Optimized energy landscape exploration for nanosciences using ab-initio based methods

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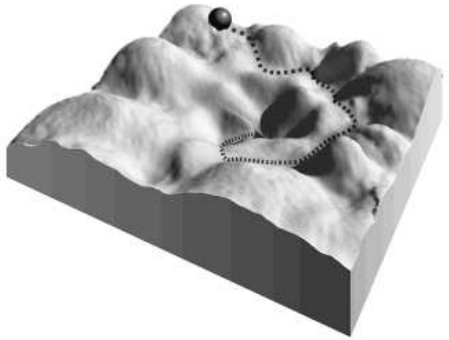
Energy Landscapes

Generic problem

How to explore the space of variables of a high dimensional cost function?



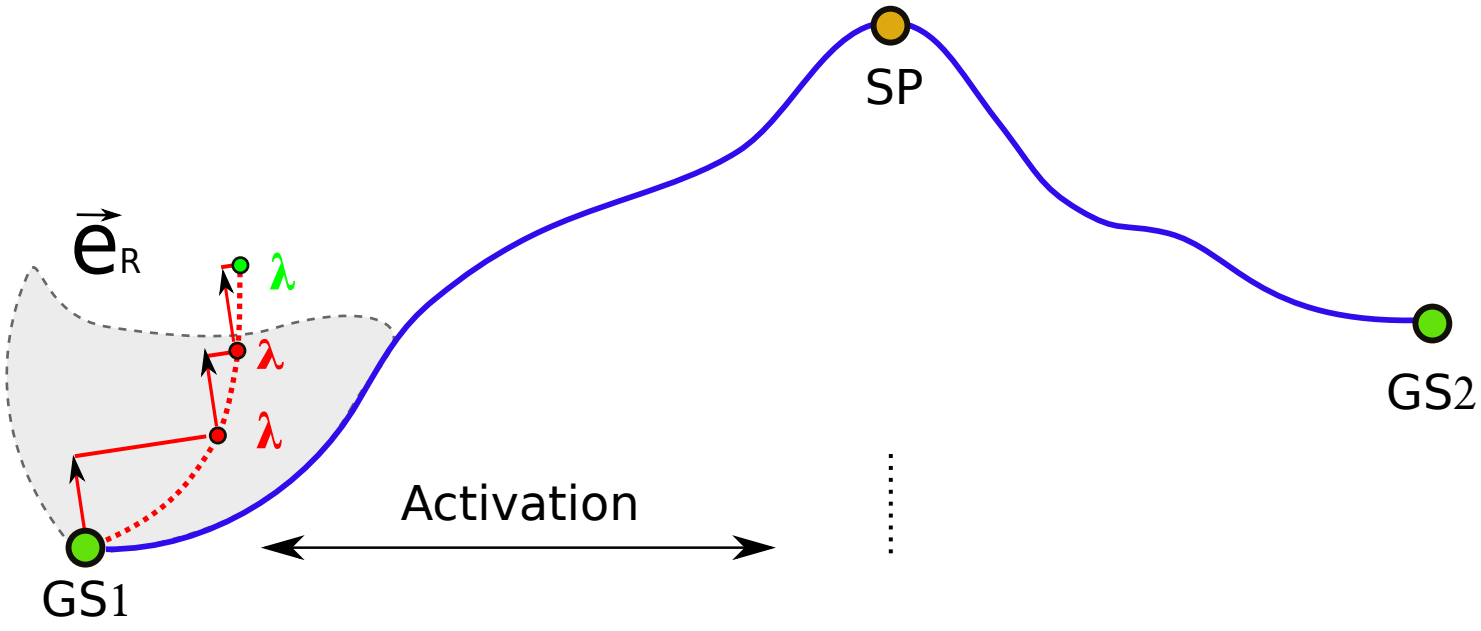
ART nouveau : Zero temperature method

Samples the local minima only, going through common saddle point, generating a continuous trajectory.

- Barkema *et al*, PRL 1996 and Malek *et al*, PRB 2000
- Marinica *et al*, PRB 83, 094119 (2002)

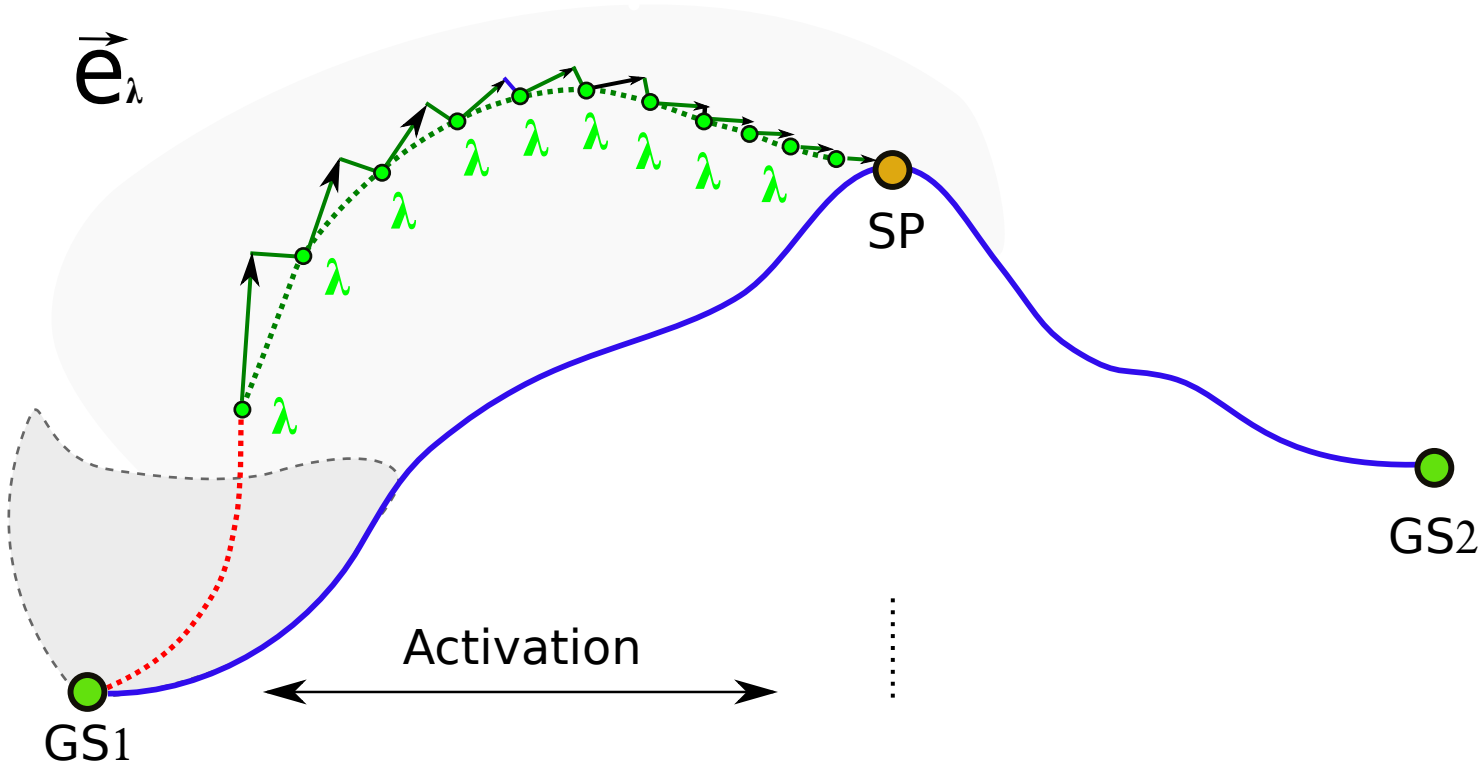
Disordered systems, polymers and proteins

