Density Functional based Tight Binding and its implementation in deMonNano

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deMonNano

`http://demon-nano.ups-tlse.fr`

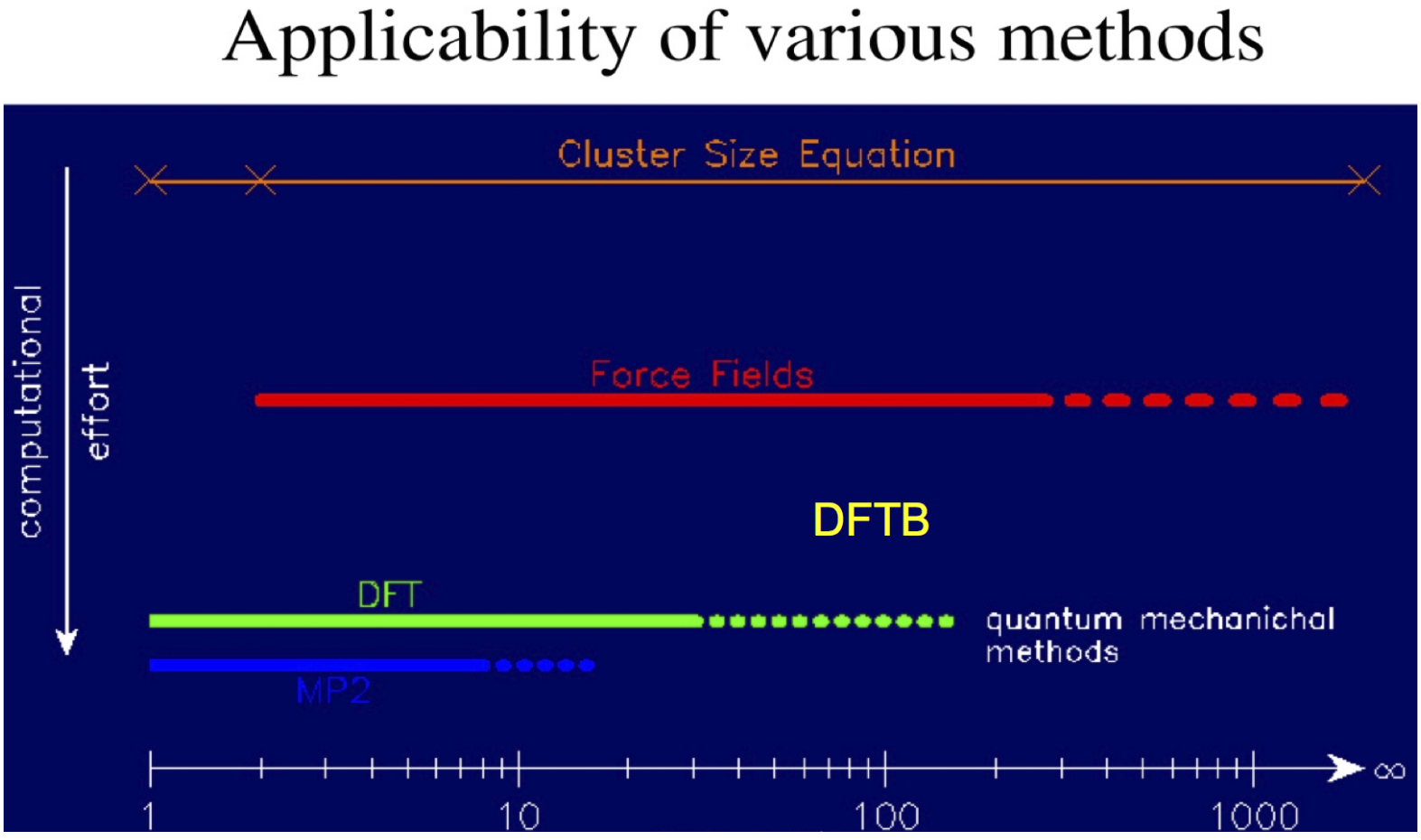
When do I need Tight Binding ?

There is a field of applications for which

- *ab intio* schemes are too much time costing
- An explicite description of the electronic system is usefull (to reduce the number of parameters, excited states, ...)

This is where Tight Binding approaches are usefull in terms of **compromise between accuracy and computational cost**

When do I need Tight Binding ?



Density Functional based Tight Binding

How can we reach a TB expression from DFT ?

