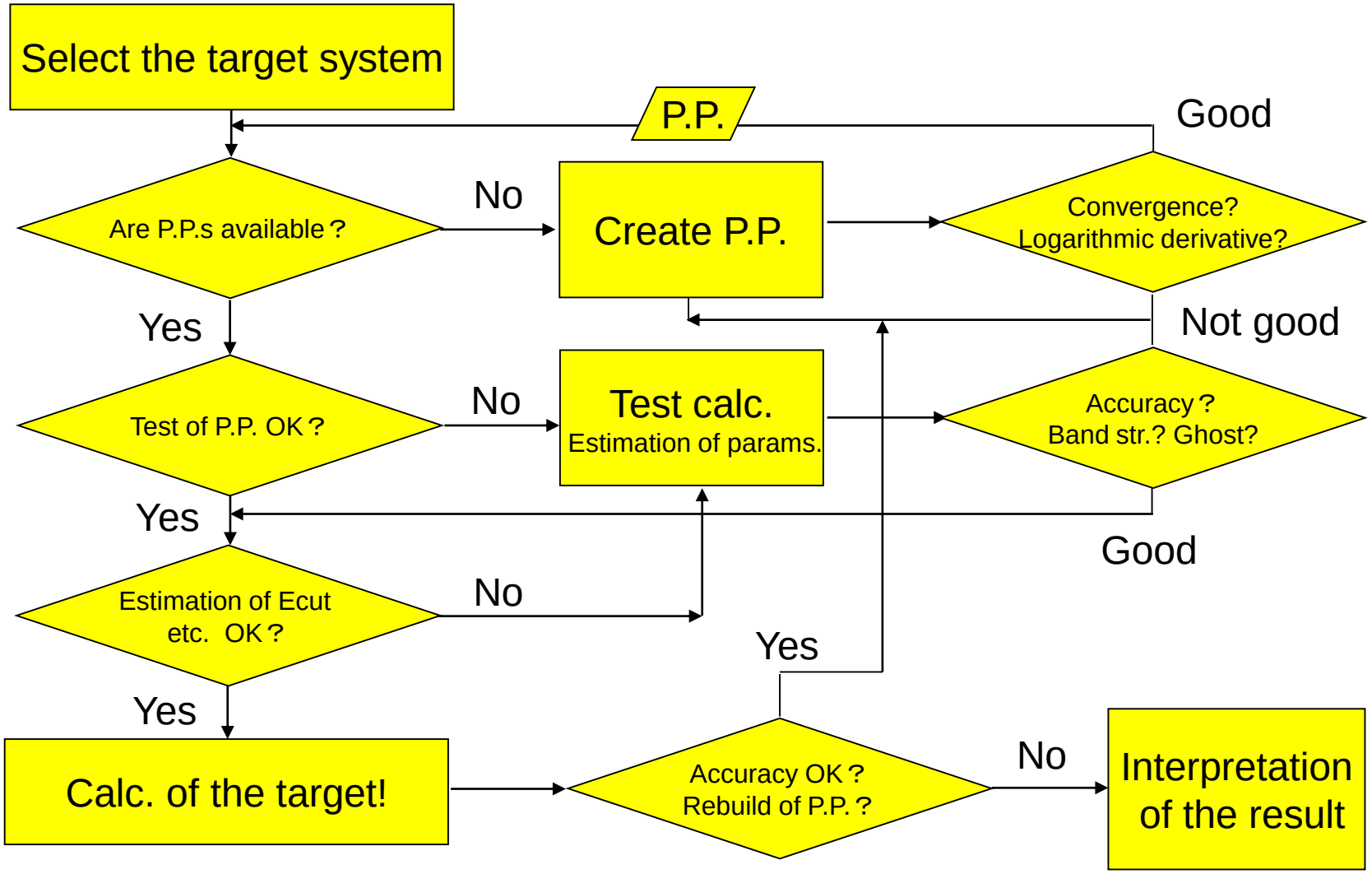
```
[stud**@rl ~/ESopt-CMD32-fw]$ cd utility/cBN_scripts
[stud**@rl cBN_scripts]$ cp CORD_5 ../../INPUT_DATA/CORD
[stud**@rl cBN_scripts]$ cd ../../
[stud**@rl ~/ESopt-CMD32-fw]$ head makefile
[stud**@rl ~/ESopt-CMD32-fw]$ make < input_make
[stud**@rl ~/ESopt-CMD32-fw]$ cd cBN
[stud**@rl cBN]$ qsub qsub
```

- Create a0ene.dat and a0ene.dati. (An example is in utility/cBN_scripts)
- You can do the fitting by asking murnfit in fit_esopt.

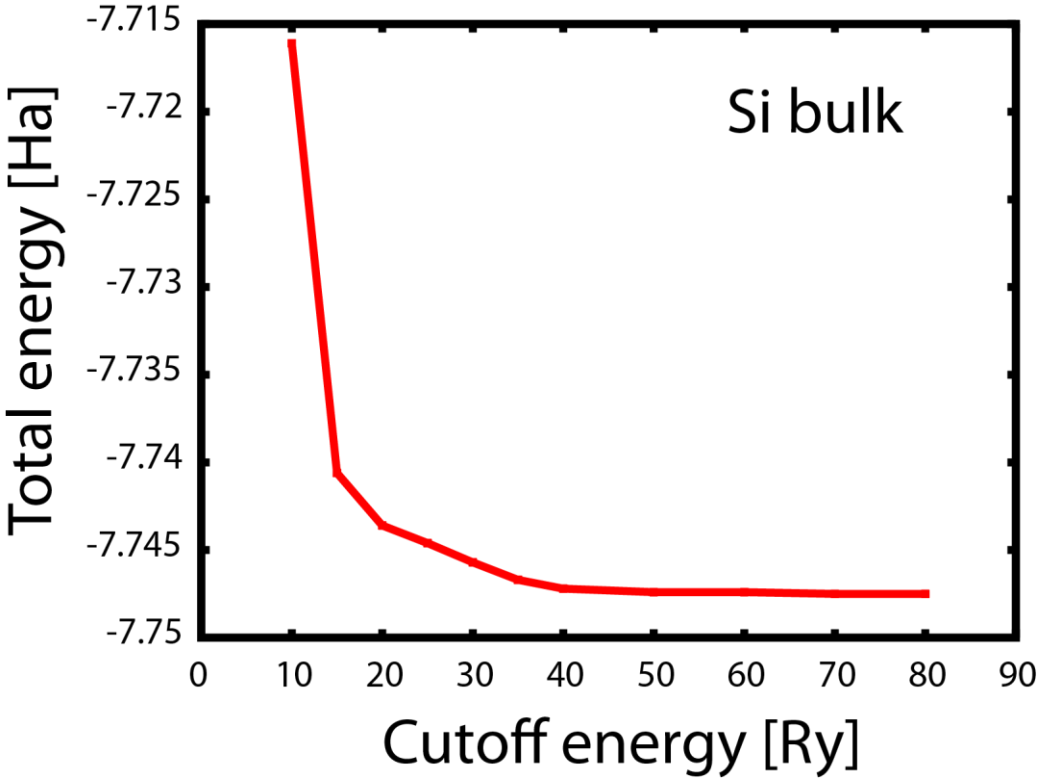
```
[stud**@rl cBN]$ pushd ../fit_esopt
[stud**@rl fit_esopt]$ make
[stud**@rl fit_esopt]$ popd
[stud**@rl cBN]$ ../fit_esopt/murnfit
```

Equilibrium volume: V_0
Bulk modulus: B_0
Pressure deriv. of bulk modulus: B_0’

Flow diagram to check accuracy



E_{cut} dependence of the total energy



calc_mode: bas
band_calc: metal

For an ordinal use, 40 Ry may be allowed.
To have a converged stress tensor, E_{cut} > 60 Ry would be required.

Trial 2: Cutoff check of PP

- Select an element among “Al, Ca, Cu, Mg, Mn, Si”.
- You can see an example of “CORD” for them in INPUT_DATA.
- Change the directory to the destination in “makefile” like,

  DESTDIR=Al <= you may rewrite this name.
- Using an example, try the cutoff test.