Activation: Leave the harmonic basin



- Random $\mathbf{e_R}$ deformation (global, local, guess)
- Inflection point Follow $\mathbf{e_R}$ until an λ become negative

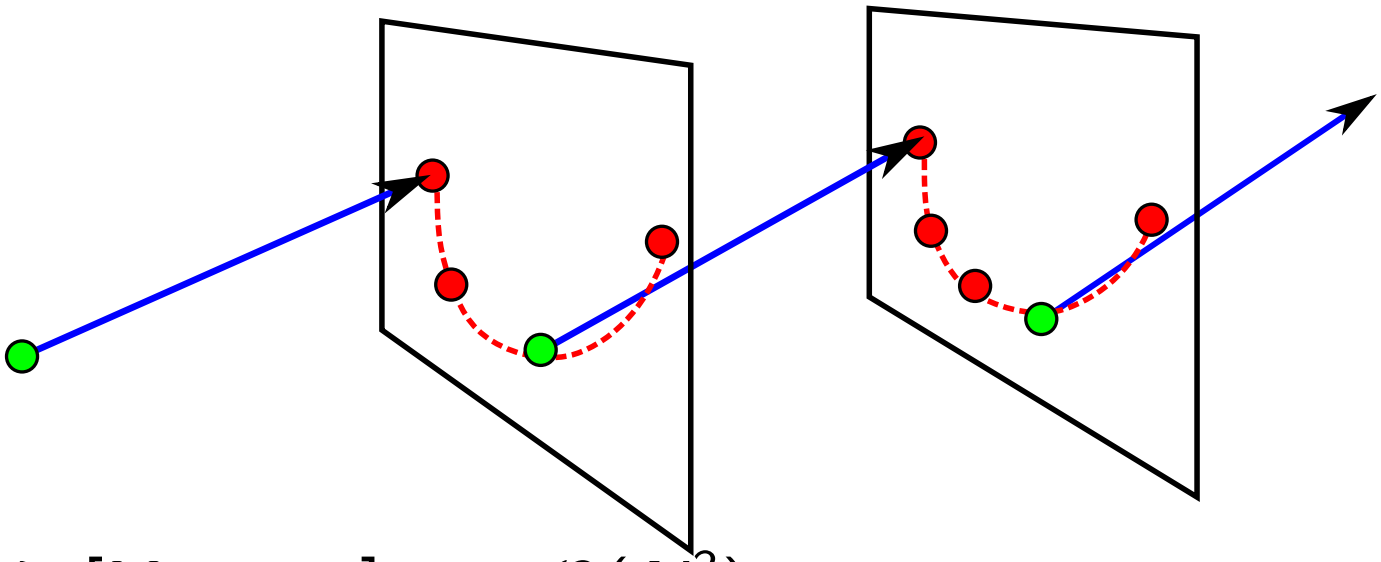
Activation: Converging to a saddle point



- Push the configuration up along the direction $\mathbf{e}_\lambda$
- Convergence Zero total force & negative eigenvalue λ

Some detail of the step

$$\vec{q_{i+1}} = \vec{q_i} + \widehat{e_\lambda} \cdot \delta$$



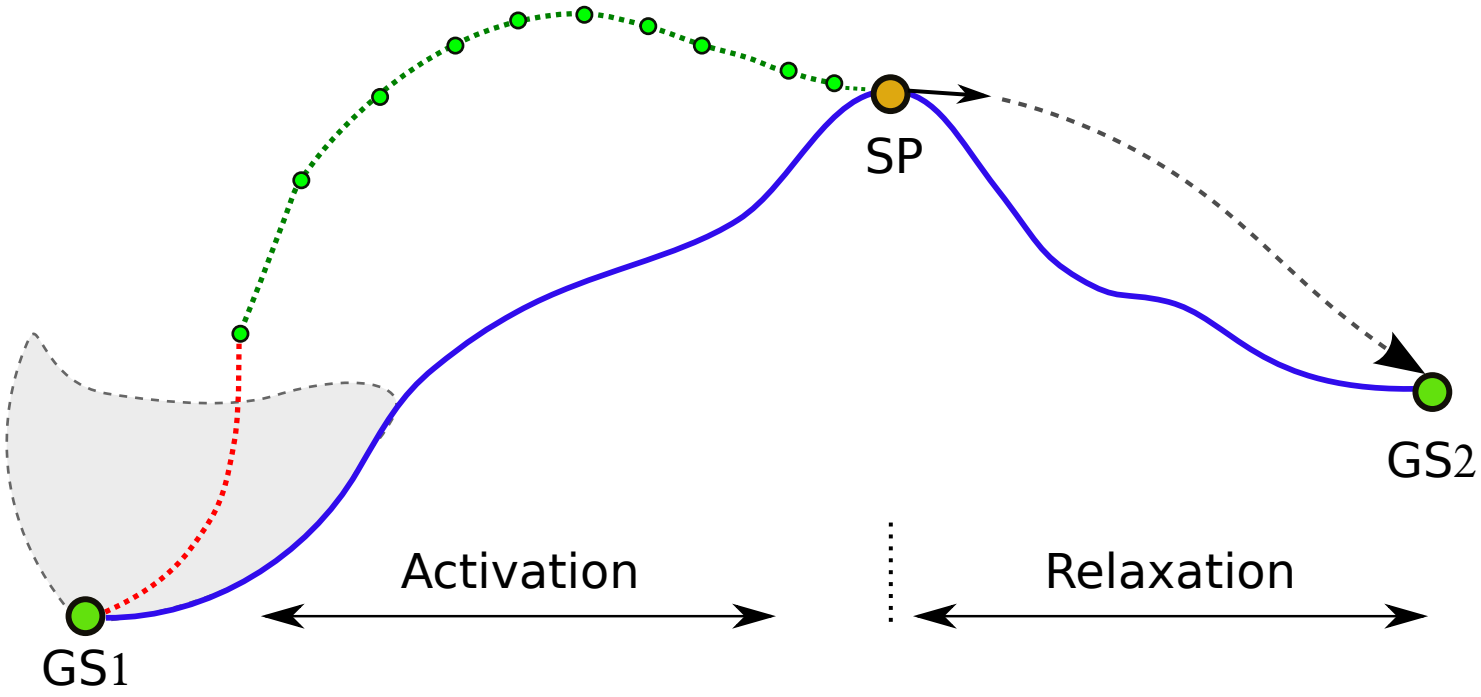
$$\lambda_1[\mathbf{H_{3N\times 3N}}] \rightarrow \mathcal{O}(N^3)$$