- Use of a minimal basis
- Use Tight Binding approximation (two center terms) to compute integrals
- Taylor expansion of the DFT energy with respect to a reference density $\rho = \rho_0 + \delta\rho$ with $\rho_0 = \rho_0^A + \rho_0^B + \rho_0^C + ..$
  $E^{DFTB} = E^{DFT}[\rho_0] + \int \frac{\delta E^{DFT}}{\delta \rho}|_{\rho_0} \delta\rho$

Density Functional based Tight Binding

$$E^{DFTB} = \sum_{A,B} E^{rep}_{AB}(R_A - R_B) + \sum_i n_i \sum_\mu \sum_\nu c_{i\mu} c_{i\nu} H^0_{\mu\nu}$$

with $H_{\mu\nu} = < \chi_\mu | f^{KS}[\rho_0] | \chi_\nu >$

- Variational principle of DFT : minimize the energy with a constraint of othonormality :
- $H^0 C_i = \epsilon_i S C_i$

A DFTB code needs parameter files (Slater Koster files) for each pair of involved atoms.

Density Functional based Tight Binding, SCC version

DFTB refined in 1998 by Elstner et al. to include second order terms in the Taylor expansion (SCC-DFTB) .

- $E^{DFTB} = E^{DFT}[\rho_0] + \int \frac{\delta E^{DFT}}{\delta \rho}|_{\rho_0}\delta\rho + \frac{1}{2}\int\int' \frac{\delta^2 E^{DFT}}{\delta\rho\delta\rho'}|_{\rho_0}\delta\rho\delta\rho'$

Density Functional based Tight Binding, SCC version

$$E^{DFTB} = \sum_{A,B} E^{rep}_{AB} + \sum_i n_i \sum_\mu \sum_\nu c_{i\mu} c_{i\nu} H^0_{\mu\nu} + \frac{1}{2} \sum_{A,B} \Delta q_A \Delta q_B \gamma_{AB}$$

- Variational solution with orthonormality constraint
- $HC_i = [H^0 + H^1(q)]C_i = \epsilon_i S C_i$
- $q \rightarrow H^1 \rightarrow H \rightarrow C \rightarrow q$
- The second order term reintroduces the self consistent scheme, over the charges $\rightarrow$ SCC

LR-TD-DFTB

Linear-response Time Dependent -DFT

- Perturbative treatement of Time Dependant KS equations
- Often implemented with Casida's equation
- It is possible to adapt DFTB approximation to TDDFT equation to compute excited states. (Niehaus et al. PRB 63, 085108, 2001)

LR-TD-DFTB

- The excitation energies ω_I found by solving (for singlet)

$$\sum_{ij}[\omega_{ij}^2\delta_{ik}\delta_{jl} + 4\sqrt{\omega_{ij}}K_{ij,kl}\sqrt{\omega_{kl}}]F_{ij}^I = \omega_I^2 F_{kl}^I$$

with $\omega_{ij} = \epsilon_j - \epsilon_i$; i,k occupied, j,l virtual

$$K_{ij,kl} = \int \psi^i\mathbf{r})\psi^j(\mathbf{r})[\frac{1}{\mathbf{r}-\mathbf{r}'} + \frac{\delta^2 E_{xc}}{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')}]\psi^k(\mathbf{r}')\psi^l(\mathbf{r}')$$

LR-TD-DFTB

$$K_{ij,kl} = \int \psi^i \mathbf{r})\psi^j(\mathbf{r})[\frac{1}{\mathbf{r}-\mathbf{r}'} + \frac{\delta^2 E_{xc}}{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')}]\psi^k(\mathbf{r}')\psi^l(\mathbf{r}')$$

- Transition dipole density :
  $\rho^{ij}(r) = \psi^i(\mathbf{r})\psi^j(\mathbf{r}) = \sum_A q_A^{ij} F^0(r - R_A)$
- Mulliken approach : $q_A^{ij} = 0.5 \times \sum_{\mu\in A,\nu} c_\mu^i c_\nu^j S_{\mu\nu} + c_\mu^j c_\nu^i S_{\mu\nu}$

