

# Accelerated ab-initio Molecular Dynamics by Quantum Monte Carlo

**Sandro Sorella**

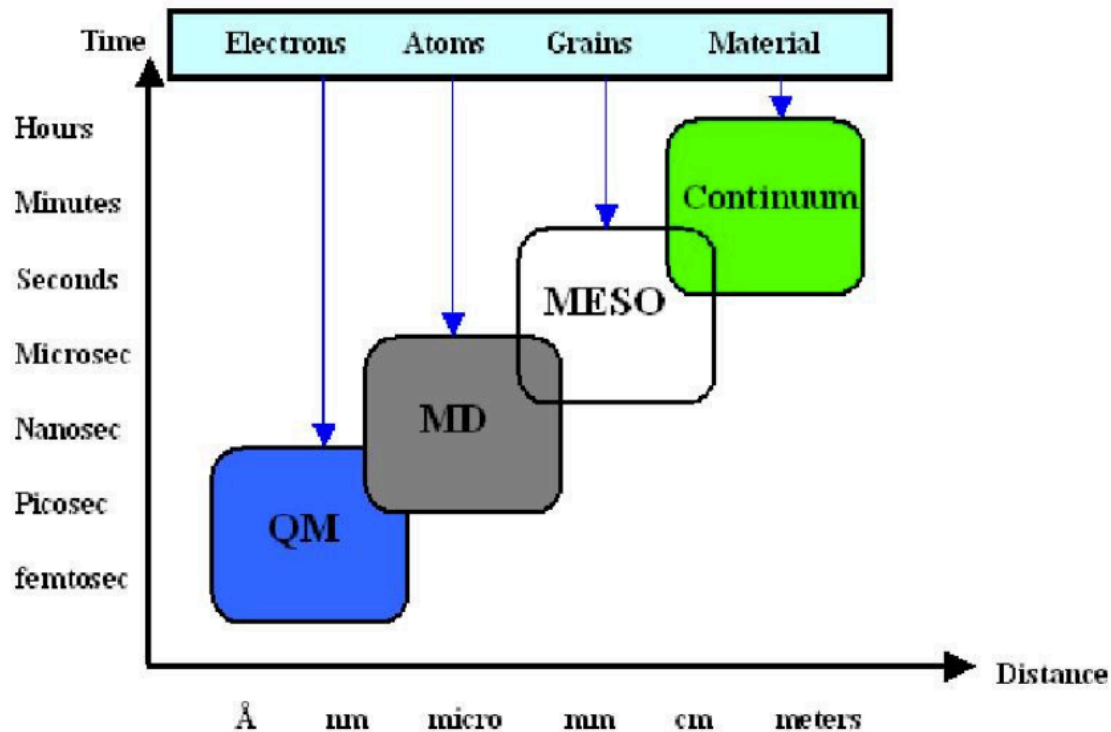
**Sissa Trieste**

**in collaboration with:**

**G.Mazzola, ETH-Zurich**

# Time scales and system size

QM=Ab-initio Molecular dynamics (with no QMC!)



Our **dream** would be QM-QMC with  $10^{11}$  fs and  $10^3$  atoms, eg protein folding of the simplest protein

## First order Langevin dynamics

**Task:** sample  $\rightarrow P_{eq}(\vec{R}) = \frac{\exp(-V(\vec{R})/T)}{Z}$

**Tool:** Stochastic differential equation:

$$\dot{\vec{R}} = -\frac{\partial V}{\partial \vec{R}} + \sqrt{2T}\vec{\eta}$$

$$\langle \vec{\eta}(\vec{R}(t))\vec{\eta}(\vec{R}(t')) \rangle = \delta(t - t')\delta_{i,j}$$

**Proof:** Fokker-Planck equation:

$$\partial_t P(\vec{R}, t) = \partial_{\vec{R}} \left[ \frac{\partial V}{\partial \vec{R}} + T\partial_{\vec{R}} P(\vec{R}, t) \right]$$

Indeed (Parisi '81):  $P(R, t) = \Phi(\vec{R}, t) \sqrt{P_{eq}(\vec{R})}$

$$\partial_t \Phi(\vec{R}, t) = -H \Phi(\vec{R}, t)$$

$$H = -T \partial_{\vec{R}}^2 + V_{eff}(\vec{R})$$

$$V_{eff}(\vec{R}) = \frac{1}{4T} |\partial_{\vec{R}} V|^2 - \frac{1}{2} \partial_{\vec{R}}^2 V$$

Thus for an harmonic potential:  $V(R) = \frac{1}{2} K x^2$

$$V_{eff}(\vec{R}) = \frac{K^2}{4T} x^2 - \frac{K}{2}$$

Thus the approach at equilibrium of  $P(R,t) \rightarrow$   
**exact** by solving an equivalent harmonic problem:

$$m = \frac{1}{2T} K_{eff} = \frac{K^2}{2T}$$
$$E_n \rightarrow \sqrt{\frac{K_{eff}}{m}} \left( n + \frac{1}{2} \right) - \frac{K}{2} = nK$$

The correlation time  $\tau = \frac{1}{K}$  **independent of T**

Thus a **faster** MD should be **faster** at T=0 (structural optimization)

At T=0 when we discretize the LD Equations:

$$\vec{R}_{n+1} = \vec{R}_n - \Delta \partial_{\vec{R}} V(\vec{R})$$

i.e. the “**steepest descent**” and for harmonic case:

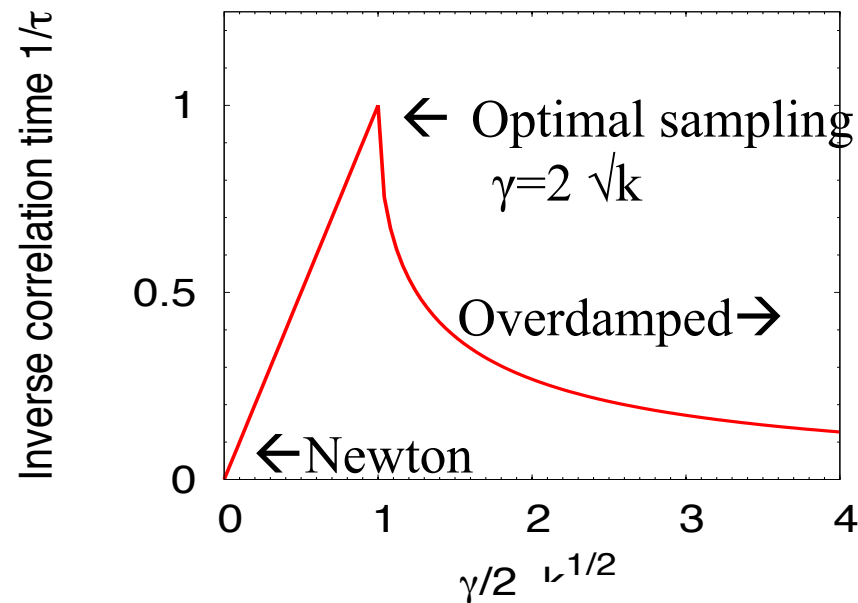
$$\Delta \lesssim \frac{1}{K_{max}} \text{ but } \tau_{max} \simeq \frac{1}{K_{min}} \text{ thus we need}$$

$$n_{opt} = \frac{\tau_{max}}{\Delta} \gtrsim \frac{K_{max}}{K_{min}} \quad \text{MD steps} \gg 1 !!!$$

Also 2<sup>nd</sup> order Newton dynamics suffers...

to sample the canonical distribution  $\exp(-E/T)$

one add some damping:  $\ddot{\vec{R}} = -\gamma\dot{\vec{R}} + f_{\vec{R}} + \sqrt{2T}\vec{\eta}$



Several works on this:

M.Tassoni, F. Mauri & R. Car PRB'94

G.Bussi & M.Parrinello PRE'07

M.Ceriotti et al. JCP '10

See Y. Luo, A. Zen & SS JCP'14

Eventually  $\tau_{max} \sim 1/\sqrt{K_{min}}$  and  $\Delta \lesssim \frac{1}{\sqrt{K_{max}}}$

and  $n_{opt} \sim \sqrt{\frac{K_{max}}{K_{min}}}$  is an unavoidable fact.