Lanczos method

$\Longrightarrow \mathbf{L}_{n\times n}$ $\Longrightarrow$ Still costly

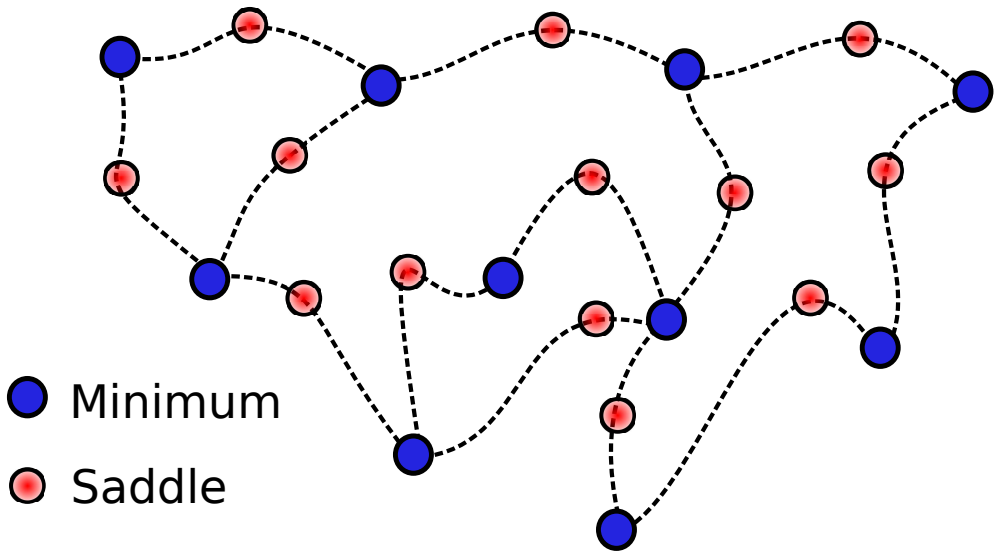
Typically, $15 < n < 20$ n force evaluations

Relax to a new local minimum



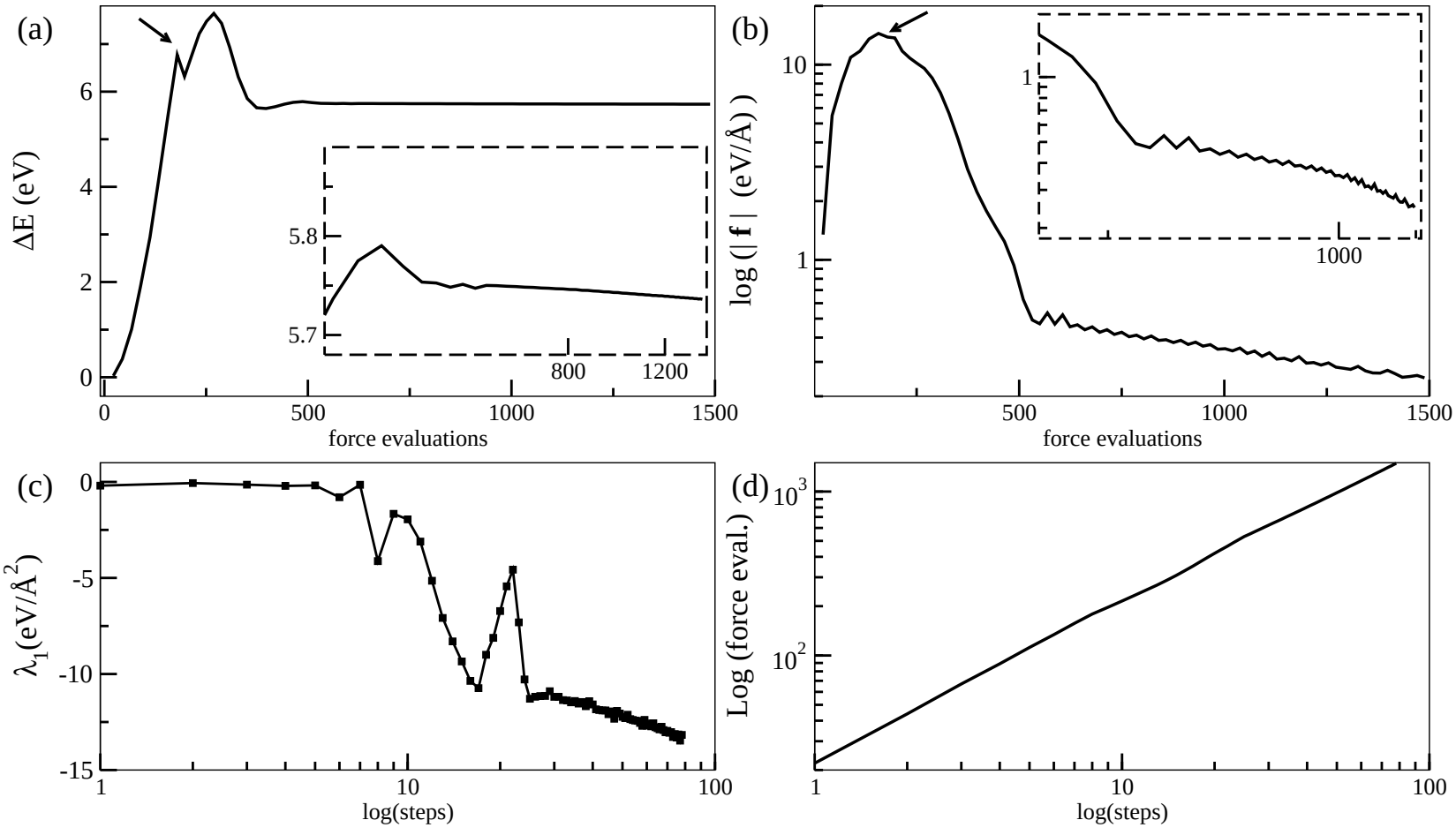
- Push the configuration slightly over the saddle point
- Kick: Relaxation (FIRE)
- Metropolis test
- Warning: The path is not the MEP