$$K_{ij,kl} = \sum_{A,B} q_A^{ij} q_B^{kl} \gamma_{AB}$$

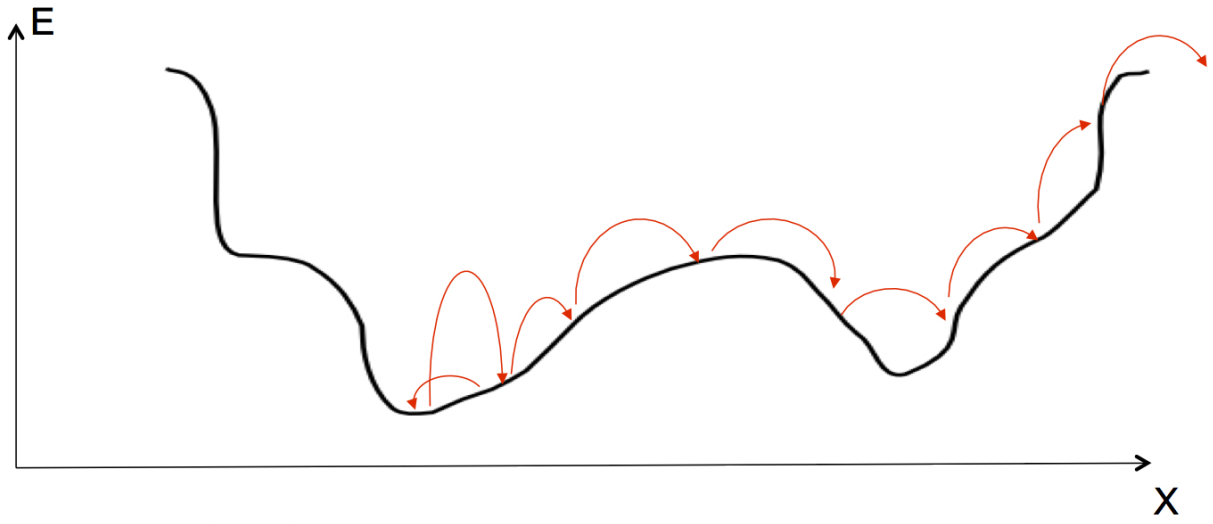
Quaternion definition

QUATERNION = a powerfull tool for rigid body systems

Euler's theorem : Any rotation or sequence of rotation of a rigid body is equivalent to a rotation by a given angle θ about a fixed axis $\vec{u} = a\vec{u_x} + b\vec{u_y} + c\vec{u_z}$.
The quaternion is befined by $q = (cos(\theta/2), \vec{u}sin(\theta/2))$
$q = (cos(\theta/2), a\ sin(\theta/2), b\ sin(\theta/2), c\ sin(\theta/2)$
To place a molecule, we need
1- A reference geometry (the MOLECULES file)
2- The position of the mass center (3 numbers)
3- The quaternion to define its rotation (4 numbers)
Quaternions are automatically normalized in deMonNano

Monte Carlo simulations

Simple Monte Carlo Metropolis scheme



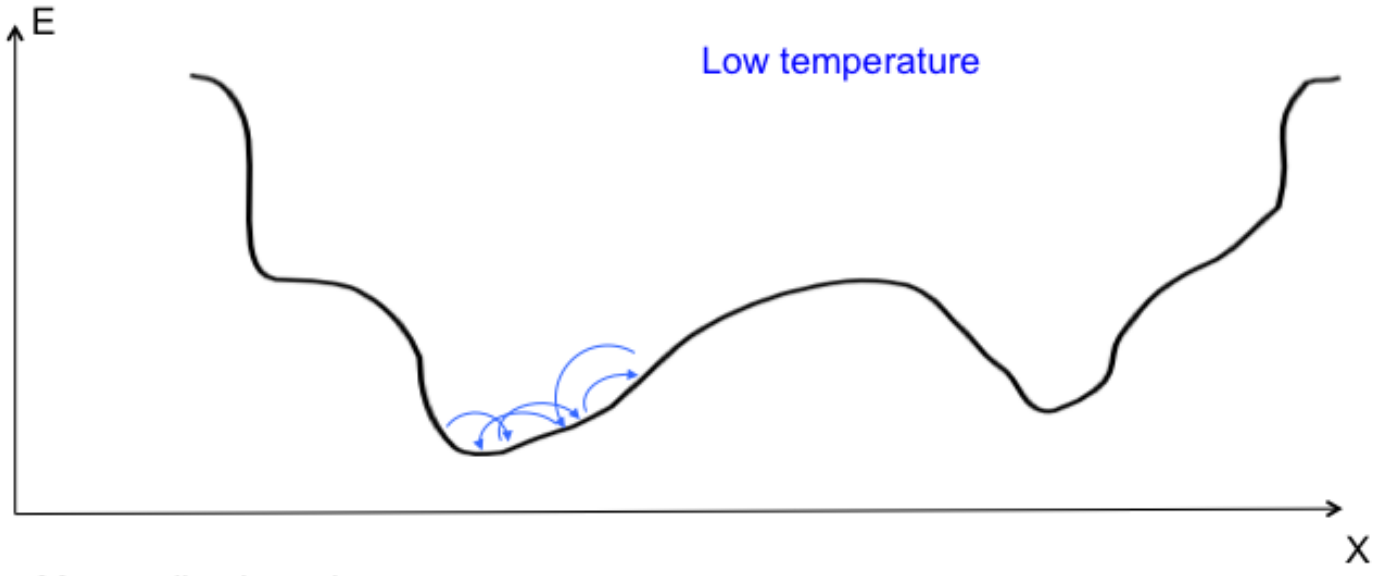
Metropolis algorythm

- Xn, E_n
- $X_{n+1}=X_n+\text{rand}()*\text{step}$
- Compute : E_{n+1}
- Displacement accepted with the probability

$$\begin{cases} 1 & if \quad E_{n+1} < E_n \\ e^{-(E_{n+1}-E_n)/kT} & if \quad E_{n+1} > E_n \end{cases}$$