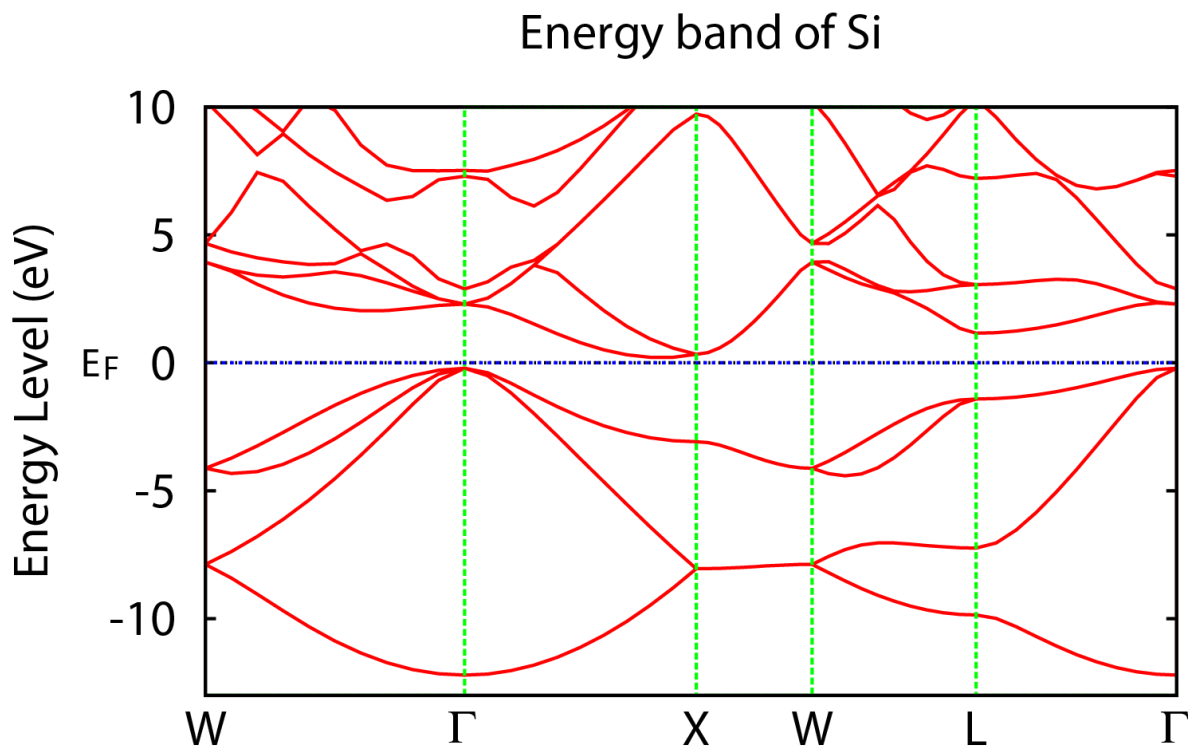
```
[stud**@rl ~/ESopt-CMD32-fw]$ cp INPUT_DATA/CORD-Al INPUT_DATA/CORD
[stud**@rl ~/ESopt-CMD32-fw]$ emacs INPUT_DATA/CORD
… please “edit” the input file “CORD”.  …
[stud**@rl ~/ESopt-CMD32-fw]$ head makefile
[stud**@rl ~/ESopt-CMD32-fw]$ make < input_make
[stud**@rl ~/ESopt-CMD32-fw]$ cd Al
[stud**@rl Al]$ qsub qsub
```

- Create a data file of “the lattice constant a” v.s. “the total energy”.
- Total energy may be seen in MONIT/energy, RESULTS/Htot001 (for basic mode), or STRUCT/result0001 (for extended mode).

Some post-processing commands

- For writing a band structure calculation,
  - Select band_calc = ‘bands’ in INPUT_DATA/CORD,
  - Do ‘make’ after checking
    - INPUT_DATA/kpoint
    - Top of the ‘makefile’
  - Do run your job by ‘qsub qsub’ in the working directry.
  - After finishing the job, you can type,
    - $ ../utility/vbpef2gp –s –e fort.50
    - $ gnuplot
  - We now see the functions of ‘xcrysden’ by seeing ‘axsf’ file in your ‘Si-band’.

Kohn-Sham band structure of Si

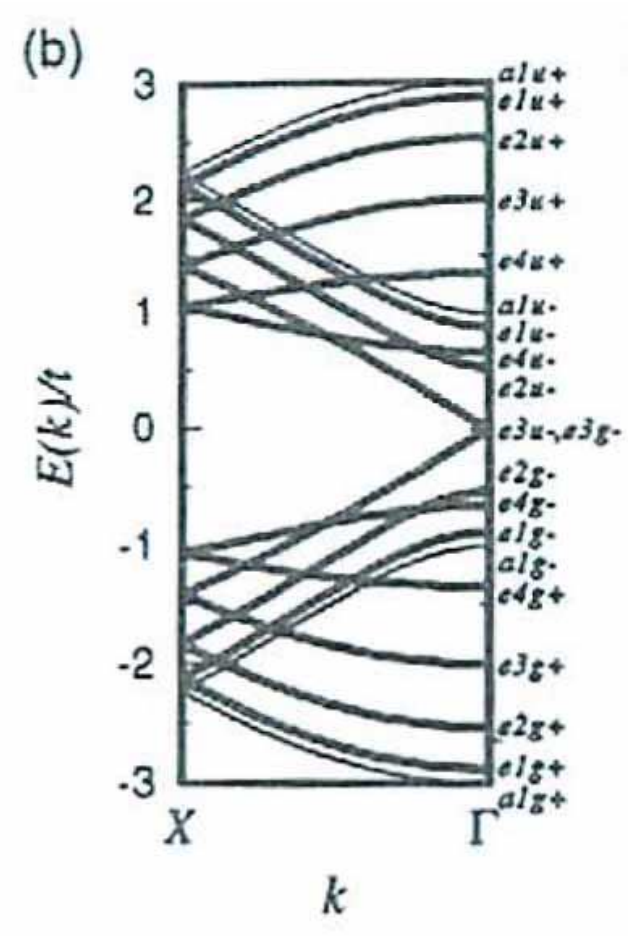


calc_mode: bas
band_calc: bands

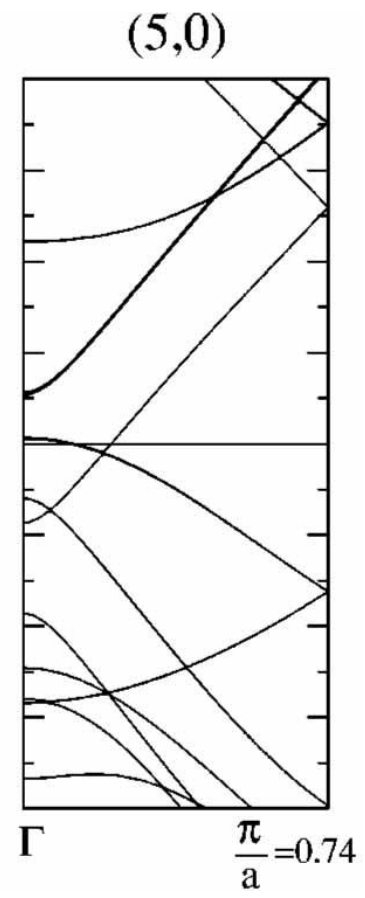
For this band calculation, E_{cut} = 60 Ry is used.
ncband=6 in CORD is used to obtain unoccupied levels.