But why we have to be limited to the steepest descent in ab-initio MD?

In Tassoni, Mauri & Car PRB'94 they noted that with 2<sup>nd</sup> order MD the optimization is faster:

$$n_{opt} \rightarrow \sqrt{\frac{K_{max}}{K_{min}}}$$

Some progress has been made later (e.g. Ceriotti et al. JCP'10) here we observe that with the Newton method

$$n_{opt} = 1$$



In fact if  $V$  **quadratic**

$$V(\vec{R}) \simeq \frac{1}{2} \sum_{i,j} S_{i,j} R_i R_j - \sum_i f_i R_i$$

$$\text{Min}_{\vec{R}} V(\vec{R}) = V(\vec{R}_{min})$$

$$\vec{R}_{min} = S^{-1} \vec{f}$$

Namely time step “optimal” **for all scales**

## Proposed accelerated Langevin dynamics

**Task:** sample  $\rightarrow P_{eq}(\vec{R}) = \frac{\exp(-V(\vec{R})/T)}{Z}$

**Tool:** Accelerated stochastic differential equation:

$$\dot{\vec{R}} = -S^{-1}(\vec{R}) \frac{\partial V}{\partial \vec{R}} + \sqrt{2T} \vec{\eta}$$

$$\langle \eta_i(\vec{R}(t)) \eta_j(\vec{R}(t')) \rangle = \delta(t - t') S_{i,j}^{-1}(\vec{R})$$

**Proof:** Fokker-Planck equation:

... see supplementary information

# QMC framework

Unlike DFT, QMC is a many body approach and deals with electronic correlations.

$$J = \exp \left[ \sum_{i < j} u(\vec{r}_i, \vec{r}_j) \right]$$
$$J |MF\rangle$$
$$\psi_i(\mathbf{r}) = \sum_{a=1}^M \sum_{\mu_a=1}^{L_a} c_i^{a, \mu_a} \phi_{a, \mu_a}(\mathbf{r})$$

JASTROW: two and three body term

SLATER DET: made with  $\psi_i(\mathbf{r})$   
molecular orbitals expanded on  
localized at. basis

+ Avoid DFT xc functional approximations, systematic improvable and fully ab-initio.

+ Excellent scaling with system size and (now important) with the number of processors.

- Error bars: few digits accuracy / noisy quantities.

- Huge computational cost, before this work only a few water molecules possible by QMC

# The wavefunction for realistic systems

$$u(\vec{r}, \vec{r}') = u_{lr}(|\vec{r} - \vec{r}'|) + \sum_{a,b,i,j} \lambda_{i,j}^{a,b} \psi_i^a(\vec{r}) \psi_j^b(\vec{r}')$$

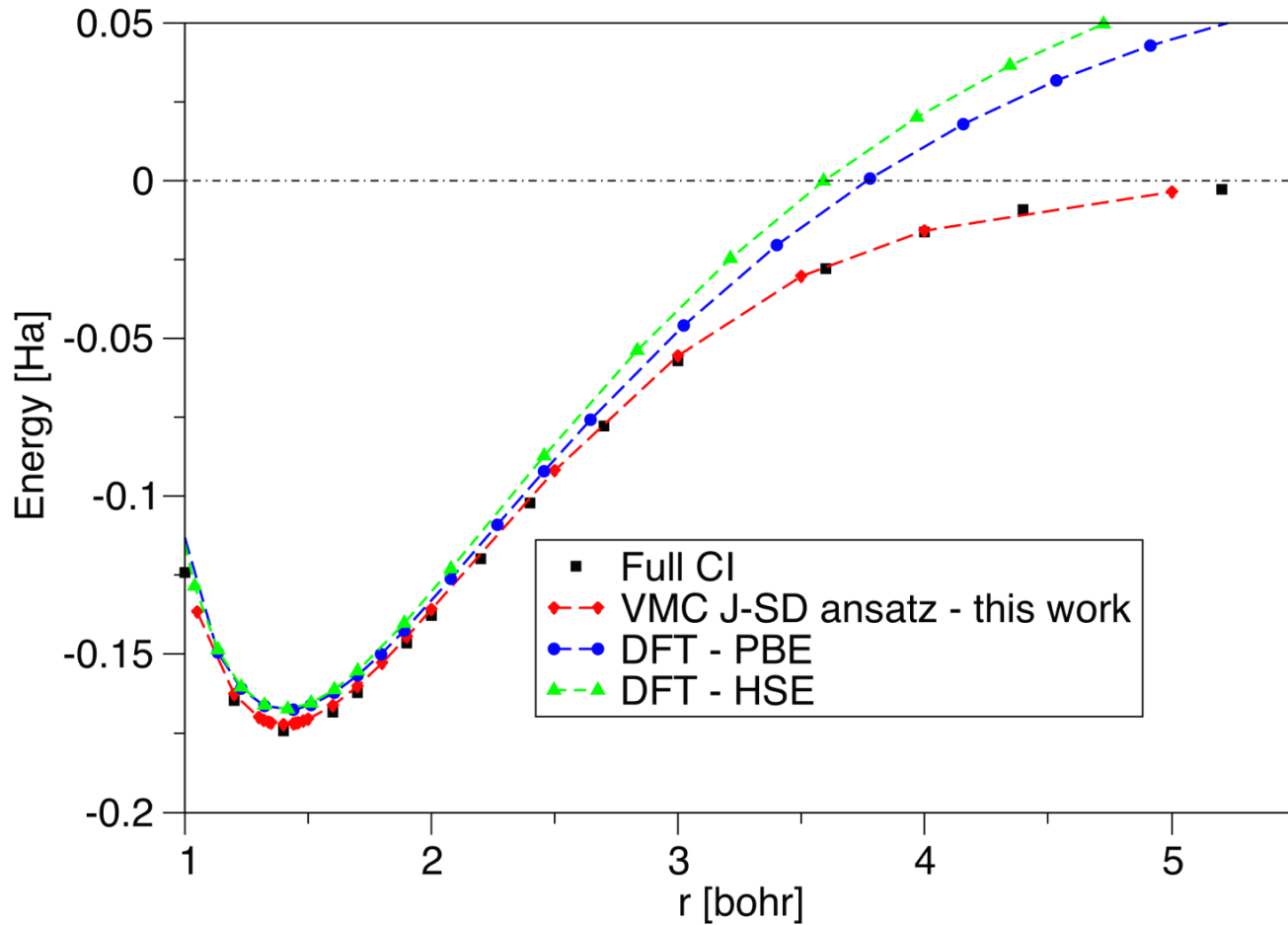
$$u_{lr}(r) = \frac{1}{2} \frac{r}{1 + Br} \quad \text{"a(b)" labels atom positions } R_a(R_b)$$

The non-homogeneous part  $a=b$  is local named **3J**  
less # parameters (no 4-body) than full named **4J**

e.g.  $\psi_k^a(\vec{r}) = \exp[-Z_k |\vec{r} - \vec{R}_a|^2]$ , i.e. localized atomic orbitals, many

variational parameters (say ~1000) determined by:  $\min_{\lambda_{kl}^a, SD} \frac{\langle SD | JHJ | SD \rangle}{\langle SD | J^2 | SD \rangle}$

# Quantum Monte Carlo vs DFT, is it worth? In $H_2$ clear



For the **Hydrogen chain**  
 $H_N$  up to 66 ( $N/2$  odd)  
Jastrow+1Det works!  
See L.Stella, C. Attaccalite, SS  
and A. Rubio, PRB, 245117 (2011)

Absence of Mott transition  
equivalent to Hubbard  $U > 0$

With a very small basis (2 gaussians/atom) one gets the essentially exact dispersion for  $H_2$

# Choice of the acceleration matrix S

In QMC we have statistical error on atomic forces:

$$f_i = -\frac{\partial V(\vec{R})}{\partial R_i} + \text{QMC noise}$$

$$\langle f_i f_j \rangle - \langle f_i \rangle \langle f_j \rangle = \text{Cov}_{i,j}$$

$$\text{Cov}_{i,i} = (\delta f_i)^2$$

$$\text{Signal/Noise} = \frac{|f_i|}{\delta f_i}$$

But there is a special direction:  $\vec{R} \rightarrow \vec{R} + \Delta\vec{x}$

That maximizes the signal/noise ratio:

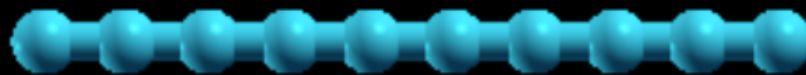
$$\text{Max}_{\vec{x}} \left( \frac{(\sum_i x_i f_i)^2}{\sum_{i,j} \text{Cov}_{i,j} x_i x_j} \right)$$

Thus

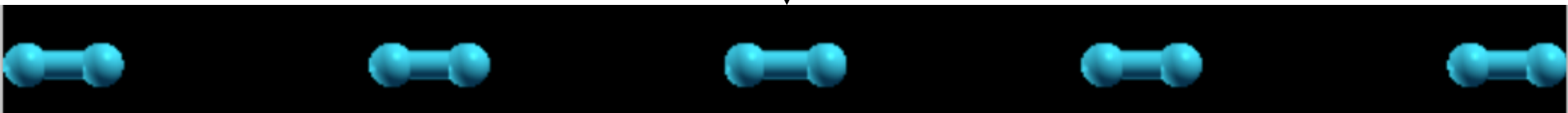
$$\vec{x} = \text{Cov}^{-1} \vec{f}$$

is the **best direction** to move for minimizing the Born-Oppenheimer Energy surface in QMC, e.g. in structural optimization.

We started with a compressed 10 H sytem



$\sim 5$  a.u.



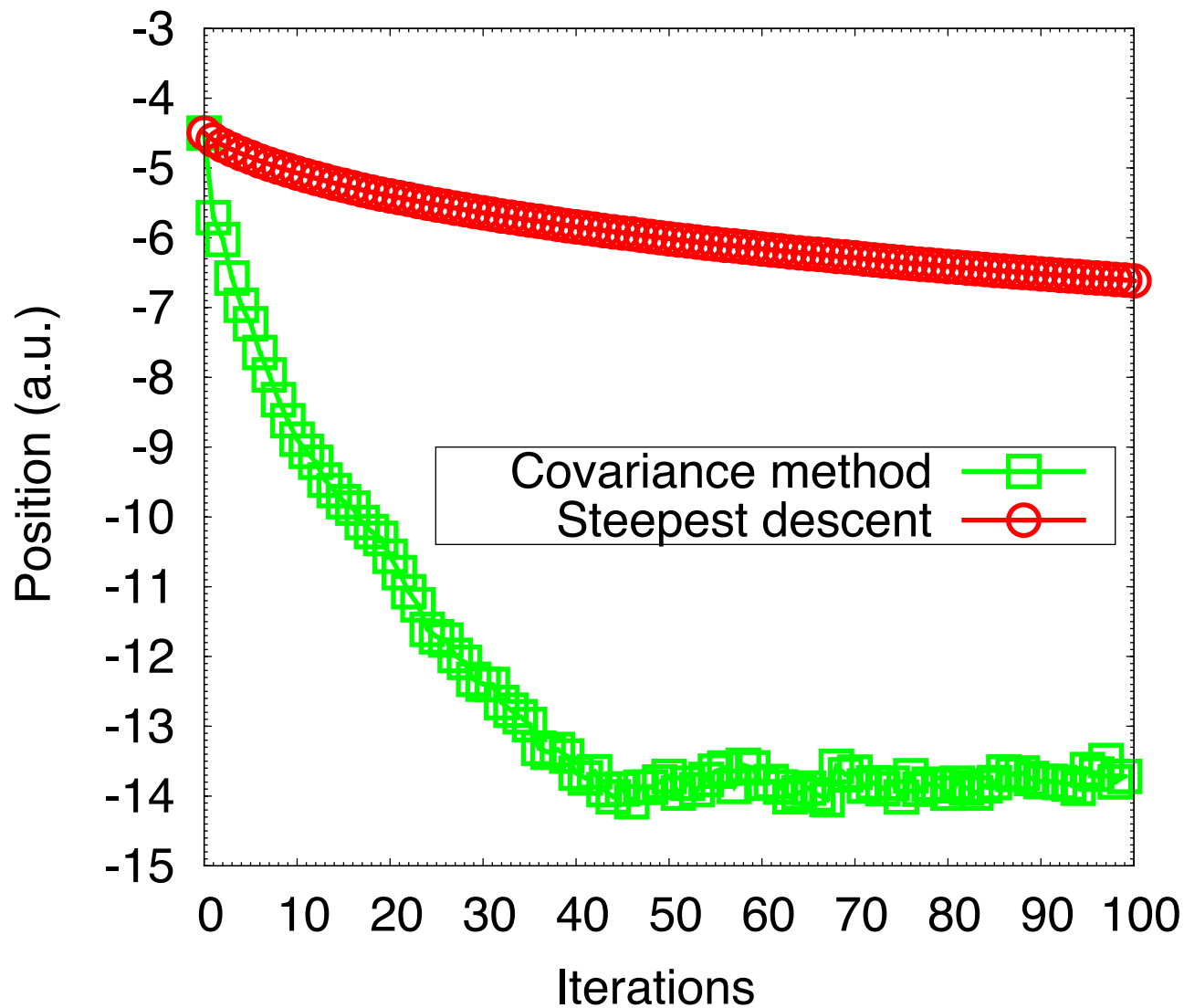
The final molecule is very weakly bound due to dispersive interactions taken into account by the Jastrow factor. With the covariance method we solved the problem of dealing with two very different energy scales

$$\frac{K_{max}}{K_{min}} \simeq 200$$



Covariance method :  $\vec{R}_{n+1} = \vec{R}_n - \Delta Cov^{-1} \partial_{\vec{R}} V(\vec{R})$

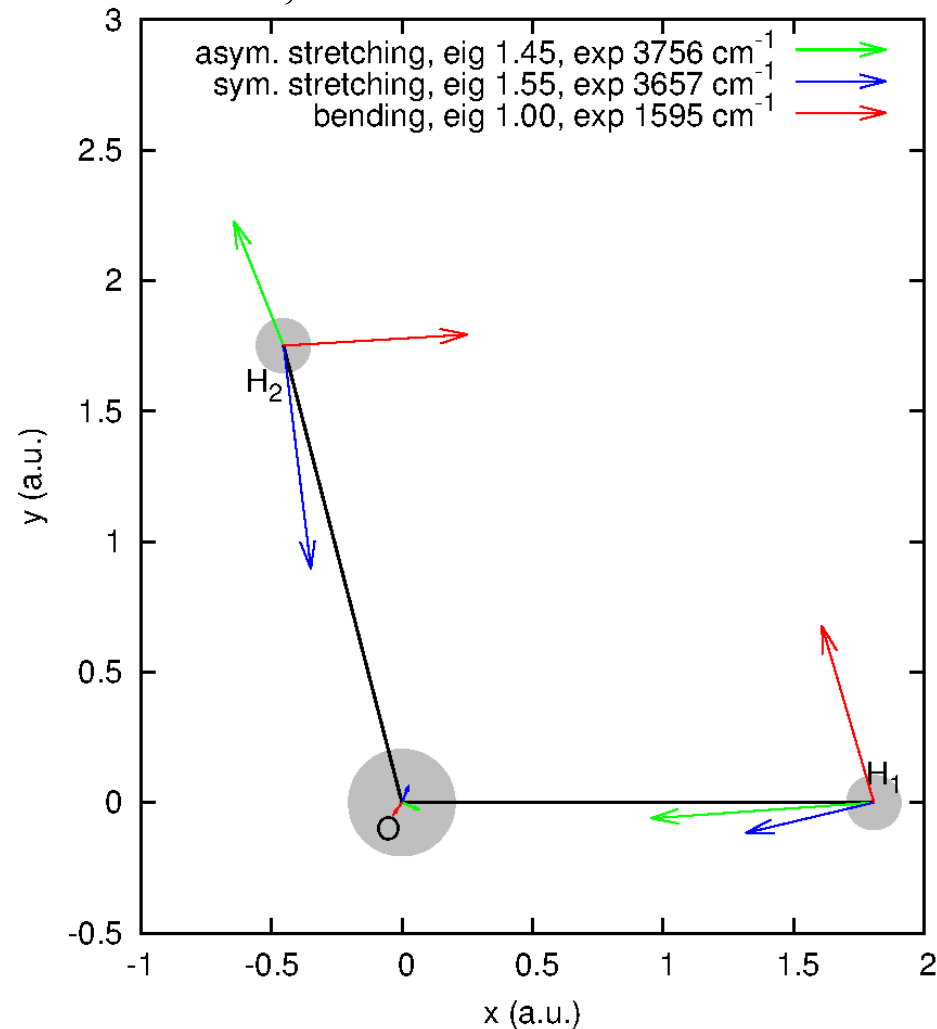
Steepest descent :  $\vec{R}_{n+1} = \vec{R}_n - \Delta \partial_{\vec{R}} V(\vec{R})$