Parallel Tempering Monte Carlo

Monte Carlo

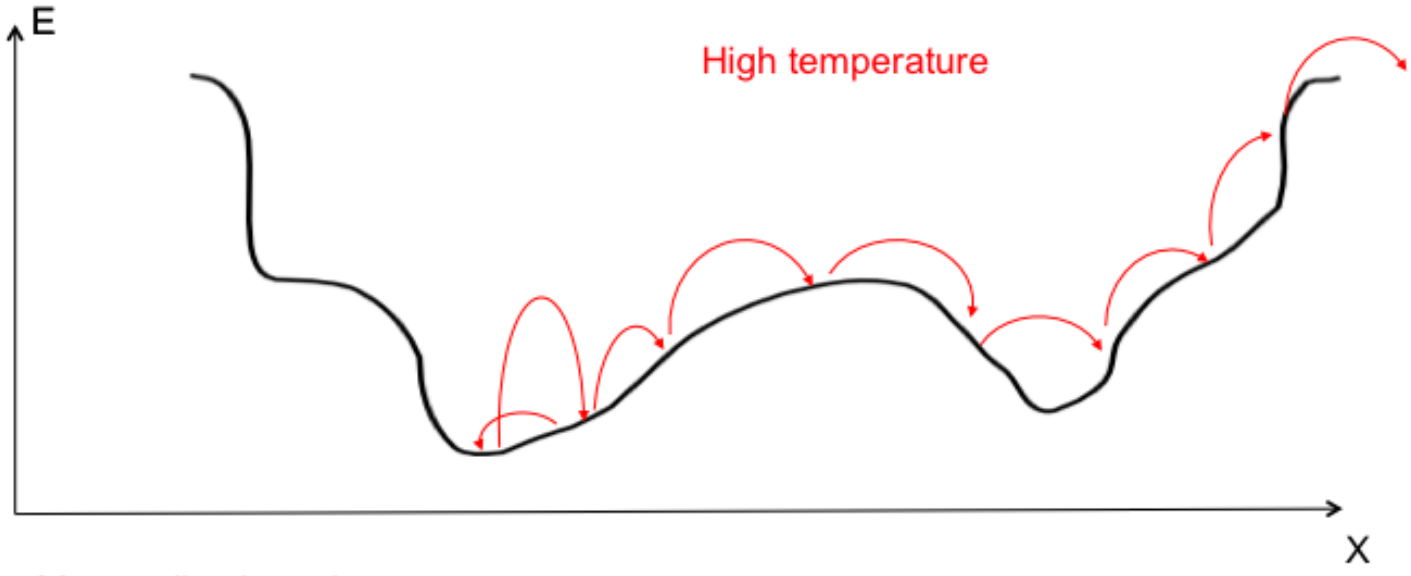


Metropolis algorythm

- E_n
- Random displacement => E_{n+1}
- Displacement accepted with the probability $\begin{cases} 1 & if \quad E_{n+1} < E_n \\ e^{-(E_{n+1}-E_n)/kT} & if \quad E_{n+1} > E_n \end{cases}$