Characteristics



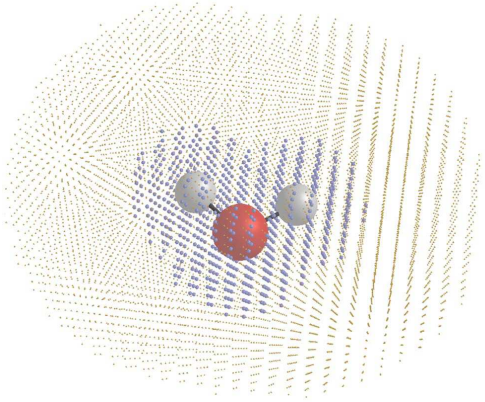
- Not sensitive to the real space complexity of activated jump nor the height of the activation energy barrier, which can be very high.
- Not biased toward pre-determined mechanisms
- Seems to sample all classes of events (ergodic)
- Events are reversible

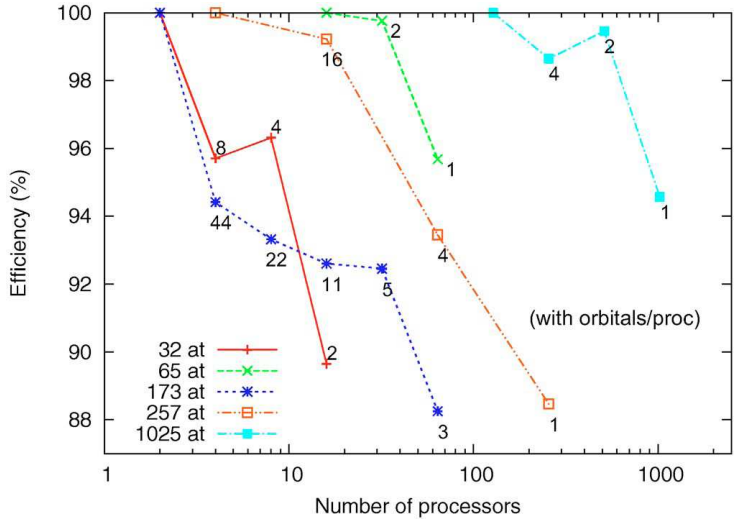
some details of an event



ab initio : BigDFT*

- Wavelets: localised in real and fourier space
- Systematic
- Placed only where are needed
- Low and high resolution
- Pseudopotentials
- Efficiency of the order of 90%, up to thousands of processors.
- Hybrid architectures (GPU)



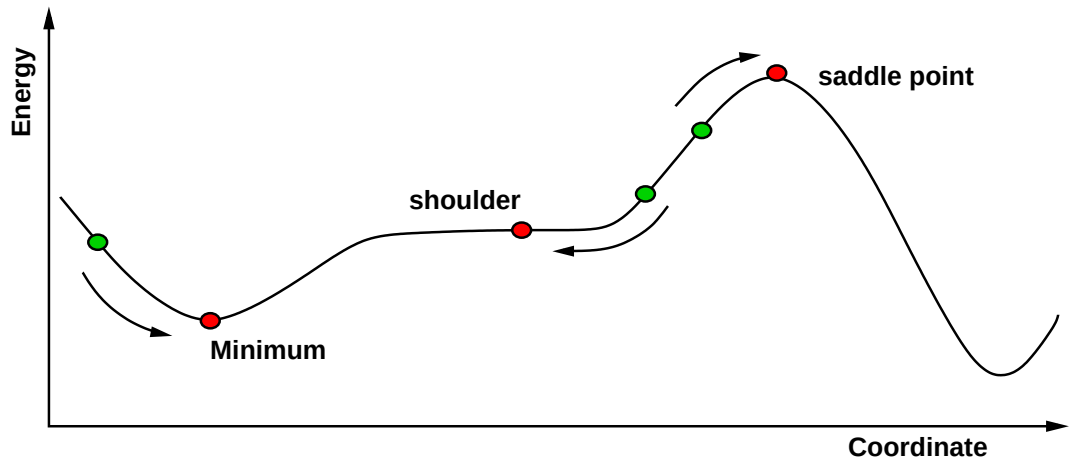


* *J. Chem. Phys.* ***129***, *014109 (2008)*

Improving convergence

Direct Inversion in the Iterative Subspace (DIIS)

- Proposed by Pulay 1980 for finding minima configurations
- Speed up the convergence when the systems is near to the SP



PROS A remarkable improvement in the efficiency

CONS detects all critical points including (shoulders)

DIIS

Use your memory

$$\mathbf{x}^* = \sum c_i \ \mathbf{x}_i \quad \mathbf{g}^* = \sum c_i \ \mathbf{g}(\mathbf{x_i}) \quad \sum c_i = \mathbf{1}$$