# Noise is useful!!!

Y. Luo, A. Zen and S.S. JCP'14

- Choice of  $S$ 
  - Great freedom
  - properly adapting time steps
  - **large** time step slow modes
  - **small** time steps for fast modes
- Our choice estimated by QMC **contains info of Hessian**



$$S_{i,j} = Cov_{i,j} = \langle \delta f_i \cdot \delta f_j \rangle_{QMC}$$

# Generalization to finite T:

S.S. and G. Mazzola arXiv:1605.08423 **now**

much more efficient than G.Mazzola and S.S. JCP (2012)

$$\begin{aligned}\vec{R}(t + \Delta) &= \vec{R}(t) + \sqrt{2T\Delta}\vec{z}(t) \\ &+ S^{-1}(\vec{R}) \left\{ \Delta\vec{f}_{\vec{R}} - \left[ \frac{S(\vec{R}(t - \Delta)) - S(\vec{R})}{2} \right] (\vec{R}(t - \Delta) - \vec{R}(t)) \right\} \\ \langle z_i(t)z_j(t) \rangle &= S_{i,j}^{-1}(\vec{R}(t))\end{aligned}$$

where: 
$$S_{ij}(\vec{R}) = \langle f_i f_j \rangle - \langle f_i \rangle \langle f_j \rangle$$

May be the optimal choice for QMC, but other choices are possible (Hessian?). And what in DFT?

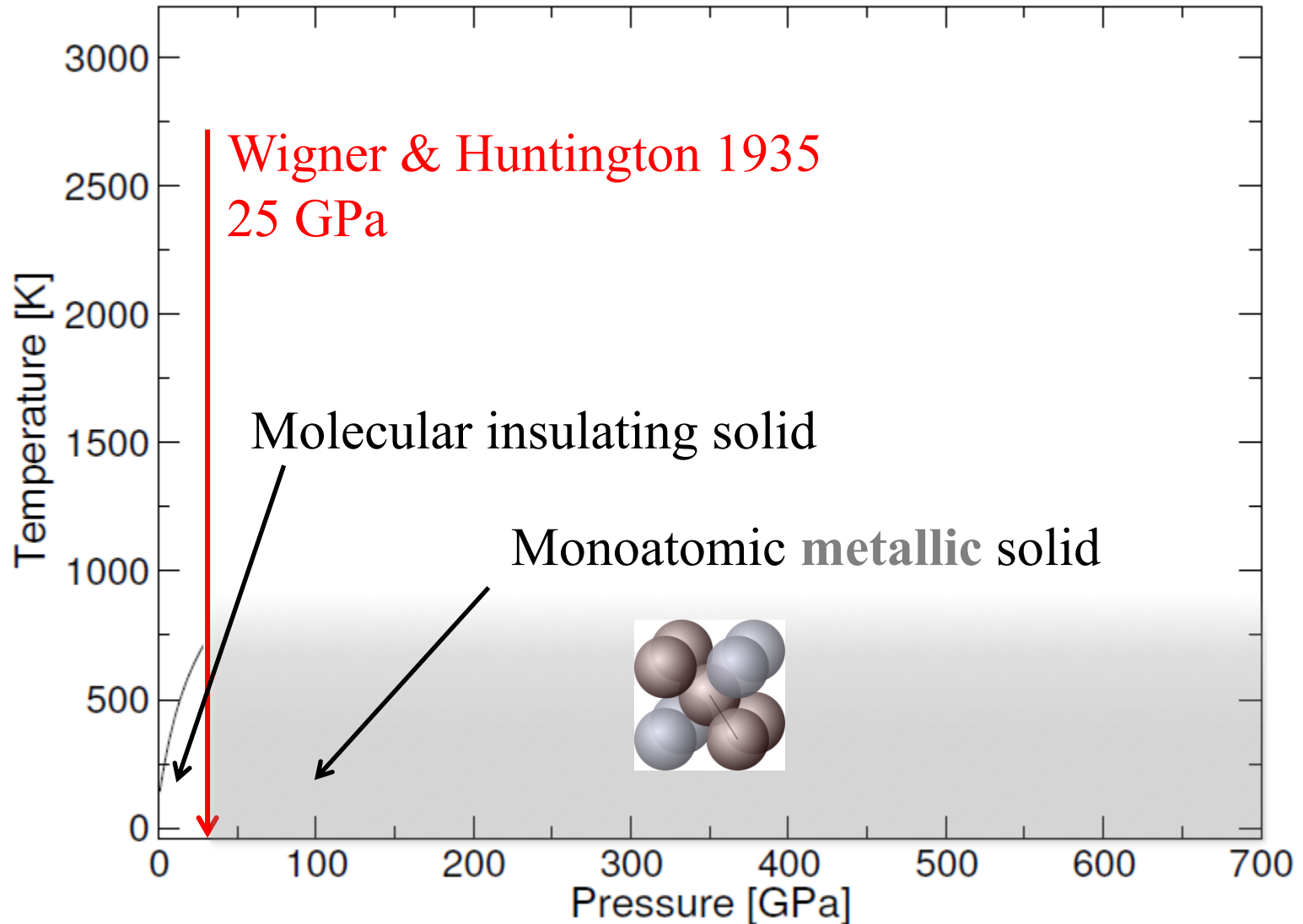
# Concluding theory part in words

A method is presented that “equalize” all time scales at given ionic positions: for appropriate acceleration matrix  $S$  when the H-C bond makes one oscillation ( $\sim 1$  fs) the “protein” downfolds to its native state ( $\sim \mu s$ )