Parallel Tempering Monte Carlo

Monte Carlo



Metropolis algorythm

- E_n
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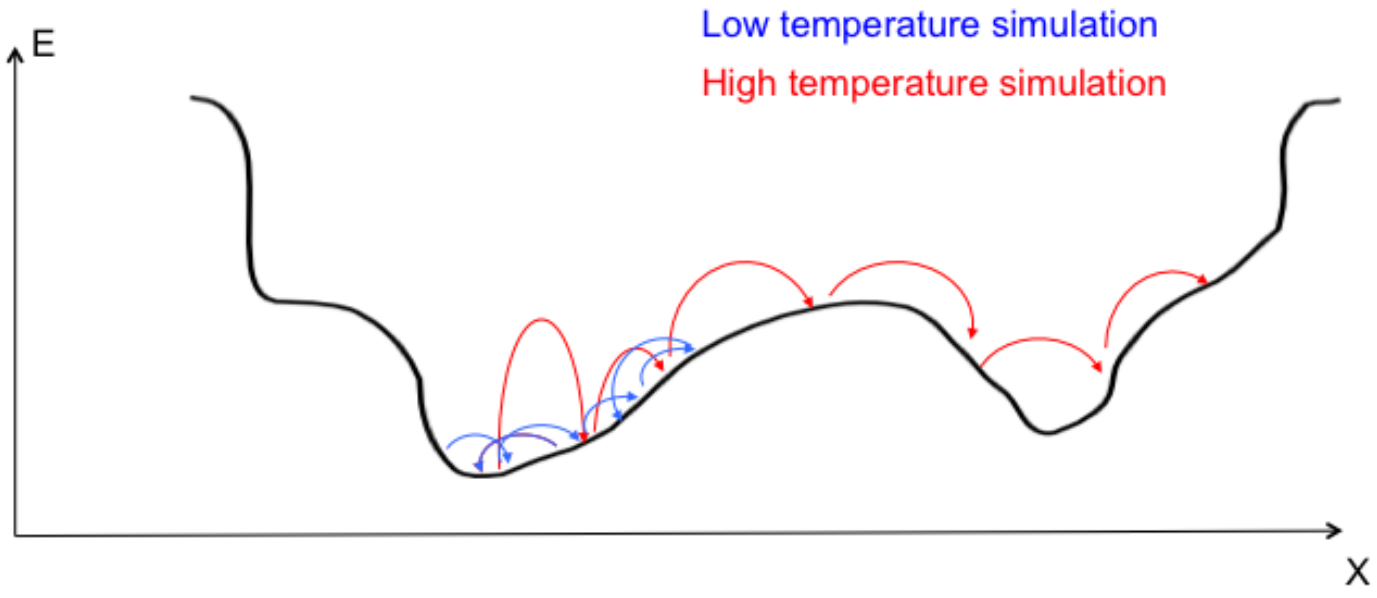
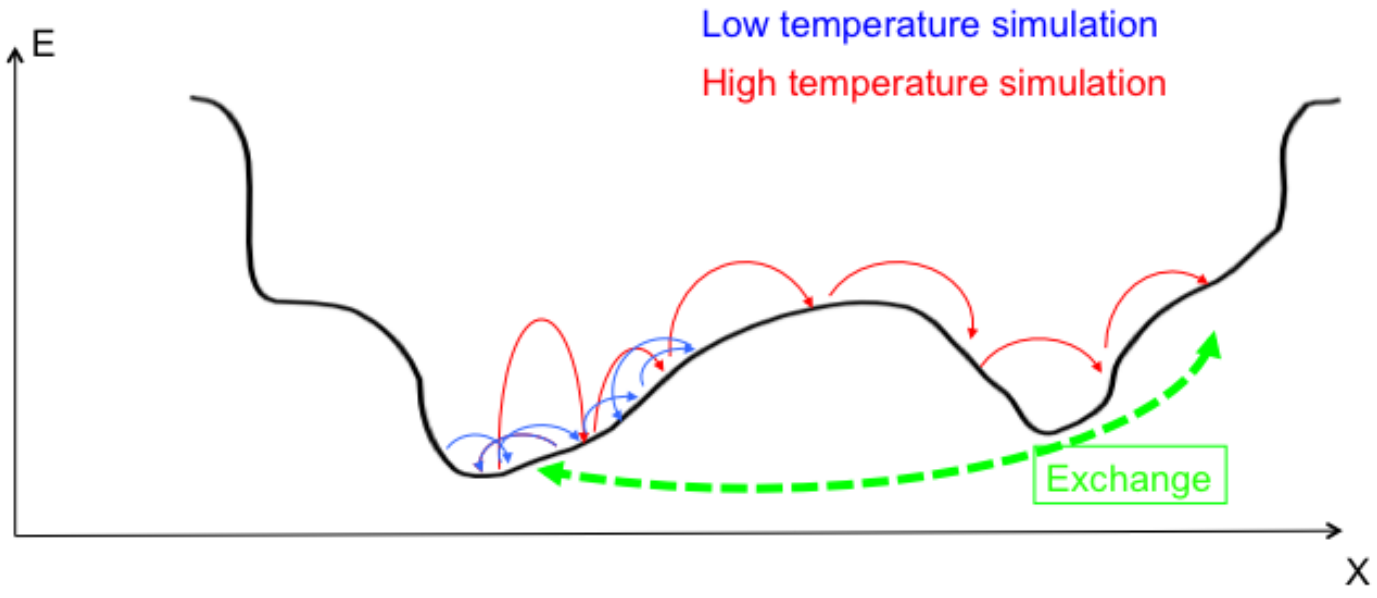
Parallel Tempering Monte Carlo