Minimize $\mid \mathbf{x^{new}} - \mathbf{x}^* \mid^2$ with respect to c_i

where $\mathbf{x}^{new} = \mathbf{x}^* + \mathbf{H}^{-1} \ \mathbf{g}$

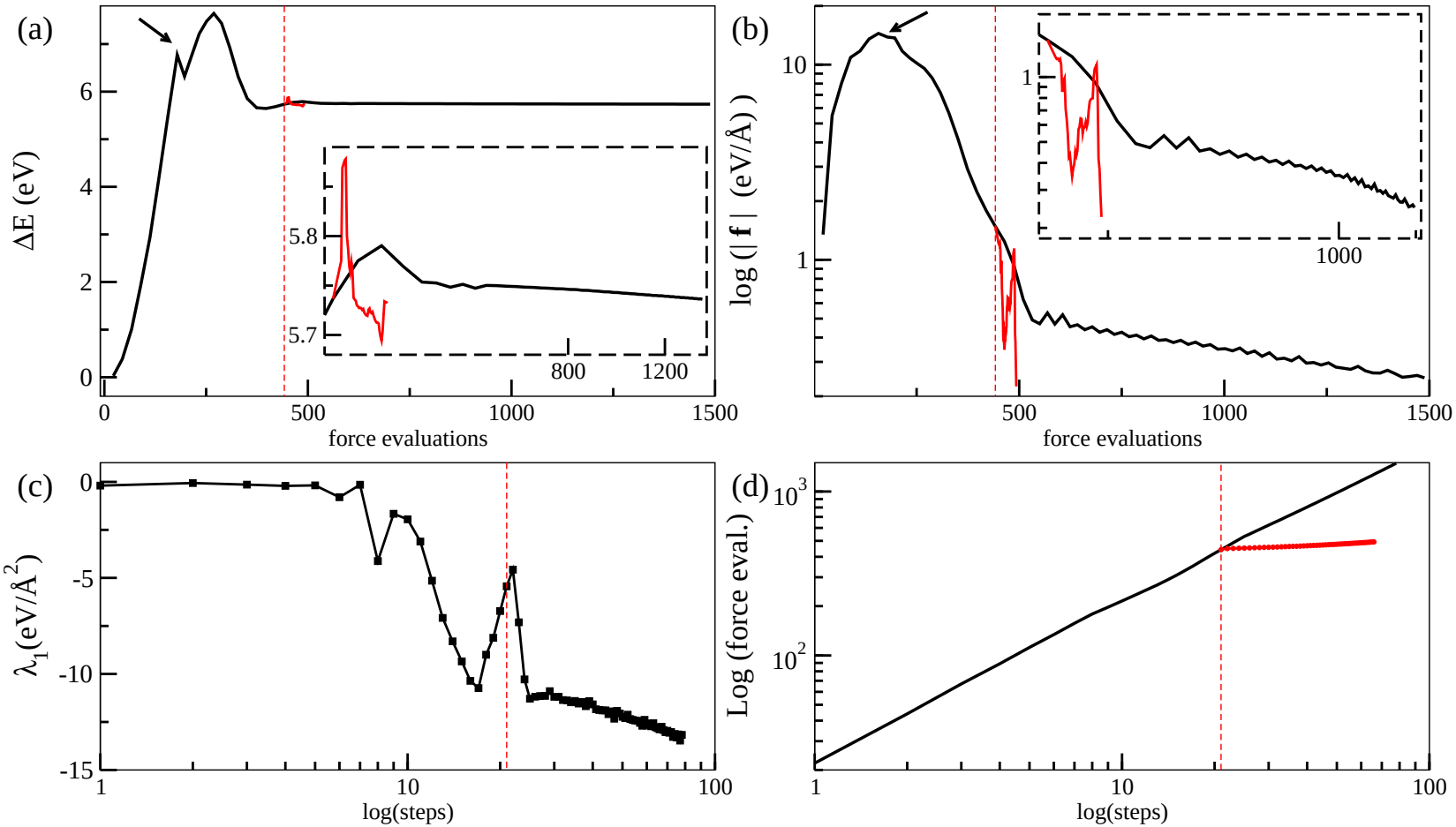
By solving

$$\begin{pmatrix} \mathbf{A} & \mathbf{1} \\ \mathbf{1} & 0 \end{pmatrix} \begin{pmatrix} \mathbf{c} \\ \lambda \end{pmatrix} = \begin{pmatrix} 0 \\ \mathbf{1} \end{pmatrix}$$

$\mathbf{A} = a_{ij} = \mathbf{g}_i^T \ \mathbf{g}_j$ and λ is the Lagrangian multiplier

Warning: We use a diagonal approximation to $\mathbf{H}^{-1}$

Lanczos + DIIS



Statistic over events

Amorphous silicon (SW semiempirical potential)

Steps after minimum in λ	∞	10	4	2
Attempted events	3021	2487	2650	2571
New events	964	968	971	965
$\langle f \rangle_s$	4885	689	670	653