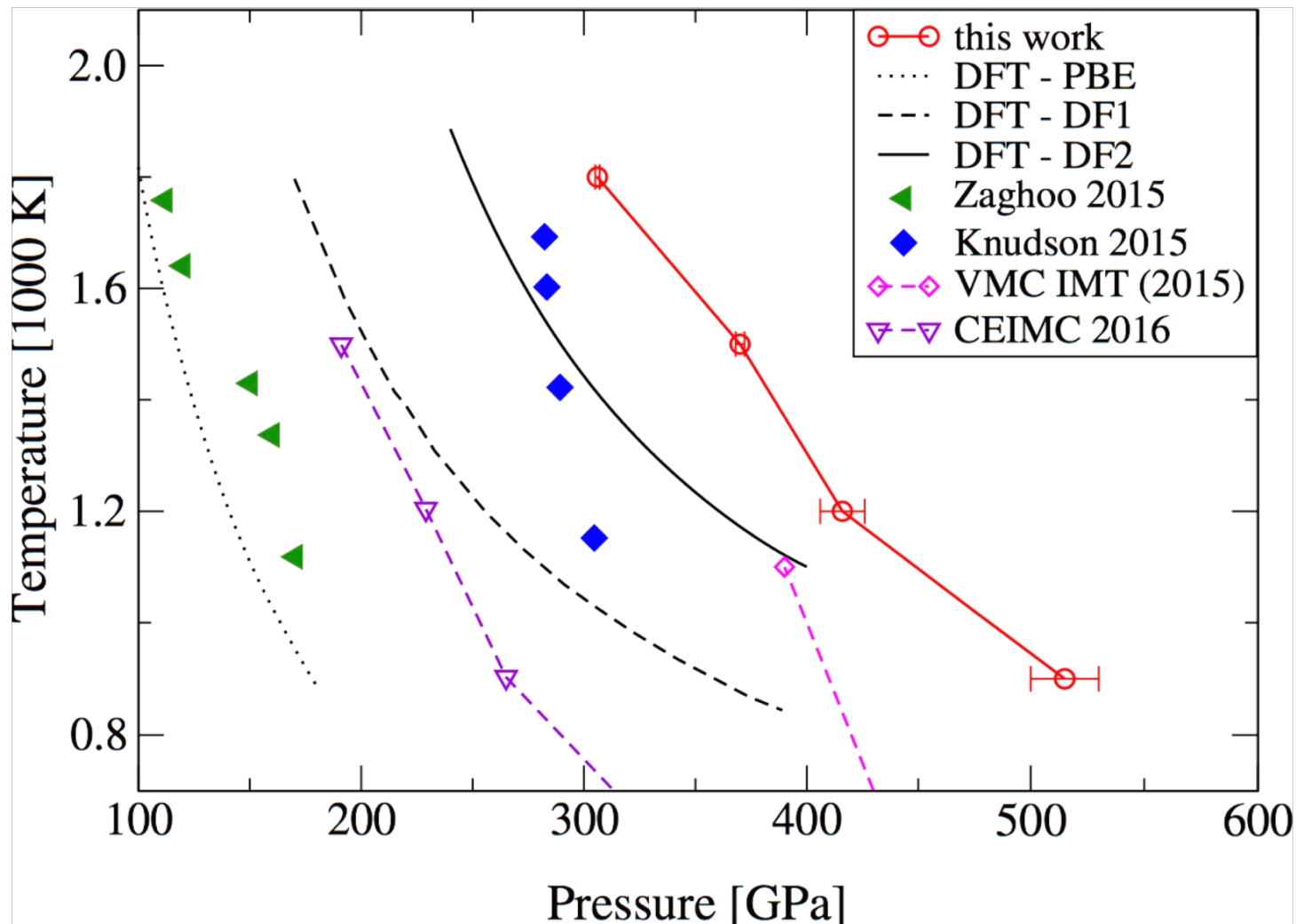
Well this is a dream...

This method cannot avoid the problem to cross free energy barriers. But other methods exist, e.g. metadynamics, Wang Landau... No problem to combine them with this “local time” equalizer.

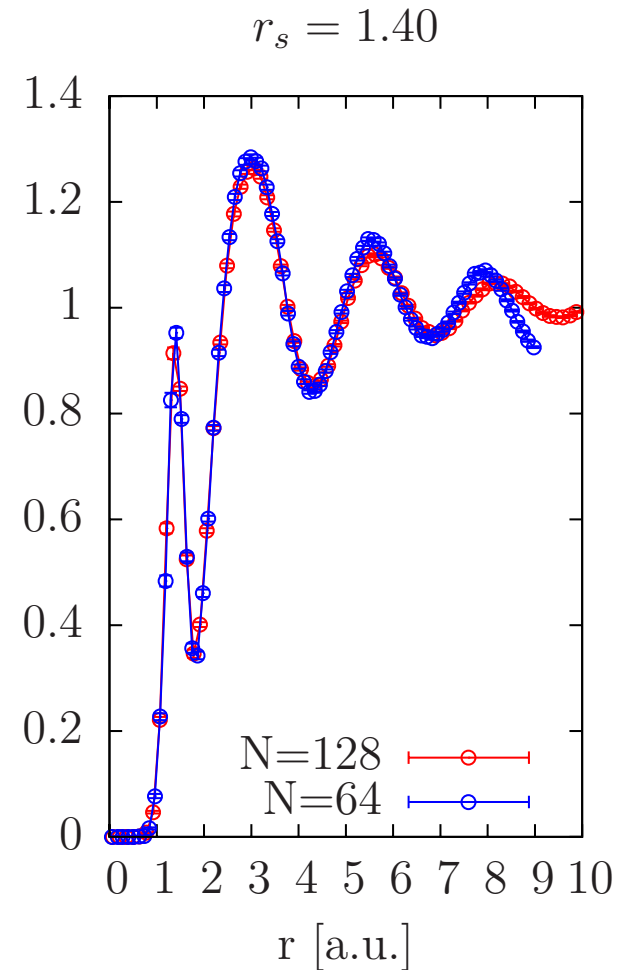
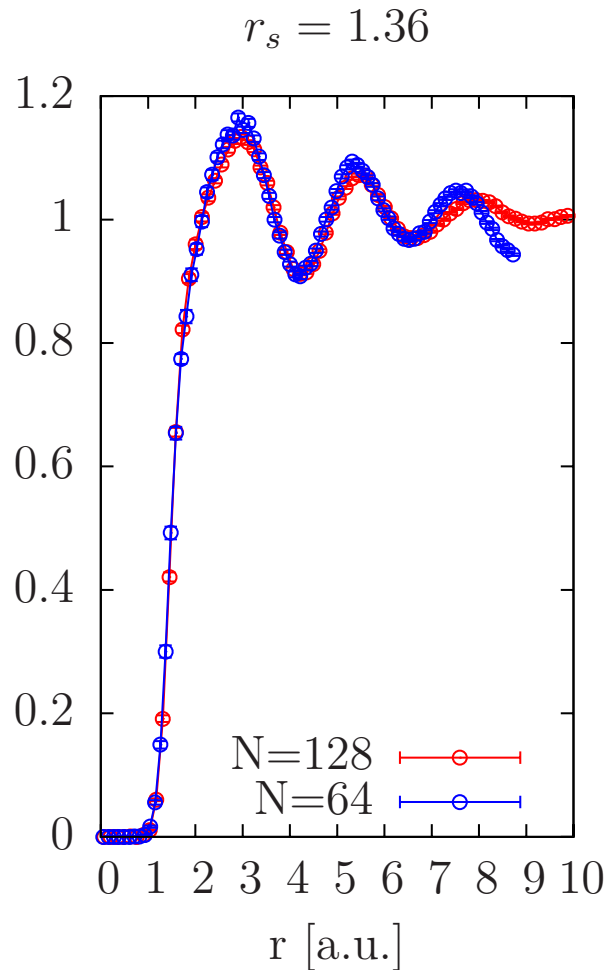
# Hydrogen phase diagram