Perform exchanges between the temperature with the probability

$$\min(1, e^{(E_{hot}-E_{cold})/(kT_{hot}-kT_{cold})})$$

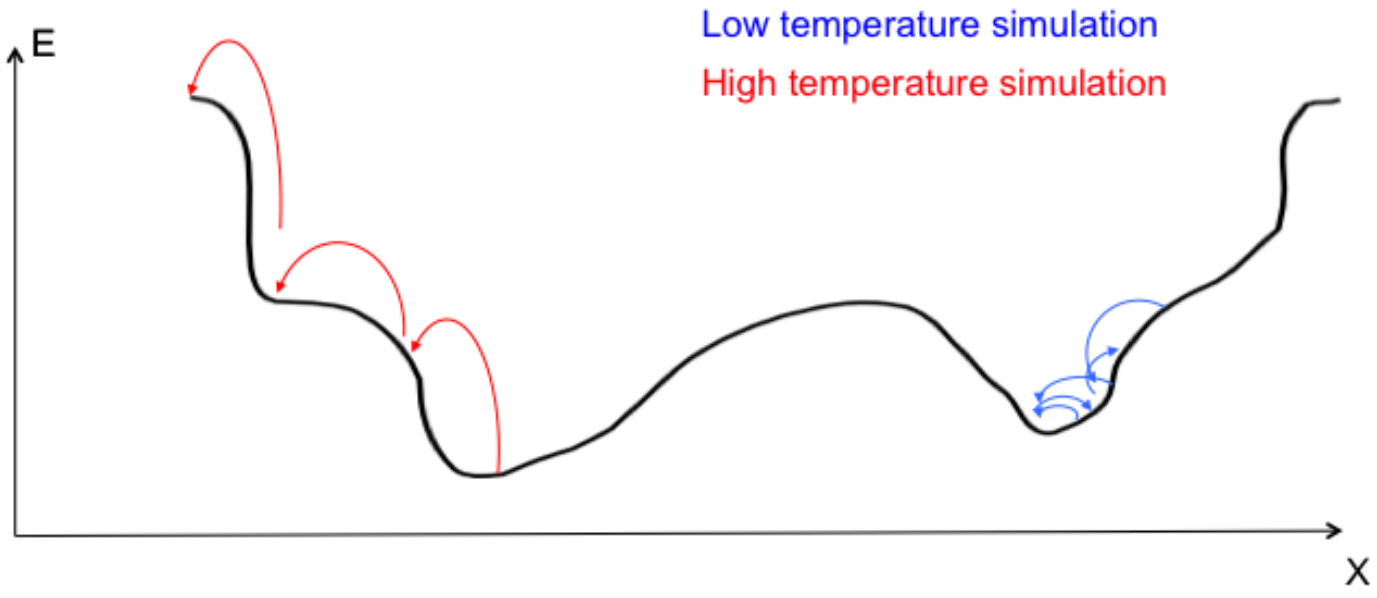
Parallel Tempering Monte Carlo



Perform exchanges between the temperature with the probability

$$\min(1, e^{(E_{hot}-E_{cold})/(kT_{hot}-kT_{cold})})$$

Parallel Tempering Monte Carlo



Perform exchanges between the temperature with the probability

$$\min(1, e^{(E_{hot}-E_{cold})/(kT_{hot}-kT_{cold})})$$

Need of about 20-30 temperatures -> few millions of single point calculations

Same approach can be applied to MD $\longrightarrow$ PTMC

Now it is time to compute

Important files

deMon.inp
deMon.out
deMon.mol $\rightarrow$ molden deMon.mol

First steps ; ex_0 ; Single point calculation

The deMon.inp file :
MAINKEYWORD SUBKEY1 SUBKEY2 ...
MAINKEYWORD' SUBKEY'1 SUBKEY'2 ...
Visit http ://demon-nano.ups-tlse.fr/ for list of keywords
$\rightarrow$
DFTB
PARAM
/usr/local/deMonNano/basis
GEOMETRY
O 0. 0. 0.
H -1.0 -1.0 0.0
H +1.0 -1.0 0.0
Exercise : Use keywords OPTIMIZATION ; PRINT DEBUG
Visualize optimization movie

First steps ; ex_0 ; Single point calculation

The deMon.out shows the different contributions to the energy.
Remember the DFTB energy expression :

$$E^{DFTB} = \sum_{A,B} E^{rep}_{AB} + \sum_i n_i \sum_\mu \sum_\nu c_{i\mu} c_{i\nu} H^0_{\mu\nu} + \frac{1}{2} \sum_{A,B} \Delta q_A \Delta q_B \gamma_{AB}$$

We call

$$E_{band} = \sum_i n_i \sum_\mu \sum_\nu c_{i\mu} c_{i\nu} H^0_{\mu\nu}$$

$$E_{electronic} = E_{band}$$

First steps ; ex_0 ; Single point calculation

The deMon.out shows the different contributions to the energy.
Remember the DFTB energy expression :

$$E^{DFTB} = \sum_{A,B} E^{rep}_{AB} + \sum_i n_i \sum_\mu \sum_\nu c_{i\mu} c_{i\nu} H^0_{\mu\nu} + \frac{1}{2} \sum_{A,B} \Delta q_A \Delta q_B \gamma_{AB}$$