Band structures of SWNT

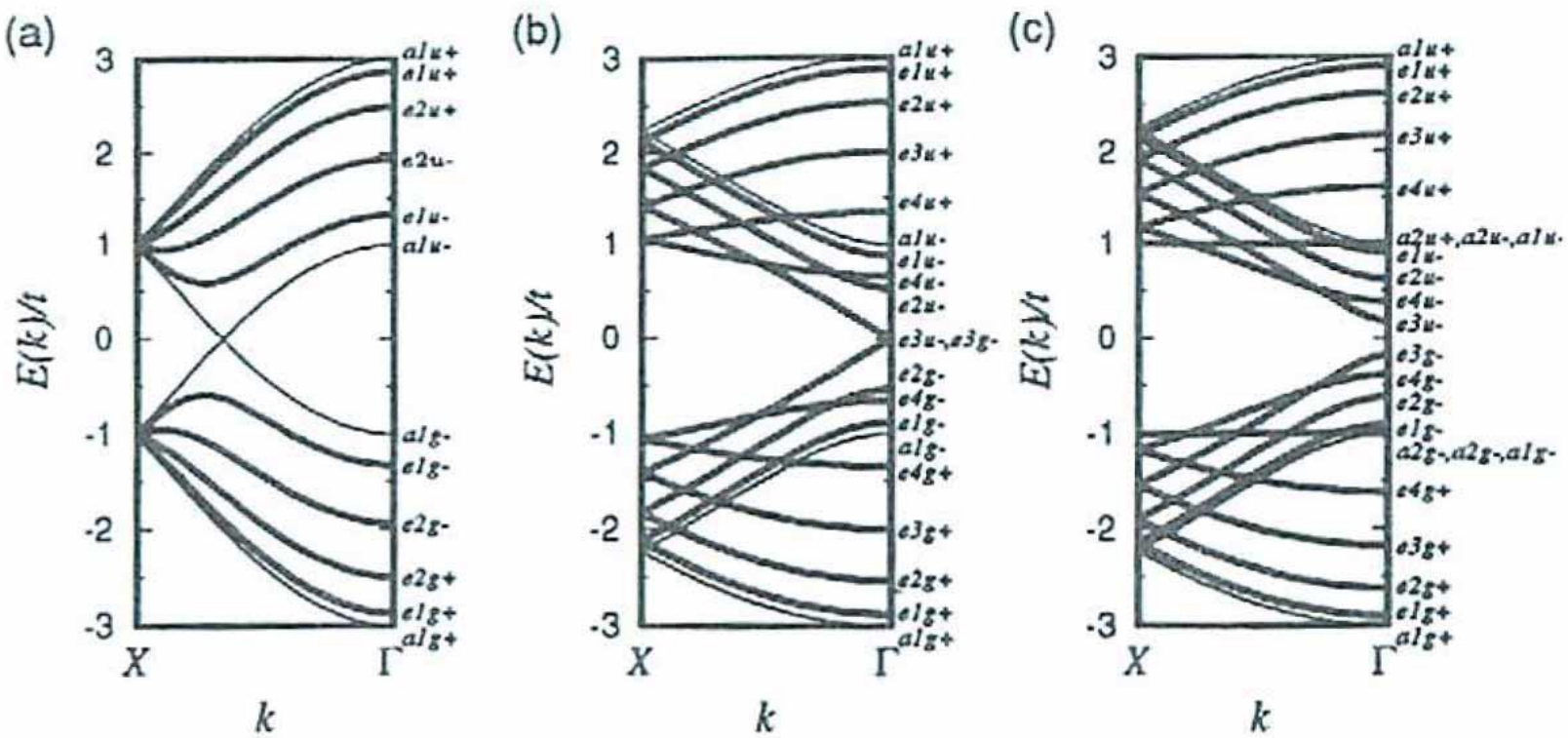
Tight binding model with π orbitals only



DFT-LDA using optimized structure



1/3-rule in a simple TBM band structure



Saito, Dresselhaus, Dresselhaus, ‘Physical Properties of Carbon Nanotubes’, Imperial College Press.

LDA band structures for thin SWNT

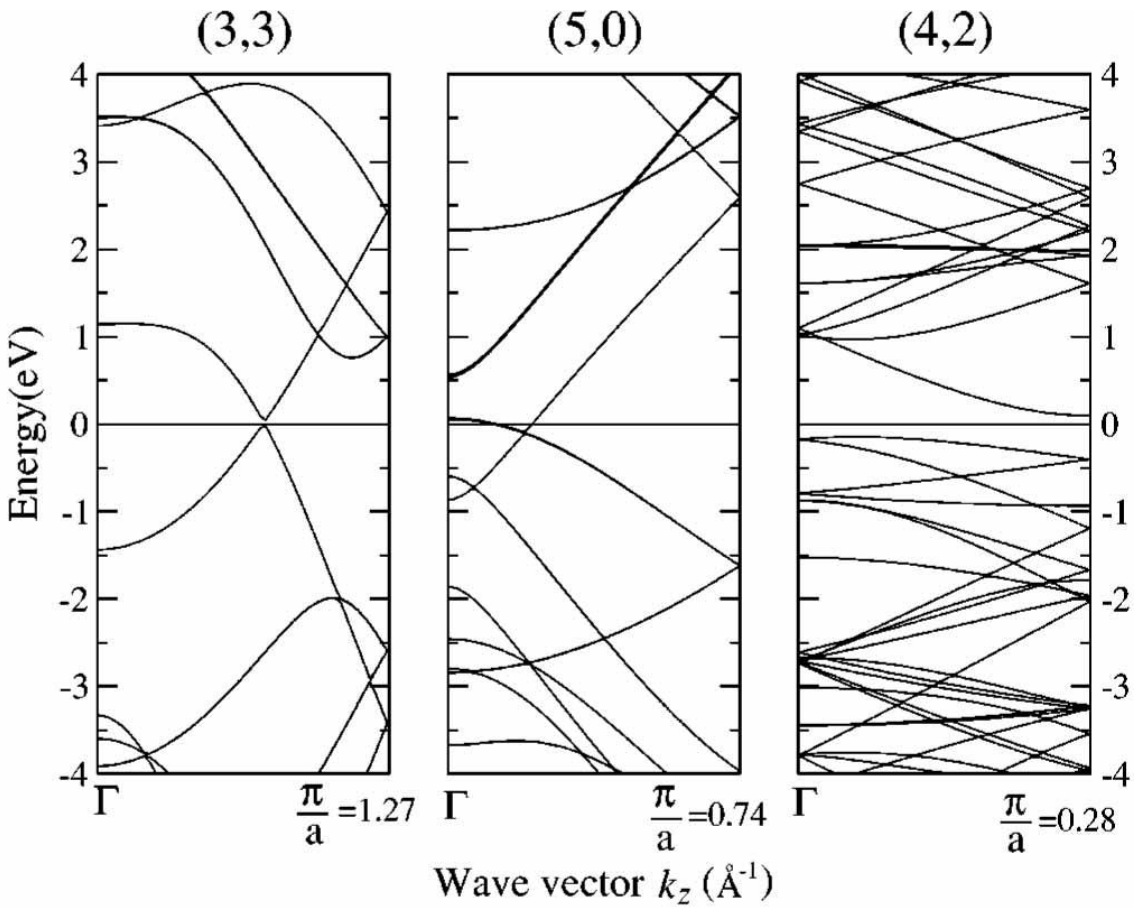


FIG. 3. Calculated electronic band structures of the relaxed 4-Å SWNT's. The Fermi level is at 0 eV.

Machón, et al. Phys. Rev. B 66, 155410 (2002).

Trial 3: band structure of CNT

- We can use prepared inputs as follows.

[stud**@rl ~/ESopt-CMD32-fw]$ cp INPUT_DATA/CORD-50Tube-b INPUT_DATA/CORD

Check E_cut in CORD

[stud**@rl ~/ESopt-CMD32-fw]$ cp INPUT_DATA/kpoint-b INPUT_DATA/kpoint

[stud**@rl ~/ESopt-CMD32-fw]$ emacs –nw makefile

<< rewrite header of makefile so that “DEST-DIR = Tube-band” >>

[stud**@rl ~/ESopt-CMD32-fw]$ make < input_make

[stud**@rl ~/ESopt-CMD32-fw]$ cd Tube-band

[stud**@rl Tube-b]$ qsub qsub

We need to wait for a while. If we need, please see the result tomorrow.