# The phase diagram



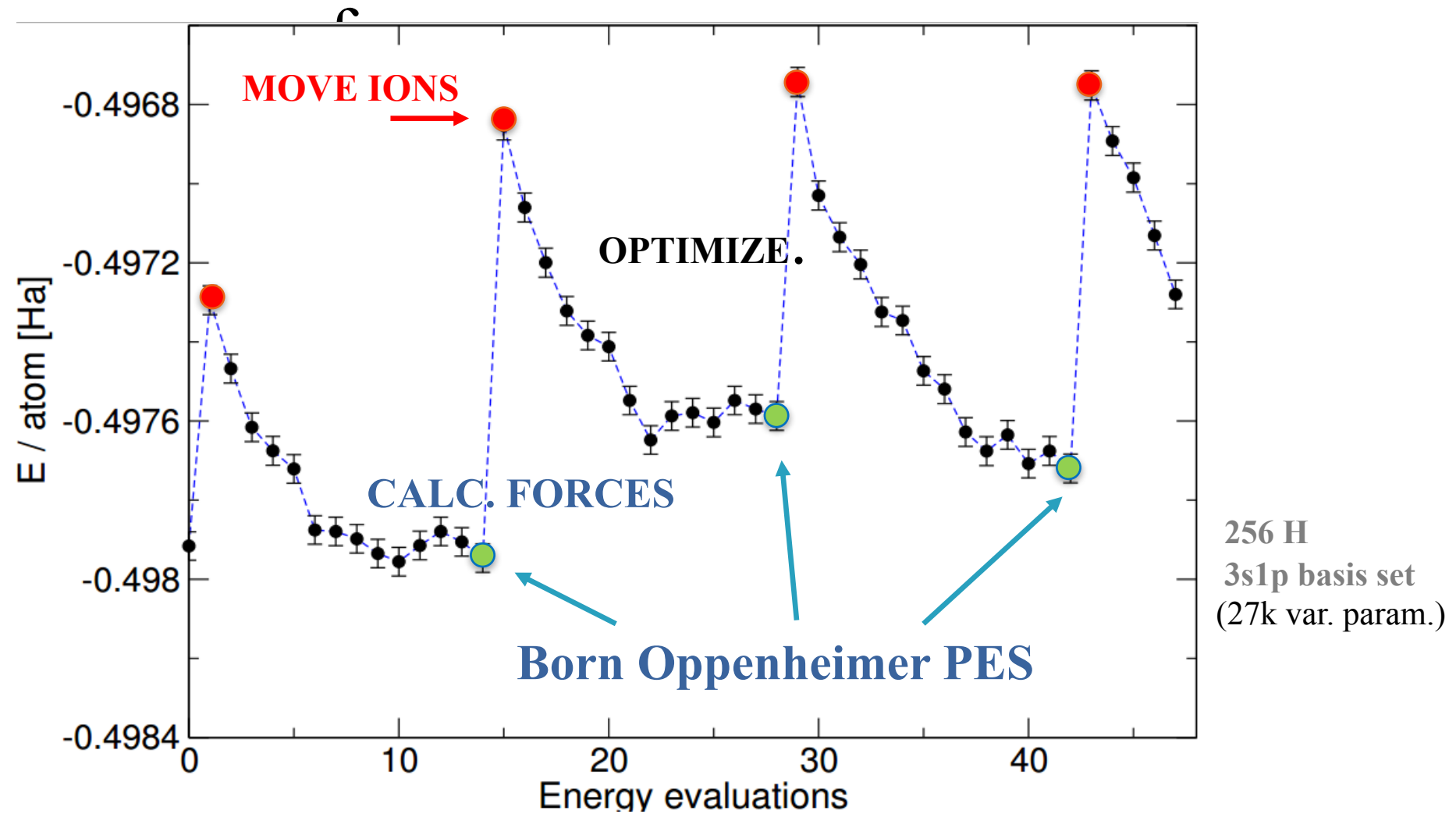
# Finite size effects with k-average



In QMC a 4x4x4 mesh is for free (C. Pierleoni et al. PNAS '16).

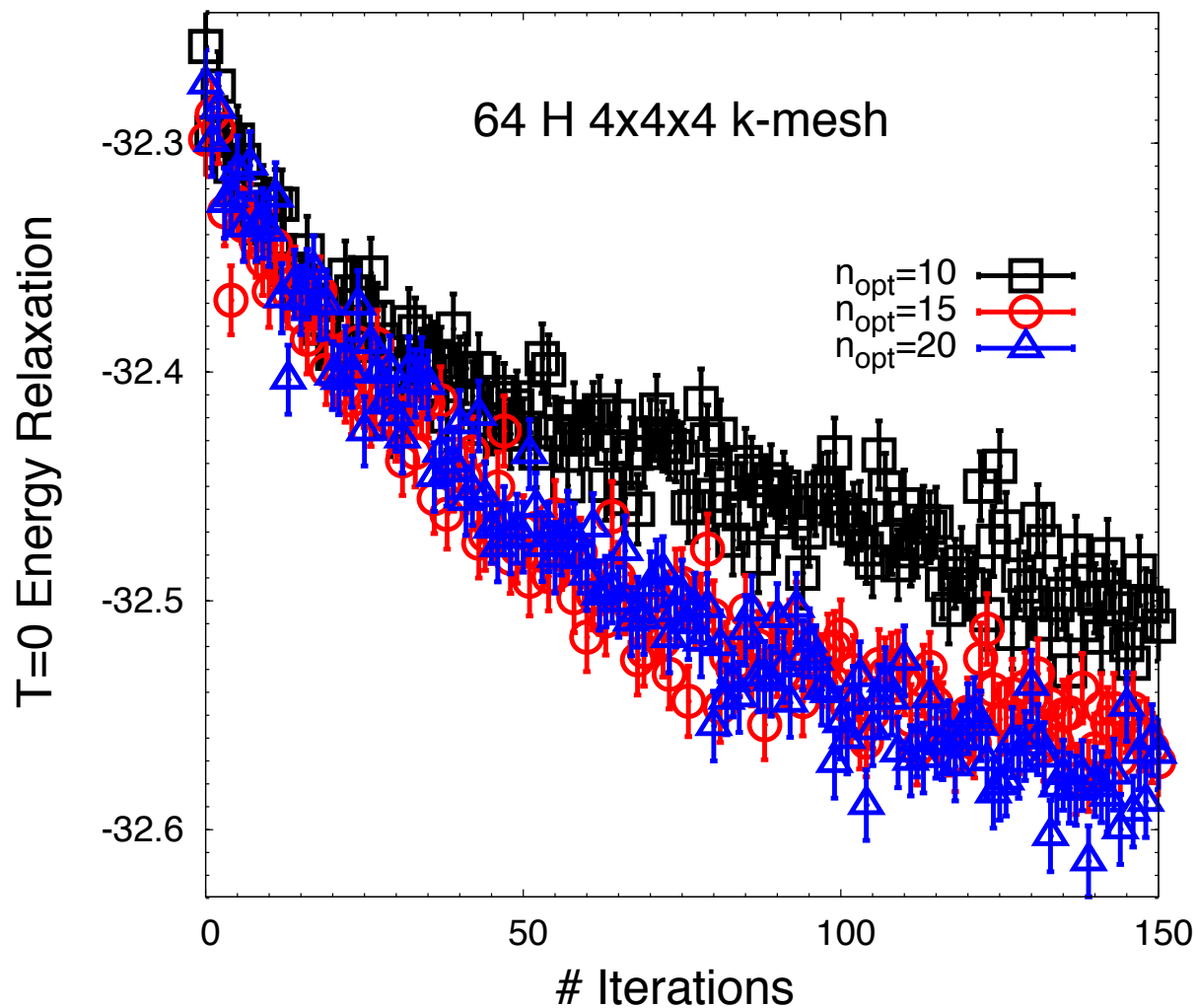
# Dynamics: WF optimization

At each MD step 6-15 steps of electronic optimization (iterative scheme) are done in order to follow the Born-Oppenheimer