We call

$$E_{band} = \sum_i n_i \sum_\mu \sum_\nu c_{i\mu} c_{i\nu} H^0_{\mu\nu}$$

$$E_{coul} = \frac{1}{2} \sum_{A,B} \Delta q_A \Delta q_B$$

$$E_{electronic} = E_{band} + E_{coul}$$

First steps ; ex_0 ; Single point calculation

DFTB SCC
PARAM PTYPE=MAT
/home/rapacioli/basis/
GEOMETRY
C 0.685236 -0.000000 0.000000
C -0.740774 -0.000000 0.000000
C 1.398621 -0.000000 1.234753
C -1.454153 -0.000000 1.234756
...
Try changing MAT by BIO

First steps ; ex_0 ; Single point calculation

All steps can be visualized with the PRINT DEBUG option →

```
DFTB SCC
PRINT DEBUG
PARAM PTYPE=MAT
/home/rapacioli/basis/
GEOMETRY
C 0.685236 -0.000000 0.000000
C -0.740774 -0.000000 0.000000
C 1.398621 -0.000000 1.234753
C -1.454153 -0.000000 1.234756
...
```

First steps ; ex_1 ; Molecular Dynamics

The deMon.inp file :

```
MDYNAMICS RANDOM=300
MDBATH NONE
MDSTEPS MAX=400 OUT=1
TIMESTEP 0.5
DFTB SCC
PARAM PTYPE=MAT
/home/rapacioli/basis/
GEOMETRY
C 0.685236 -0.000000 0.000000
C -0.740774 -0.000000 0.000000
C 1.398621 -0.000000 1.234753
C -1.454153 -0.000000 1.234756
...
```

OPTIMIZATION MAX=200
DFTB SCC
PARAM PTYPE=MAT
/home/rapacioli/basis/
GEOMETRY
C 0.685236 -0.000000 0.000
C -0.740774 -0.000000 0.000
C 1.398621 -0.000000 1.234
C -1.454153 -0.500000 1.234
C -1.454153 -0.000000 -1.234
C 1.398621 -0.000000 -1.234
...

First steps ; ex_3 ; Optimization + Frequency analysis

Harmonic spectrum computed after an optimization
OPTIMIZATION
FREQUENCY
DFTB SCC
PARAM PTYPE=BIO
../../../deMonNano/basis
GEOMETRY
O 3.945045 -0.402304 0.096123
H 3.859679 -0.169936 -0.093398
H 3.421899 0.390909 -0.118164
Visualize the frequencies with molden

Simple Monte Carlo ; ex_1

MONTECARLO MAX=10000
MCTEMP TMC=300 OUT=1
DFTB SCC DISP
PARAM PTYPE=MAT
/home/rapacioli/basis
QUATERNION NMOL=3 RIGID
1 1.0 0.0 .0 1.0 0.0 0.0 0.0
2 0. -3. 0.0 0.7 0.7 0. 0.0
3 1. -3. -4.0 1.0 0.0 0.0 0.0
MOLECULES NMOL=3
1 WAT
2 WAT
3 WAT

The MOLECULES FILE

WAT NAT=3
O 0.071715 0.071715 0.000000
H 1.016642 -0.088358 0.000000
H -0.088358 1.016642 0.000000
BZZ NAT=12
C 0.000000 0.000000 0.000000
H 0.000000 1.008000 0.000000
C 1.212436 -0.700000 0.000000
C 1.212436 -2.100000 0.000000
C 0.000000 -2.800000 0.000000
C -1.212436 -2.100000 0.000000
C -1.212436 -0.700000 0.000000
...

Simple Monte Carlo ; ex_2

MONTECARLO MAX=10000
MCTEMP TMC=300 OUT=1 **RESCALE=10**
DFTB SCC DISP
PARAM PTYPE=MAT
/home/rapacioli/basis
QUATERNION NMOL=3 RIGID
1 1.0 0.0 .0 1.0 0.0 0.0 0.0
2 0. -3. 0.0 0.7 0.7 0. 0.0
3 1. -3. -4.0 1.0 0.0 0.0 0.0
MOLECULES NMOL=3
1 WAT
2 WAT
3 WAT

Simple Monte Carlo ; ex_3

MONTECARLO MAX=10000 **WALL=6**
MCTEMP TMC=300 OUT=1 RESCALE=10
DFTB SCC DISP
PARAM PTYPE=MAT
/home/rapacioli/basis
QUATERNION NMOL=3 RIGID
1 1.0 0.0 .0 1.0 0.0 0.0 0.0
2 0. -3. 0.0 0.7 0.7 0. 0.0
3 1. -3. -4.0 1.0 0.0 0.0 0.0
MOLECULES NMOL=3
1 WAT
2 WAT
3 WAT