[stud**@rl Tube-b]$ ../utility/vbpef2gp –s –e fort.50

[stud**@rl Tube-b]$ gnuplot

gnuplot> load ‘bandfig.gp’

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Overview of optimization problems

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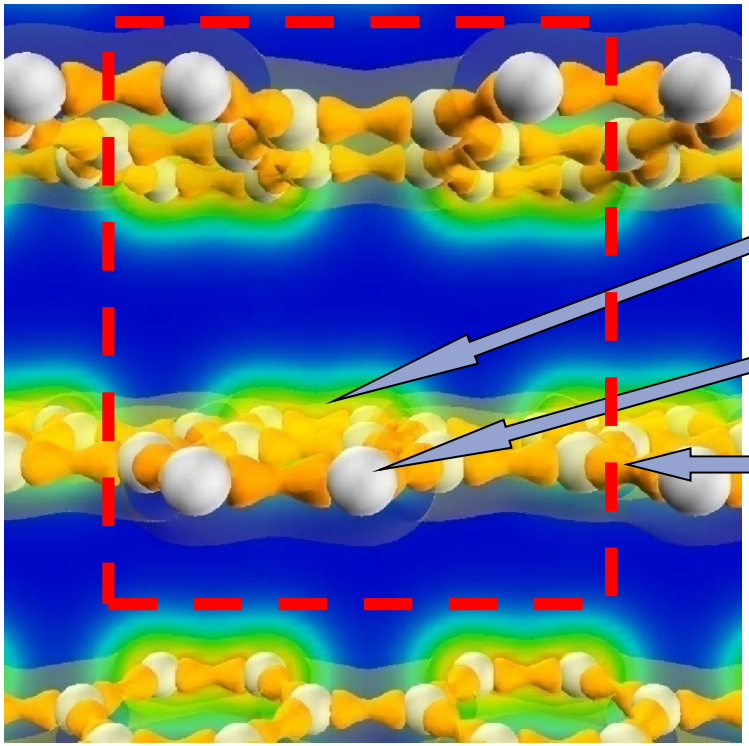
Multi-dimensional optimization problem



We regard next quantities as the variables determining of the system.

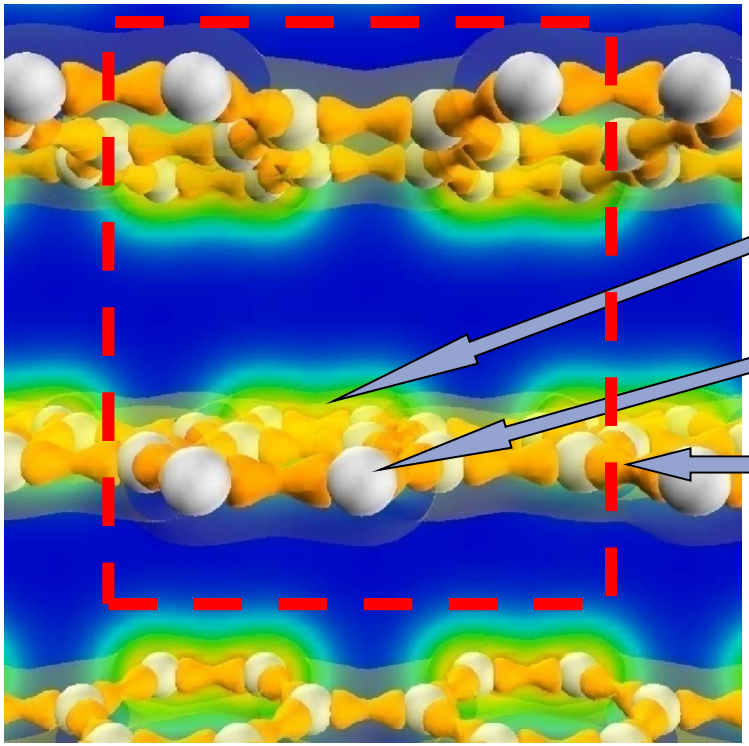
1. Electronic state

2. Atomic position

3. Unit cell (lattice parameters)

Restricted by the periodic boundary condition, various electronic states appear depending on atomic position in the variable unit cell.

Multi-dimensional optimization problem



In the actual simulation, we have

3. Electronic state

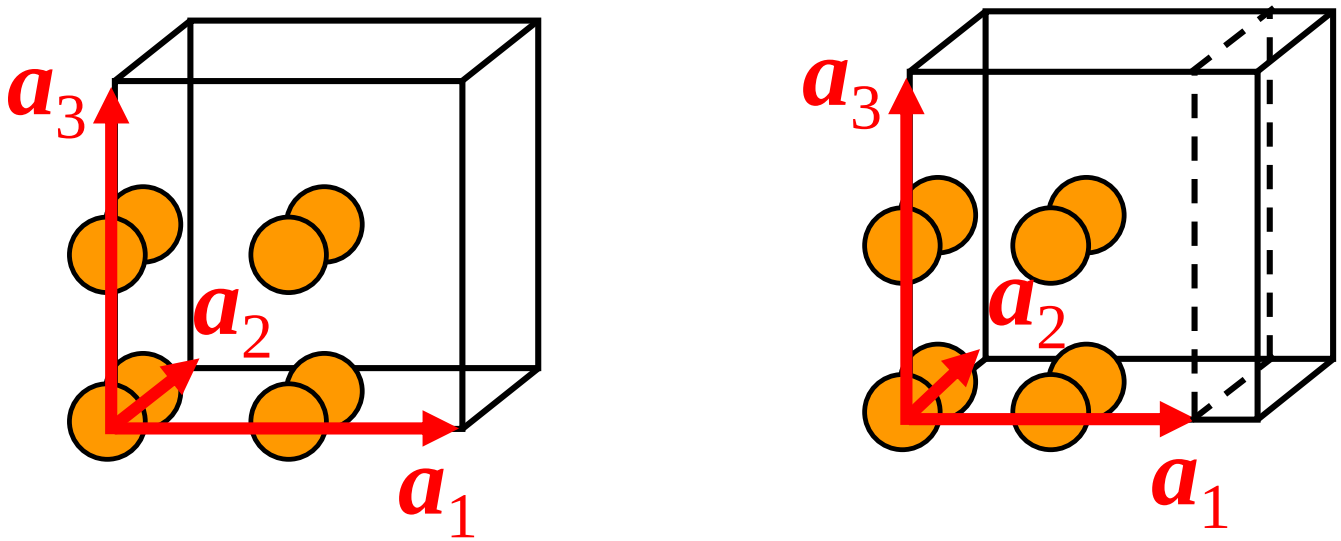
2. Atomic positions

1. Unit cell

to be optimized in an order of the number.

Multi-dimensional optimization problem

Structural change given by modification of lattice vectors induced by difference between internal stress and the external pressure.

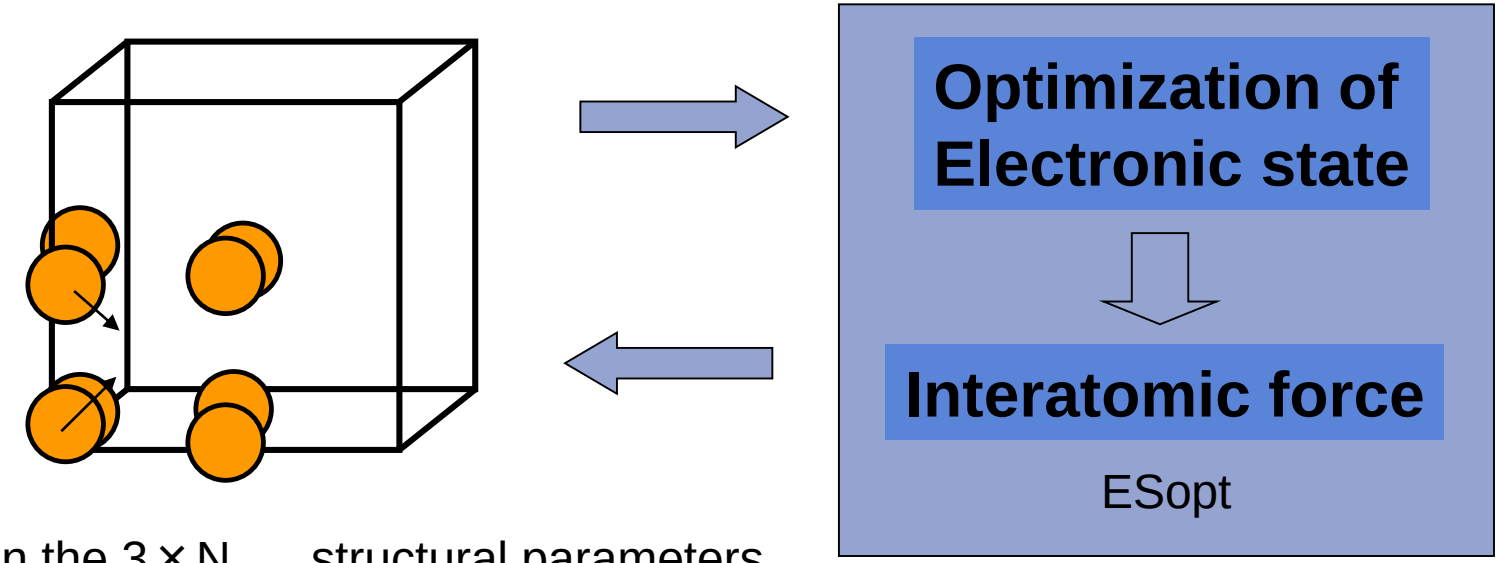


9 - 3 = 6 degrees of freedom after removing total rotation of the system.