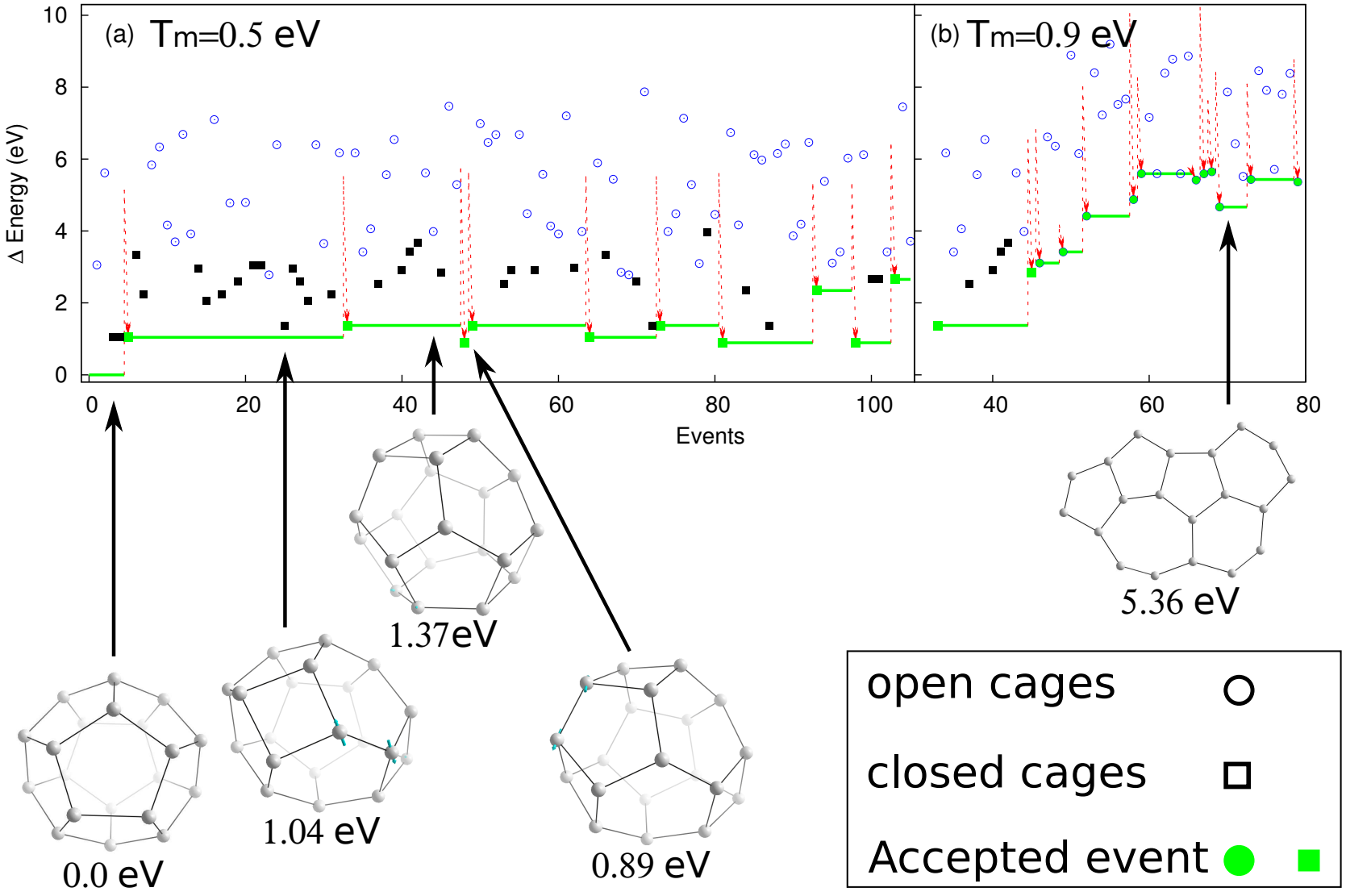
$\langle f \rangle_s$ force evaluation per successful event

Comparison between algorithms

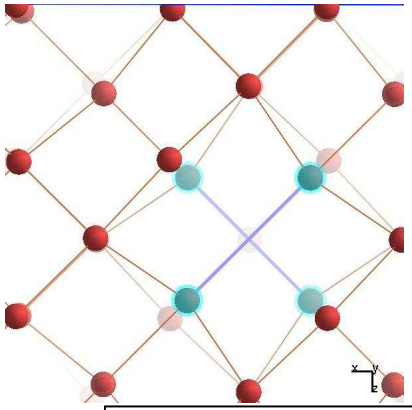
Algo.	ART nouveau			Improved dimer [a] [b]		GSM [c]
System	V_{Si}	C_{20}	SiC	C_6H_{10}	PHBH/H_2O	VO_x/SiO_2
BC	Bulk	Isol.e	Surf.	Isol.	Sol.	Isol.
Pot.	DFT	DFT	DFT	DFT	QM/MM	DFT
Method	PBE	LDA	PBE	B3LYP	AM1	B3LYP
DOF	645	60	222	48	144	90
$\langle f \rangle$	210	322	262	384	425	330
$\langle f \rangle_s$	302	718	728	-	-	-
A/S	79/78	434/201	134/75	-	-	-

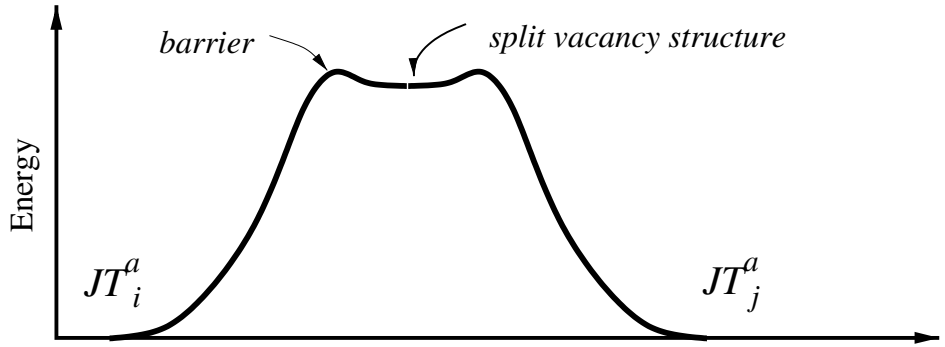
[a] *J. Chem. Phys* ***123***, *224101 (2005)*
[b] *J. Chem. Phys.* ***128***, *014106 (2009)*
[c] *J. Chem. Phys.* ***130***, *244108 (2009)*