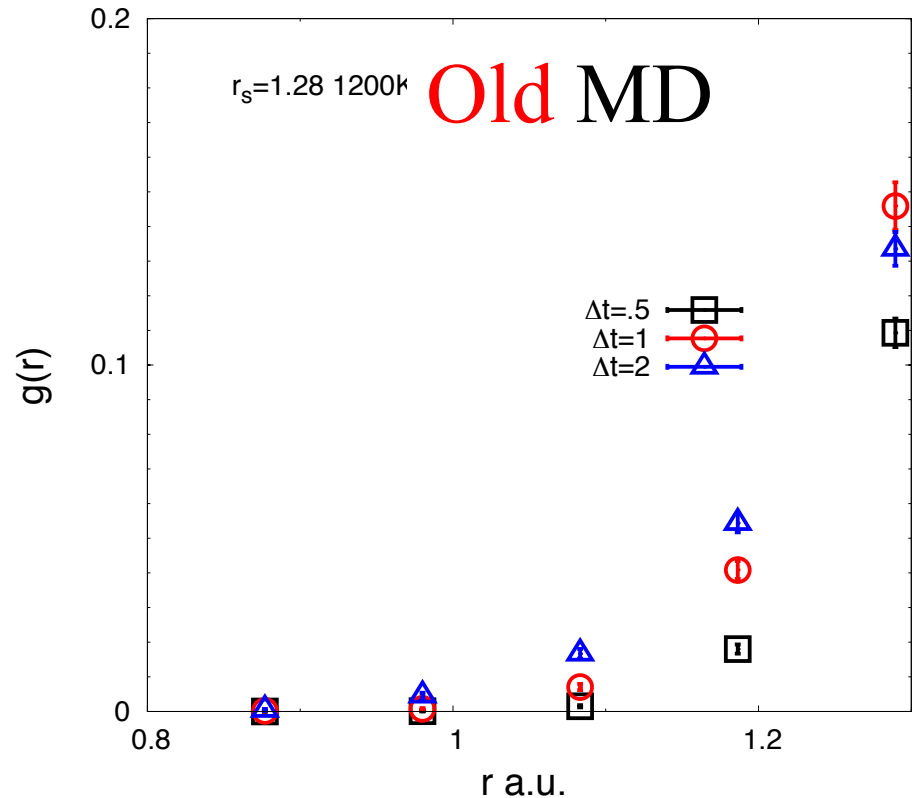
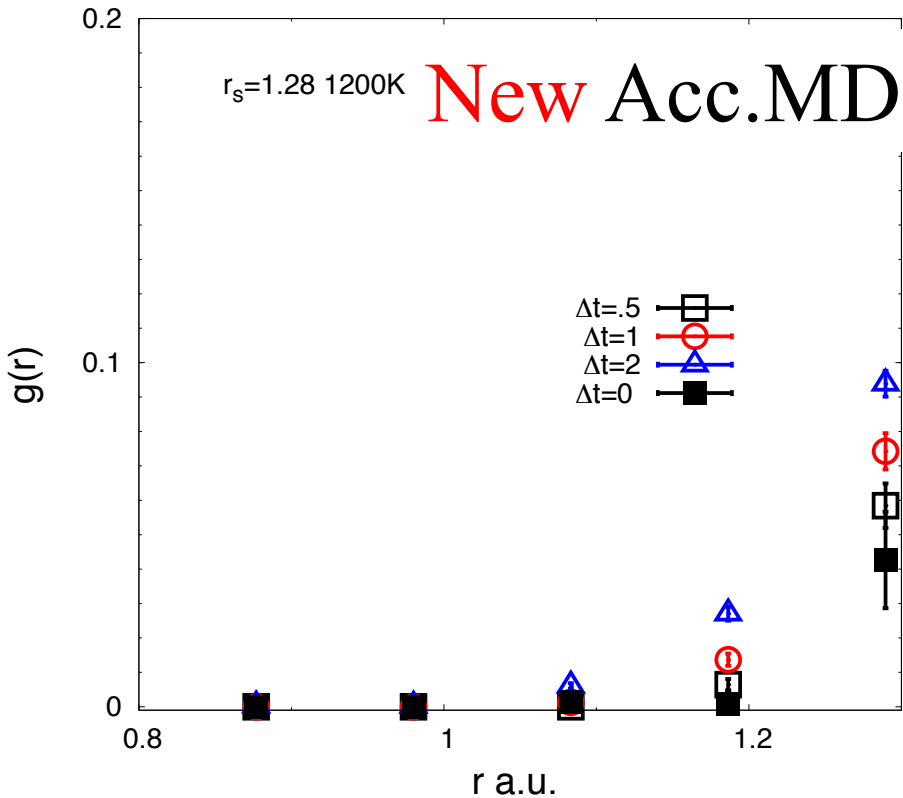


Relevance to fulfill exactly the BO constraints:  
the forces converge with at least **x 2 # opt. steps**