Simple Monte Carlo ; ex_4

MONTECARLO MAX=10000 **NDBG=ON** WALL=6
MCTEMP TMC=300 OUT=1 RESCALE=10
DFTB SCC DISP
PARAM PTYPE=MAT
/home/rapacioli/basis
QUATERNION NMOL=3 RIGID
1 1.0 0.0 .0 1.0 0.0 0.0 0.0
2 0. -3. 0.0 0.7 0.7 0. 0.0
3 1. -3. -4.0 1.0 0.0 0.0 0.0
MOLECULES NMOL=3
1 WAT
2 WAT
3 WAT

Simple Para Temp Monte Carlo ; ex_1

MONTECARLO MAX=500 WALL=6
MCTEMP **GEOM NTEMP=10 TEMPMIN=40**
TEMPMAX=300 RESCALE=10
DFTB SCC DISP
PARAM PTYPE=MAT
/home/rapacioli/basis
QUATERNION NMOL=3 RIGID
1 1.0 0.0 .0 1.0 0.0 0.0 0.0
2 0. -3. 0.0 0.7 0.7 0. 0.0
3 1. -3. -4.0 1.0 0.0 0.0 0.0
MOLECULES NMOL=3
1 WAT
2 WAT
3 WAT

Visualize the different trajectories
$\rightarrow$ molden deMon.04.mol ...

Simple Para Temp Monte Carlo ; ex_2

MONTECARLO MAX=2000 WALL=6
MCTEMP GEOM NTEMP=10 TEMPMIN=40 TEMPMAX=300
RESCALE=10 SMOD=20 **SDBG=ON**
DFTB SCC DISP
PARAM PTYPE=MAT
/home/rapacioli/basis
QUATERNION NMOL=3 RIGID
1 1.0 0.0 .0 1.0 0.0 0.0 0.0
2 0. -3. 0.0 0.7 0.7 0. 0.0
3 1. -3. -4.0 1.0 0.0 0.0 0.0
MOLECULES NMOL=3
1 WAT
2 WAT
3 WAT

Simple Para Temp Monte Carlo ; ex_2

Visualize the debug_swap file

$\rightarrow$ **gnuplot**

p 'debug_swap.dat' u 1 :2 w l ; rep '' u 1 :3 w l ; rep '' u 1 :4 w l ; ...

Study of the cluster $(C_6H_6)(H_2O)_2$

Water Benzene Water Monte Carlo ; ex_1

MONTECARLO MAX=100000 WALL=7
MCTEMP TMC=40 RESCALE=100
DFTB **MEMOSCC DISP WMULL**
PARAM PTYPE=MAT
/home/rapacioli/basis
QUATERNION NMOL=3 RIGID
1 1.0 0.0 .0 1.0 0.0 0.0 0.0
2 1.0 0.0 3.0 1.0 0.0 0.0 0.0
3 1.0 0.0 6.0 1.0 0.0 0.0 0.0
MOLECULES NMOL=3
1 WAT
2 BZZ
3 WAT

Water Benzene Water Para Temp Monte Carlo ; ex_2

```
MONTECARLO MAX=10000 WALL=7
MCTEMP GEOM NTEMP=10 TEMPMIN=40 TEMPMAX=500
RESCALE=10 SMOD=20
DFTB MEMOSCC DISP WMULL
PARAM PTYPE=MAT
/home/rapacioli/basis
QUATERNION NMOL=3 RIGID
1 1.0 0.0 .0 1.0 0.0 0.0 0.0
2 1.0 0.0 3.0 1.0 0.0 0.0 0.0
3 1.0 0.0 6.0 1.0 0.0 0.0 0.0
MOLECULES NMOL=3
1 WAT
2 BZZ
3 WAT
```

Water Benzene Water Para Temp Monte Carlo ; ex_3

MONTECARLO MAX=10000 WALL=7
MCTEMP GEOM NTEMP=10 TEMPMIN=40 TEMPMAX=500
RESCALE=10 **SMOD=2000000**
DFTB MEMOSCC DISP WMULL
PARAM PTYPE=MAT
/home/rapacioli/basis
QUATERNION NMOL=3 RIGID
1 1.0 0.0 .0 1.0 0.0 0.0 0.0
2 1.0 0.0 3.0 1.0 0.0 0.0 0.0
3 1.0 0.0 6.0 1.0 0.0 0.0 0.0
MOLECULES NMOL=3
1 WAT
2 BZZ
3 WAT


Porezag, D., Frauenheim, T., Köhler, T., Seifert, G., and Kaschner, R. (1995).
Phys. Rev. B, 51 :12947–12957.


Seifert, G., Porezag, D., and Frauenheim, T. (1996).
Int. J. Quant. Chem., 58 :185–192.