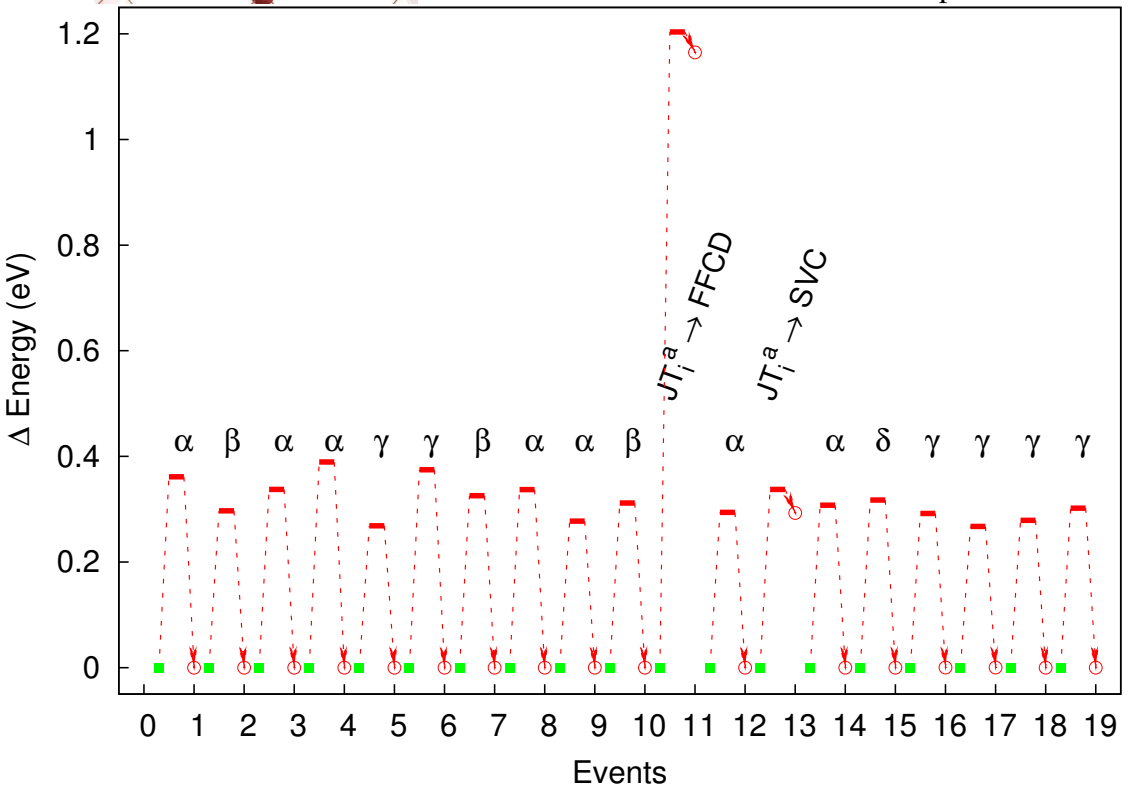
Clusters : C_{20}



Bulk: Vacancy diffusion in silicon bulk







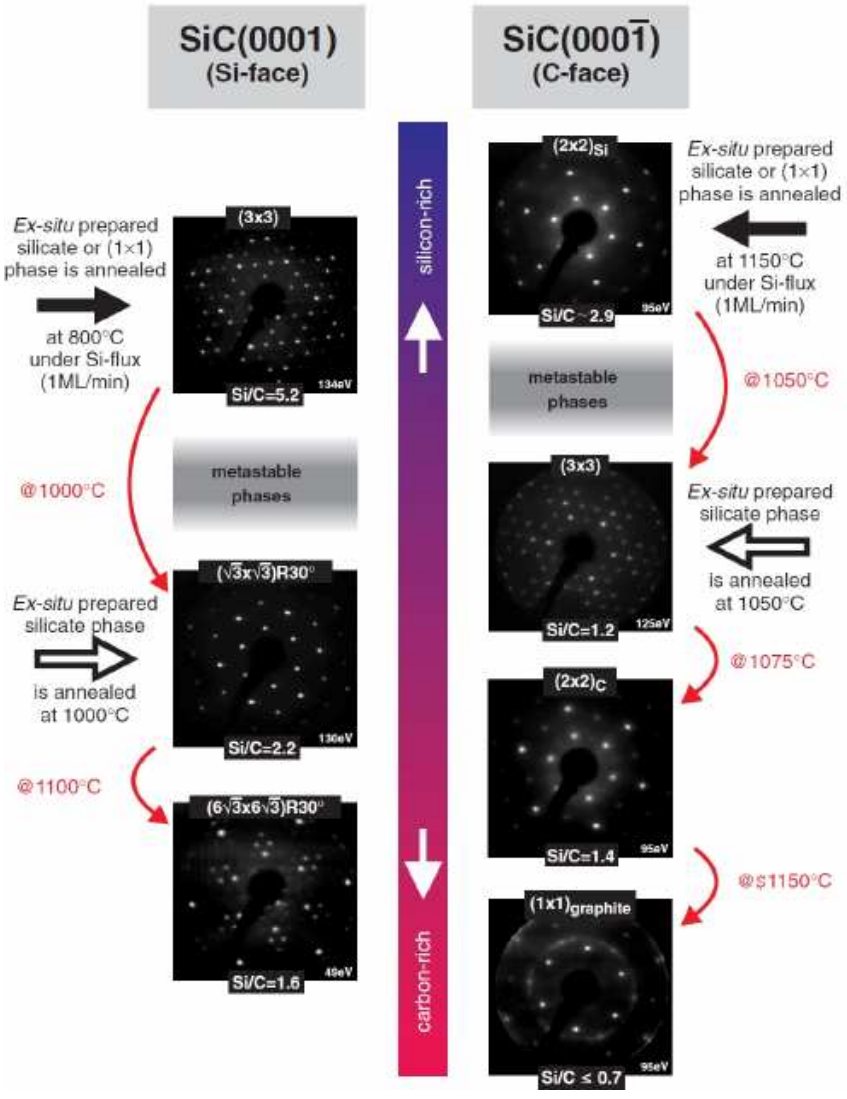
$$\alpha = JT_i^a \longrightarrow JT_j^a$$