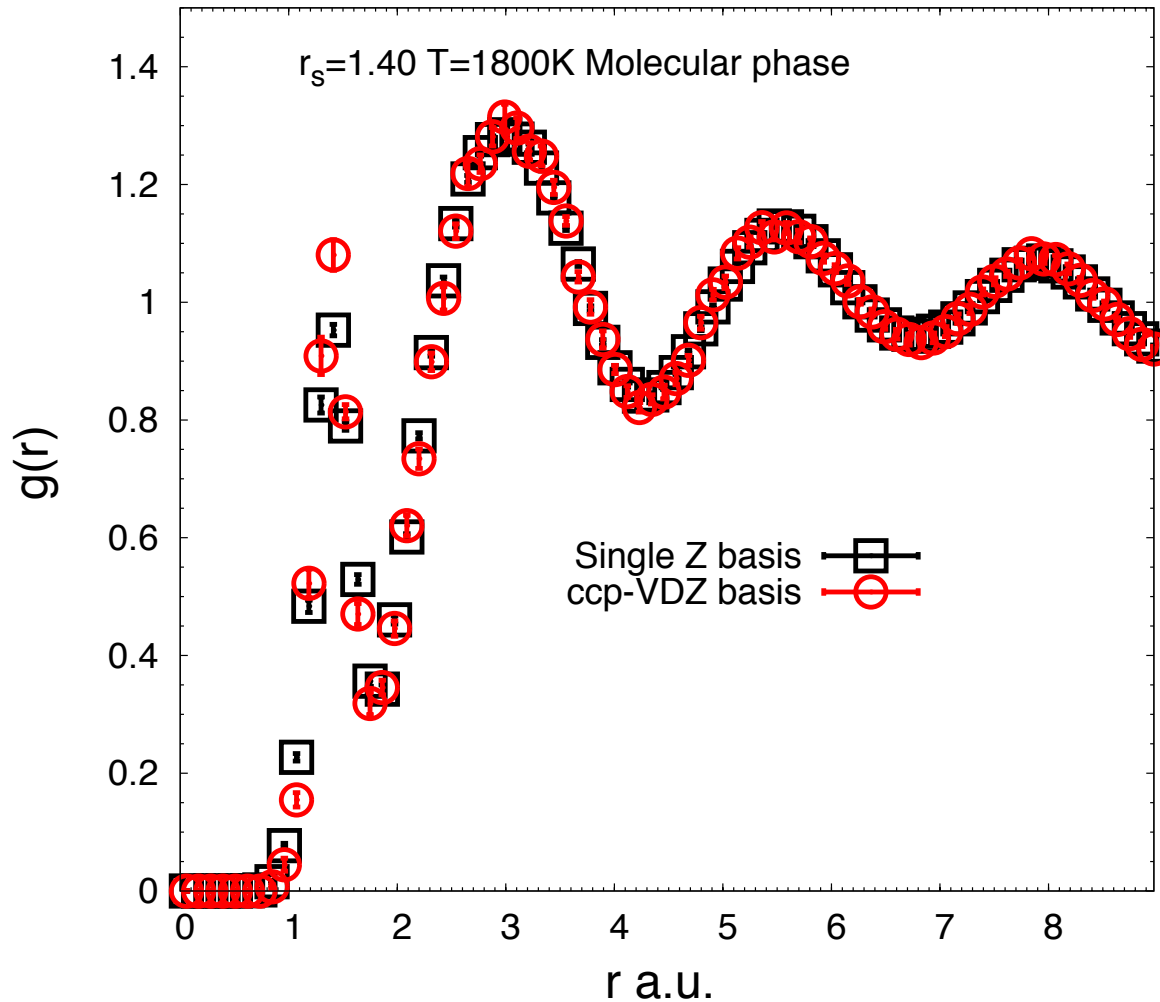


# Realistic simulation does not alter the high-energy modes:

## Time step error (ref. to max =2)

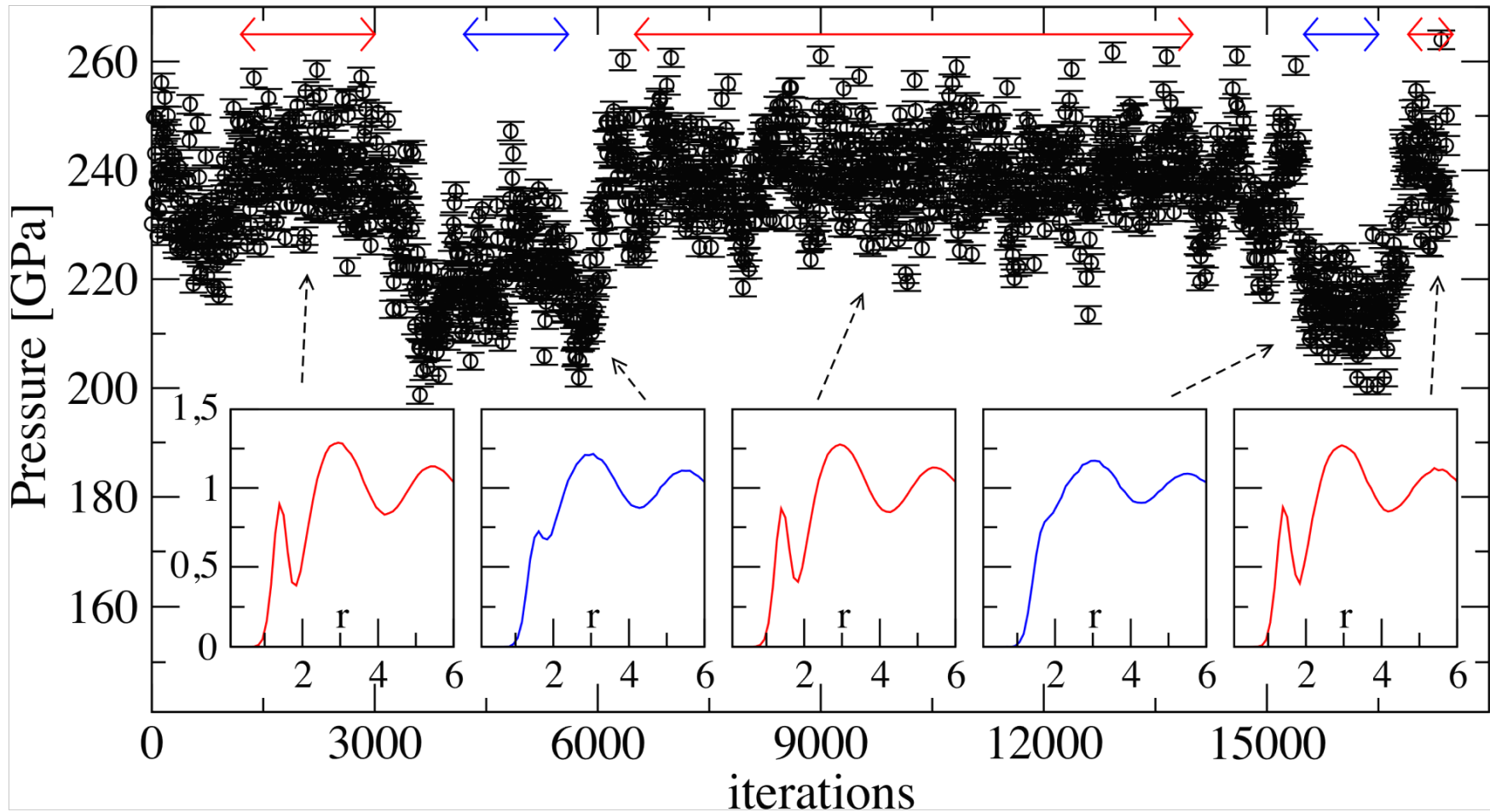


# Basis set in QMC



Larger basis favors slightly the molecular phase

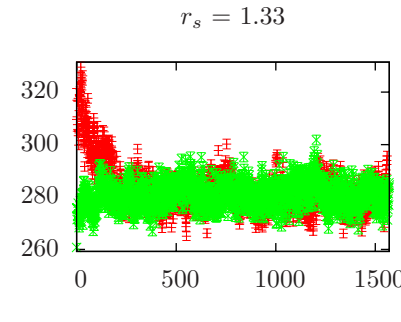
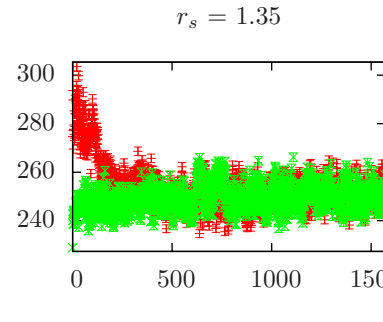
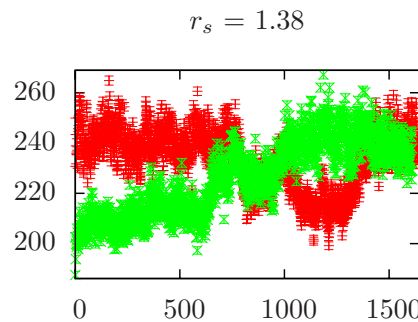
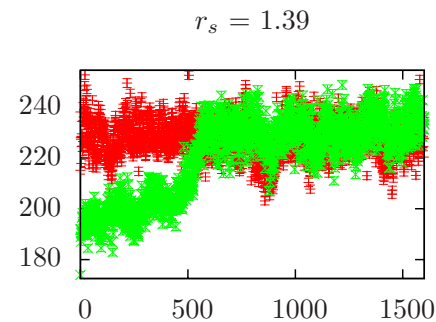
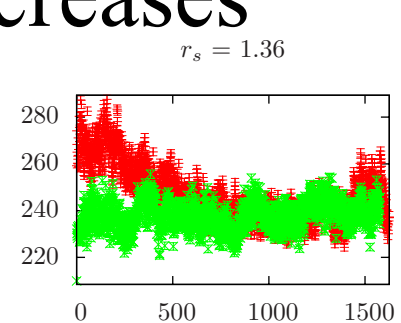
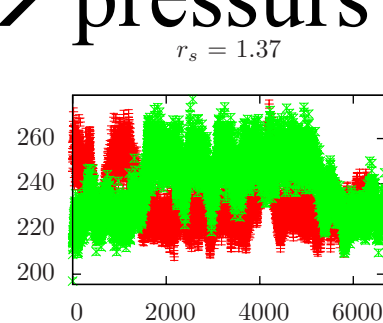
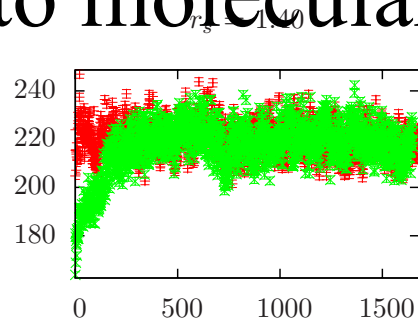
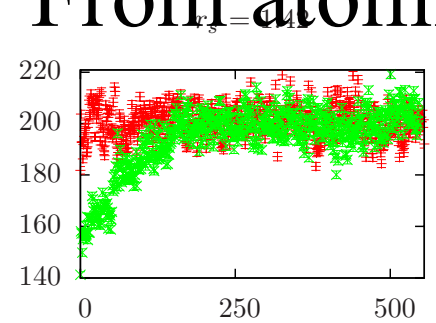
# Ergodicity issue



We start **always** with two “random” conf. (scaled) with atomic or molecular character:

From molecular to atomic  $\rightarrow$  pressure goes down

From atomic to molecular  $\rightarrow$  pressures increases



# Quantum effects within BO

As well known the PIMD approach is equivalent to a classical simulation with  $P$  beads:

$\vec{R}_1 \vec{R}_2 \cdots \vec{R}_P$  at temperature  $T_p = T \times P$

The Hessian matrix in this case is just dominated by the Harmonic part, which is exactly given by:

$$K_{ip,jl} = (PT)^2 M \delta_{i,j} (2\delta_{p,l} - \delta_{p,l+1} - \delta_{p+1,l})$$

Thus the expected speed-up in MD is :

$$\text{Speed up} \sim \begin{cases} \frac{K_{max}}{K_{min}} = \left(\frac{P}{\pi}\right)^2 & \text{vs 1st order MD} \\ \sqrt{\frac{K_{max}}{K_{min}}} = \frac{P}{\pi} & \text{vs 2nd order MD} \end{cases}$$

# Conclusions

- 1) A simple algorithm is given for accelerating MD for equilibrium properties, based on an acceleration matrix  $S$  close to the Hessian one.
- 2) In QMC a useful choice is  $S = \text{Cov}(\text{atomic forces})$ , but better choices are possible, as well as the method could work also in standard ab-initio MD based on DFT.
- 3) Application to Hydrogen  $\rightarrow$  more accurate phase diagram with MD. QMC consistent with DF2
- 4) Use of  $S$  for quantum effects extremely useful.