1. Lattice constants ← optimization of all parameters
2. Elastic constants ← deformation of stable structure
3. Structural transformation ← molecular dynamics

Multi-dimensional optimization problem

Structural change and electronic structure of the structure obtained by shift in atomic position due to the interatomic force.



Shift in the $3 \times N_{atom}$ structural parameters
Change in the crystal symmetry

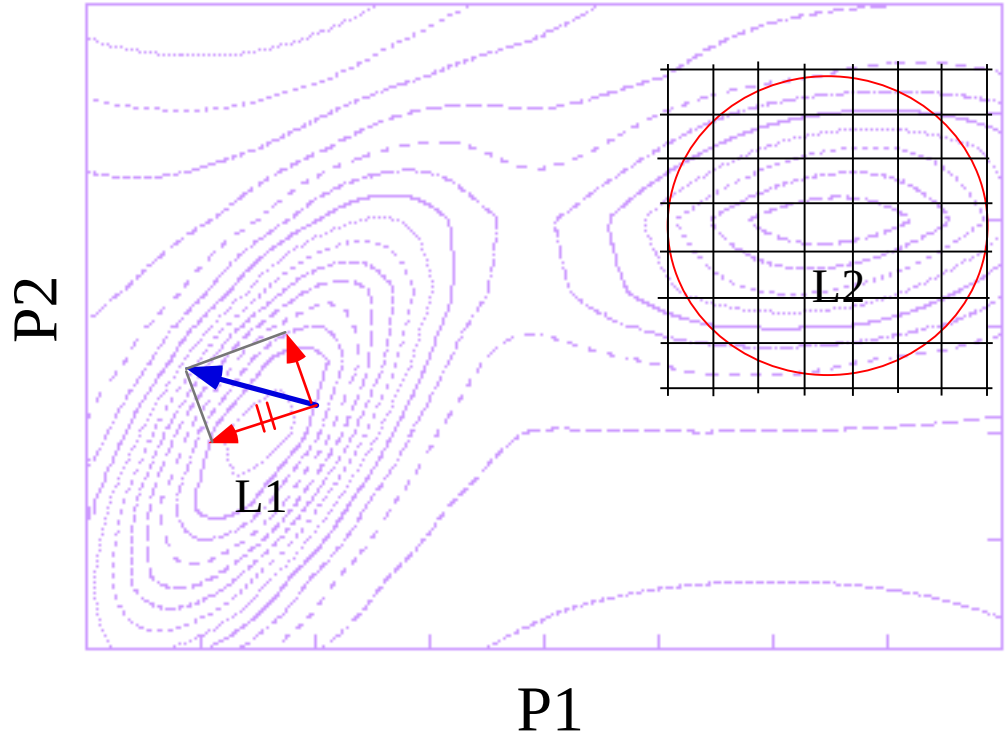
We can determine,
1. Stable atomic configuration
2. Intermediate state (transition state), reaction energy

Multi-dimensional optimization problem

- Perform optimization of essential parameters to make the energy be the lowest. The optimization is done with respect to
  - Lattice constants
  - Atomic configuration
  - Electronic structure
- The optimization process is very similar, because all of the procedure is regarded as motion of a particle on an energy surface.

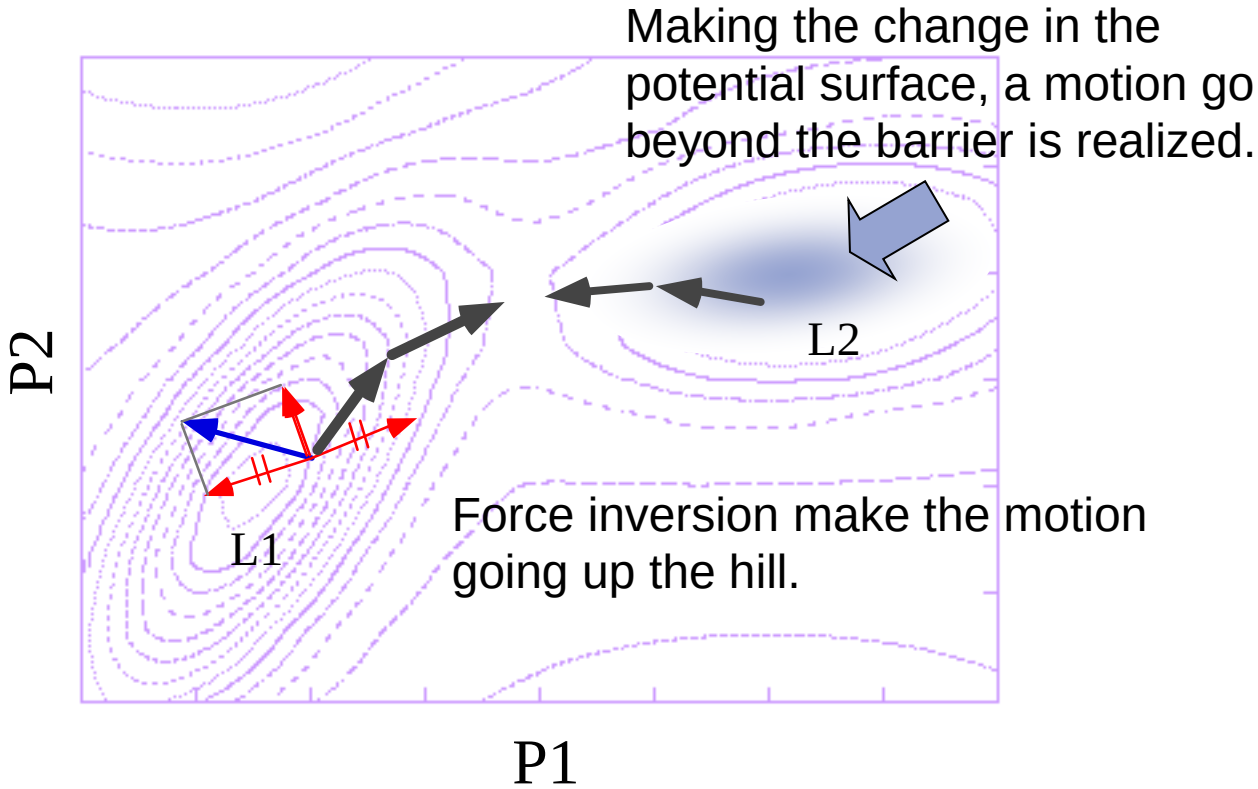
Multi-dimensional optimization problem

- Technique of the optimization
  - Global search : most powerful. Global structure of the energy surface should be known before the optimization.
  - Searching methods utilizing a gradient vector : very fast. Optimization follows a line toward the minimal point.



Multi-dimensional optimization problem

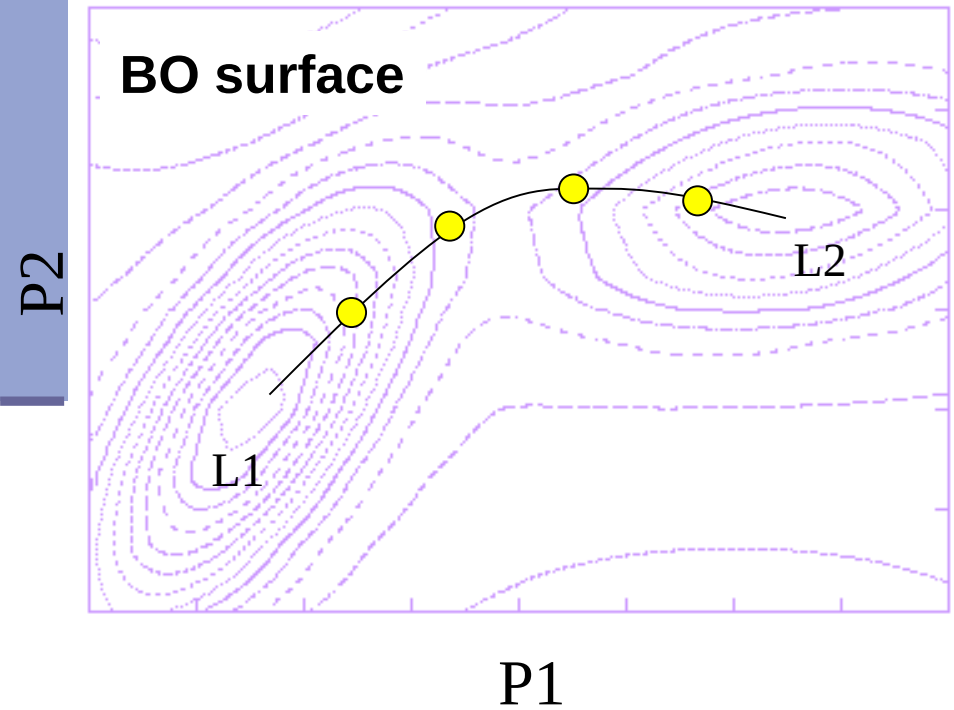
- Available methods
  - Metadynamics : search of potential minimal points beyond a potential barrier
  - Search of saddle points : force inversion technique