$$\beta = JT_i^a \longrightarrow JT_i^a$$

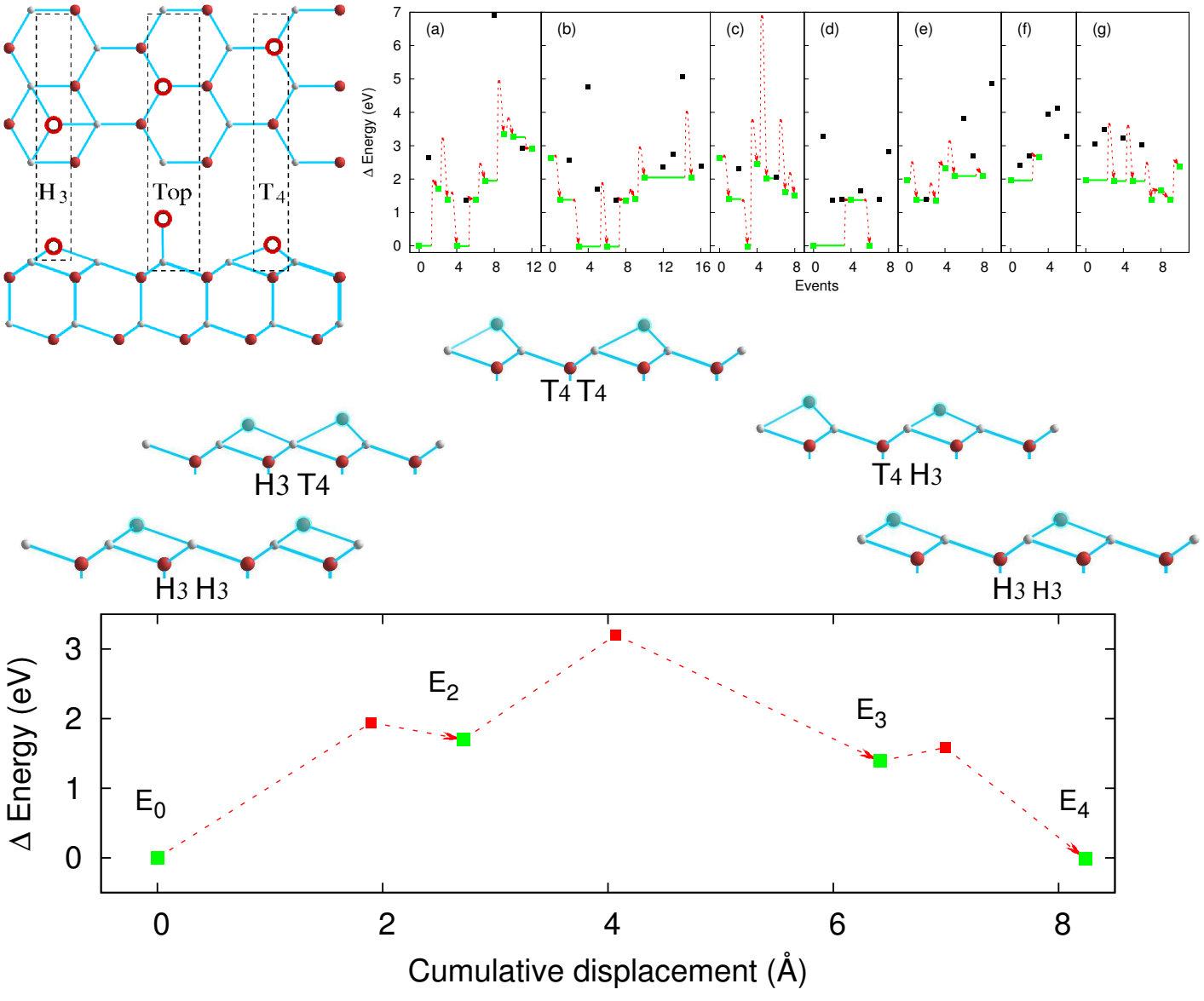
$$\gamma = JT_i^a \longrightarrow JT_i^b$$

$$\delta = JT_i^a \longrightarrow JT_j^b$$

Graphene/SiC Growth : LEED pattern



Surface: 4H-SiC $(000\bar{1})$ $(2 \times 2)_C$



Final remarks

- Lanczos + DIIS improve the convergence to saddle points by a factor of 3
- A tool for energy landscape exploration in material science simulations using ab initio forces
- Not a black box: Requires a interaction with the user
- QM/MM (SW potentials) L. Karim Béland @ U. Montréal
- Kinetic-ART N. Mousseau @ U. Montréal

People involved

Pascal Pochet

Luigi Genovese

Damien Caliste

Normand Mousseau

Université de Montréal

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Thanks for your attention !!

Look for

J. Chem. Phys. **135**, 034102 (2011)

J. At. Mol. Opt. **2012**, 925278 (2012)

http://inac.cea.fr/L_Sim/BigDFT/

http://www.phys.umontreal.ca/∼mousseau/

The Lanczos method

$$
\begin{aligned}
H|x_0> &= a_o|x_0> + b_1|x_1> \\
H|x_1> &= a_1|x_1> + b_1|x_0> + b_2|x_2> \\
H|x_2> &= a_2|x_2> + b_2|x_1> + b_3|x_3> \\
&\vdots \\
H|x_{l-1}> &= a_{l-1}|x_{l-1}> + b_{l-1}|x_{l-2}> + b_1|x_1> \\
H|x_1> &= a1|x_l> + b_l|x_{k-1}> \qquad (1)
\end{aligned}
$$

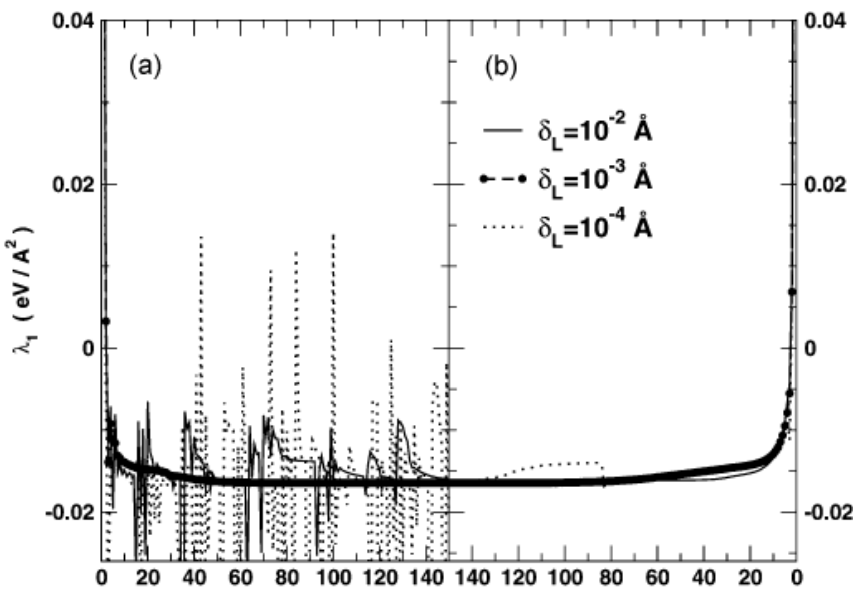
$$
L_l = \begin{pmatrix} a_0 & b_1 & & & \\ b_1 & a_1 & b_2 & & \\ & & \ddots & & \\ & & & b_{l-1} & a_{l-1} & b_l \end{pmatrix} \lambda_1[\mathbf{H}] \Rightarrow \lambda_1[\mathbf{L_l}](l \to 3N).
$$

$H[q_0]u$

by the finite difference on the forces by a Taylor expansion

$$H[q_0]u = -\frac{f(qo + \delta_l u) - f(q_0)}{\delta_l} + \mathcal{O}(\delta_l^2) \quad (2)$$

$$H[q_0]u = -\frac{f(qo + \delta_l u) - f(qo - \delta_l u)}{2\delta_l} + \mathcal{O}(\delta_l^3) \quad (3)$$



Metropolis test

$$p_{accept} = min[e^{-(E_{fin} - E_{ini}/K_B T)}, 1] \quad (4)$$

- T ia a Metropolis temperature.
- Vibrational entropic contributions are not included $\Rightarrow$ Fictitious temperature
- It is possible to thermalize the system at this temperature