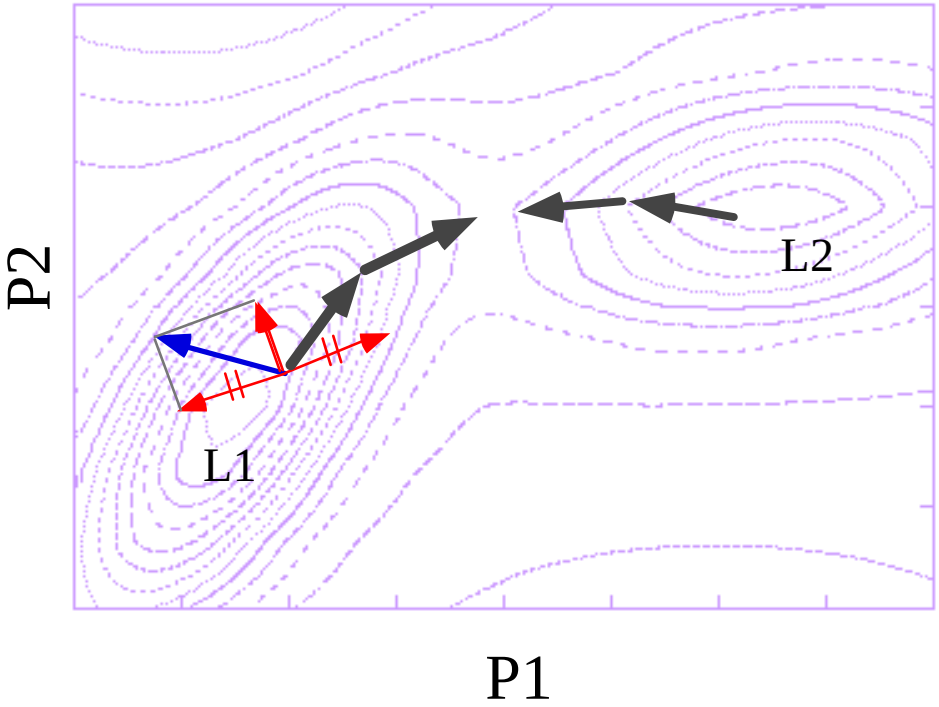


Methods to find the transition states

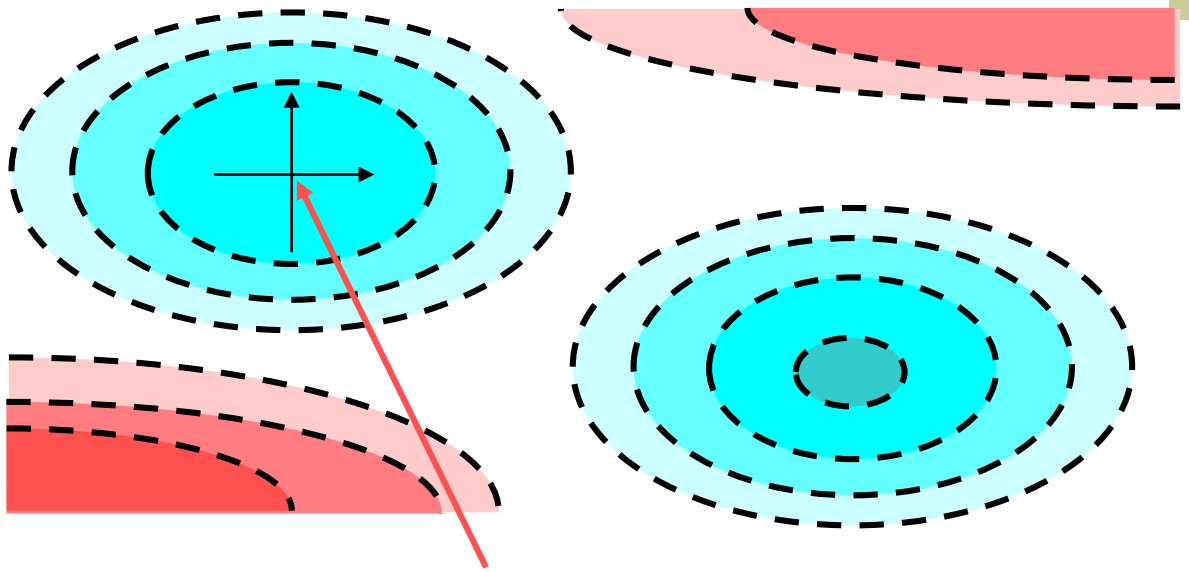
Nudged elastic band method：
- Replicas（yellow points）feel repulsion.
- They give a path through TS.

Force inversion：
- If the landscape is simple,
- The transition state is fixed.





Minimum search on the Born-Oppenheimer (BO) surface



If one look for the minimum locally around this point, one cannot find existence of another true minimum.

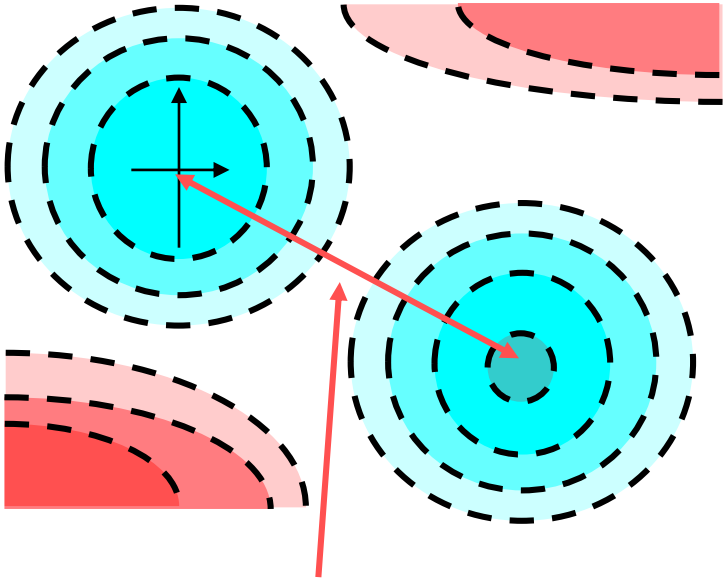
- Electronic structure at this point shows only local stability.
- Even if one make small vibration around this local minimum, only stable oscillation will appear.

In this situation, we need global search on the BO surface.
But, search in the whole $3 \times N_{atom}$-dimensional space is practically impossible.

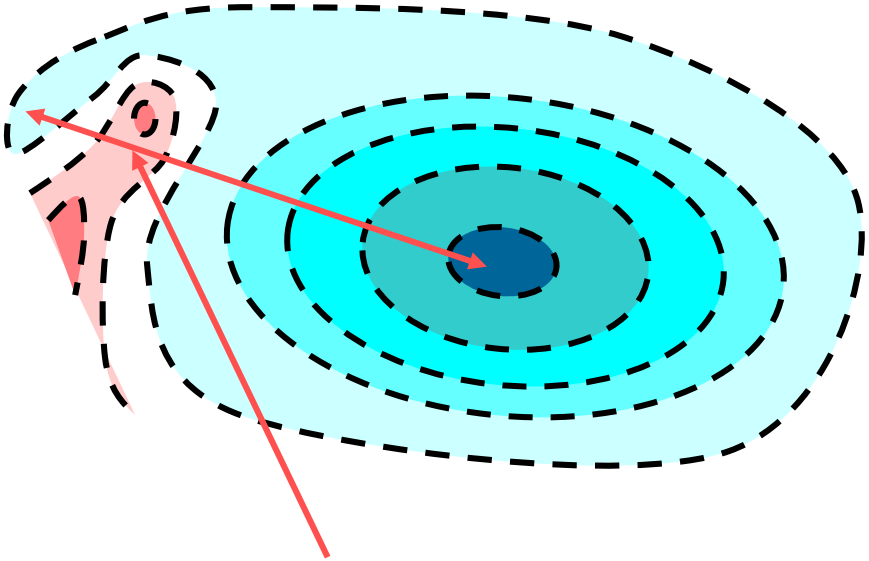
: At present, for the first-order transition, the first-principles molecular dynamics can do little without wisdom on materials.

Search for the saddle point on the BO surface

If one has some locally stable points, the saddle point of the BO surface may be found. But, we could have difficulty even in this case.

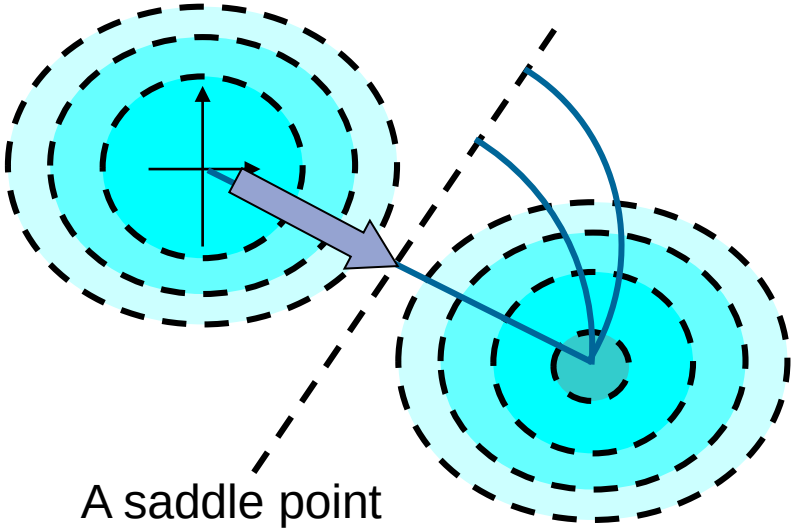


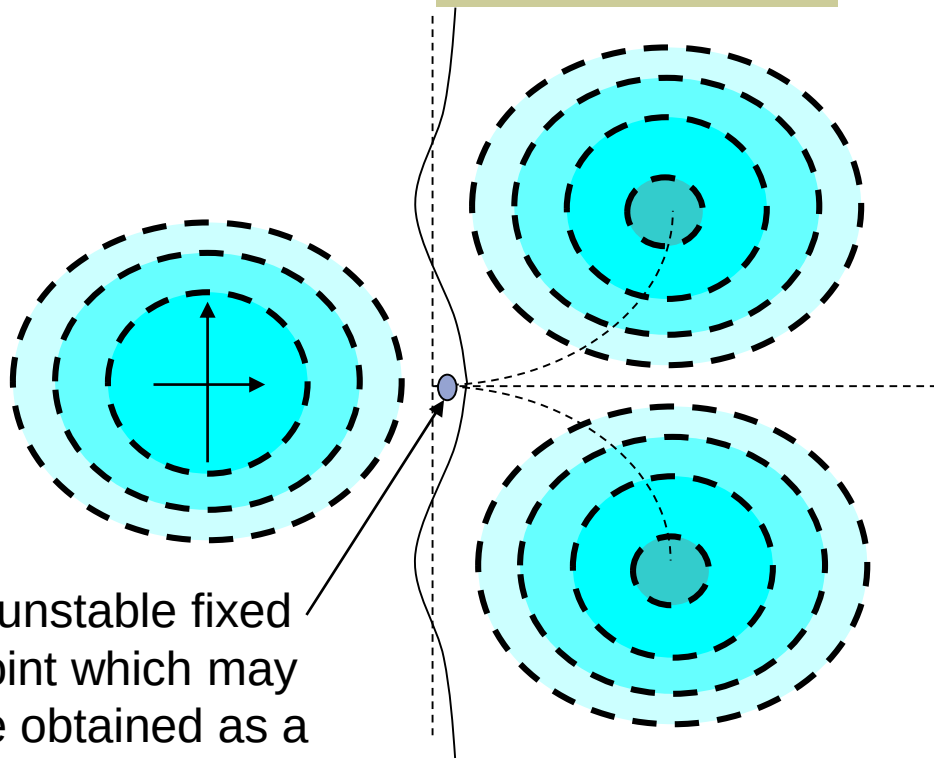
One dimensional search: Optimization methods which can search a minimum point in a section perpendicular to the reaction coordinate may give the saddle point.



In this case, this saddle point given by the one dimensional search does not tell us the true potential barrier, since we have another way to go without the barrier.

Unstable fixed points





If we optimize all the coordinate other than the reaction coordinate, the saddle point is given.

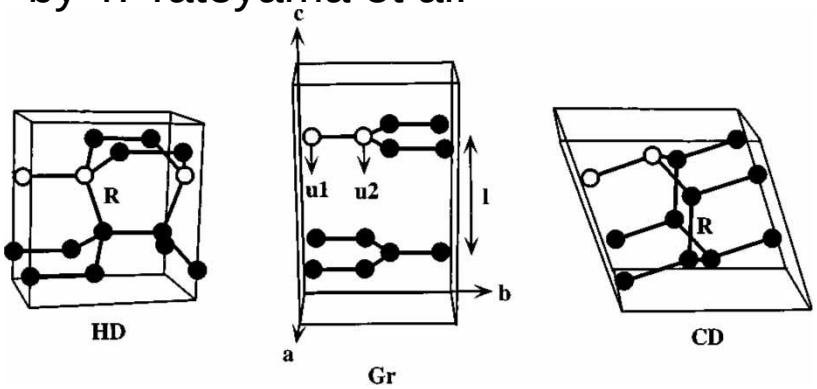
But, we may have restriction due to undesired symmetry in the simulation due to

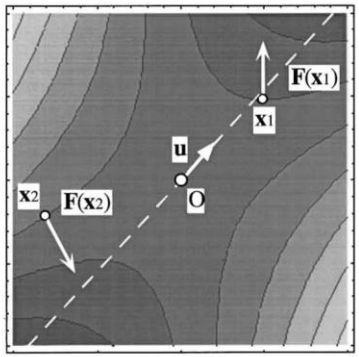
1) Finite simulation cell
2) Assumed symmetry in the run.

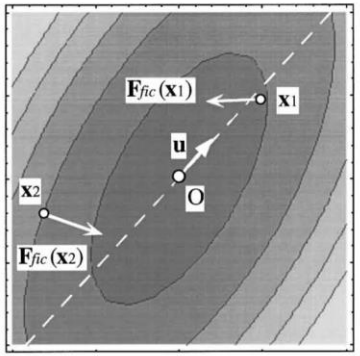
At the unstable fixed point, interatomic forces are balanced. If one look at the second-order derivative (the Hessian matrix), we may have several paths to some stable points.

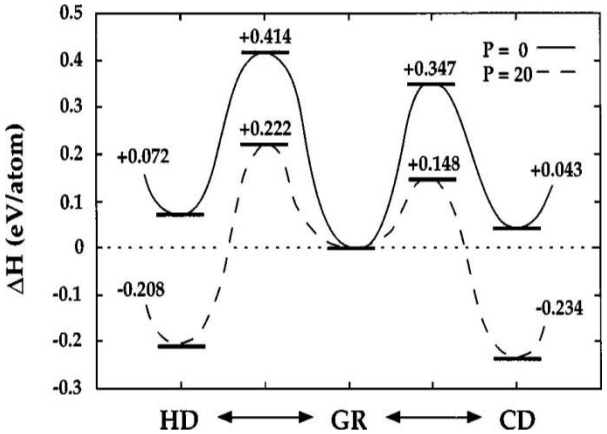
An example in the structural transformation of carbon systems

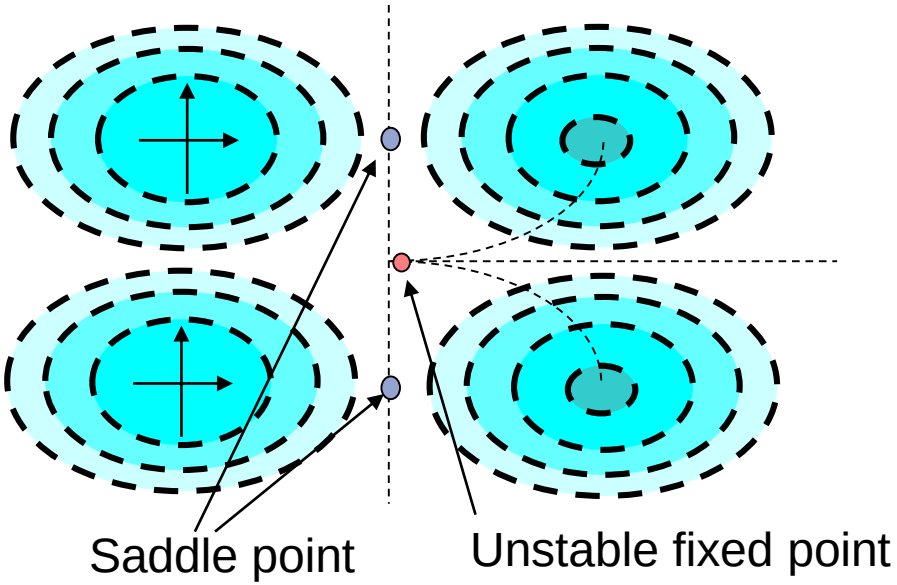
by Y. Tateyama et al.









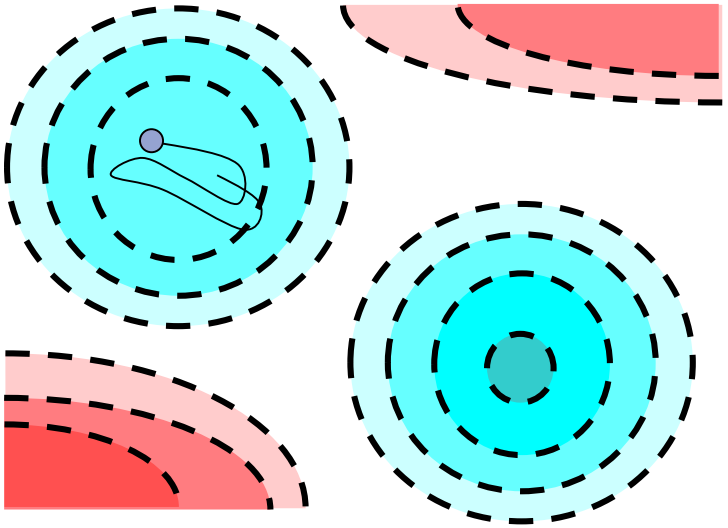


The force inversion technique determines two saddle points from the graphite to two diamond structures.

The meta-dynamics simulation

Following the motion of a system in the molecular dynamics, we add artificial potential to the true potential.

$$V_g(x) = \sum_{t_i < t} W \exp(-\left|x(t) - x(t_i)\right|^2 / 2\delta h^2)$$



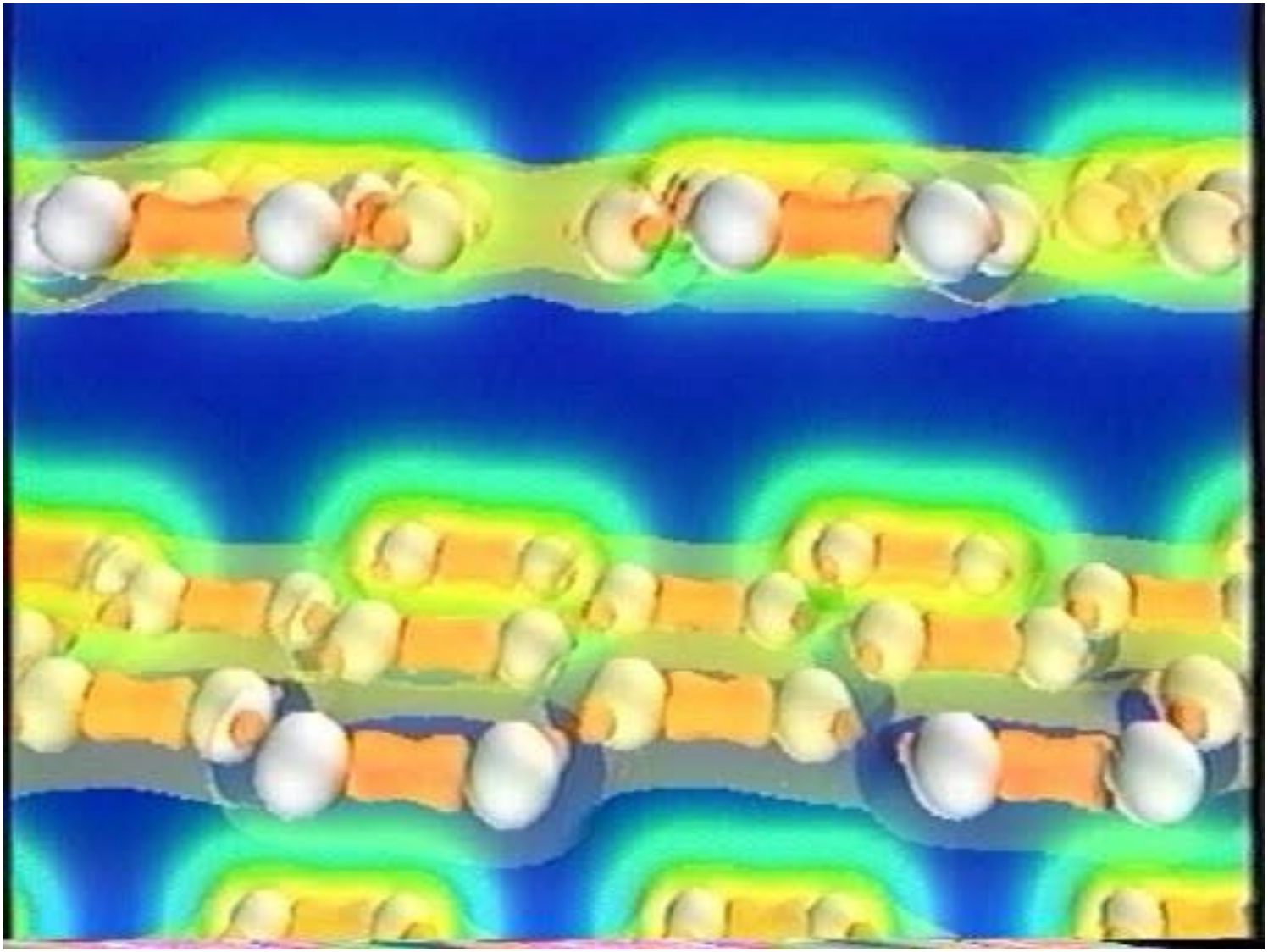
Utilizing this technique, we can reach 1) the lowest saddle point, and 2) a stable structure beyond the saddle point. If we proceed to perform this simulation without removing V_g, we should reach all of the local minima on the BO surface.

A. Laio, M. Parrinello, Proc. Natl. Acad. Sci. U.S.A. 99, 12562 (2002).
R. Martonak, et al., Phys. Rev. Lett. 90, 075503 (2003).

Recommended procedure of the structural optimization

- The case of bulk crystal structure
  - Rough estimation of the stable structure with the constant-pressure MD.
  - Optimization of the lattice constant by accurate electronic structure calculation.
  - Estimation of the bulk modulus and the elastic constants. Comparison with the experimentally observed values.
  - Confirmation of positivity in the phonon modes.
  - If an imaginary frequency appears, this may indicate that the simulation cell is too small. Try the larger simulation cell.

MD simulation of graphite in high pressure



Structural optimization method

- Optimization of bulk crystal structure
  - Estimate roughly by the constant pressure mode.
  - Improve the accuracy, optimize lattice constants for the case with the unit ε.
  - Calculate the bulk modulus and elastic constants and compare the real observation.
  - Check that phonon modes have positive real frequency. (We need the super cell technique.)
  - If an imaginary frequency appears, find a constraint in the simulation, remove the restriction and re-optimize the parameters.