Welcome to the MaZe

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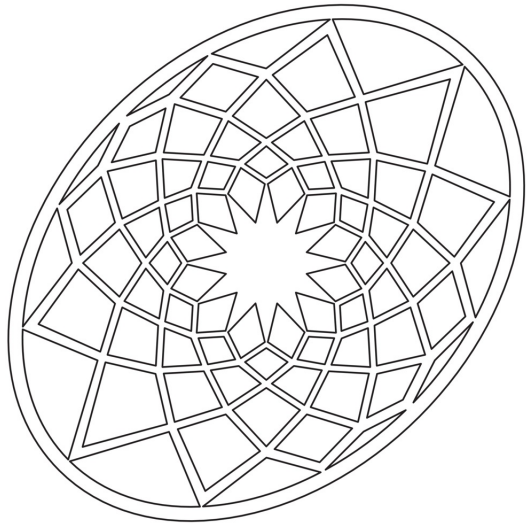

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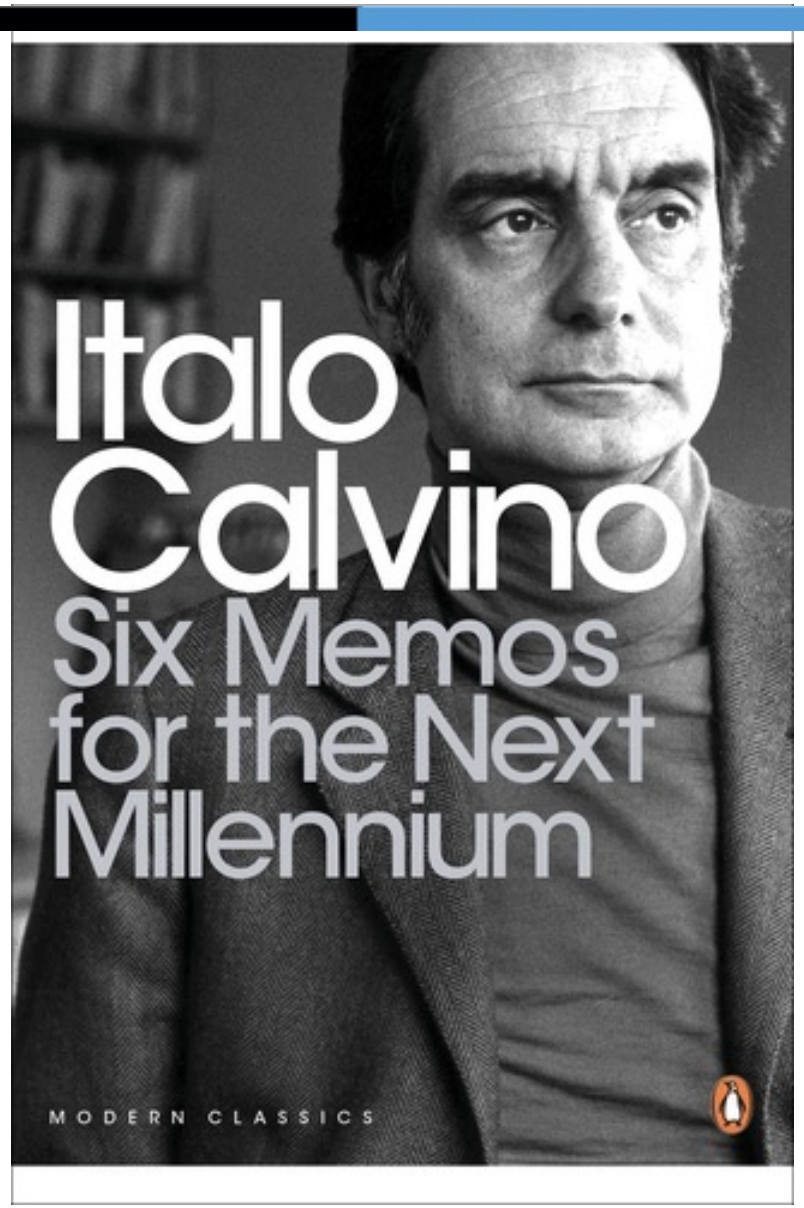
Italo Calvino 1923-1985



Lectures for the Eliot Norton Lectures
Harvard

SIX MEMOS

FOR THE NEXT MILLENNIUM

1- Lightness
2- Quickness
3- Exactitude
4. Visibility
5. Multiplicity
6- Consistency

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The general problem

Dynamics of a set of degrees of freedom that depends on parameters/variables that must satisfy specific conditions

$$V(\mathbf{R}, s)$$

Key application here **adiabatic dynamics**

$$\frac{\partial V(\boldsymbol{R}, s)}{\partial s_\alpha} = 0 \qquad \alpha = 1, \ldots, M$$

Find the set of s that satisfies the condition

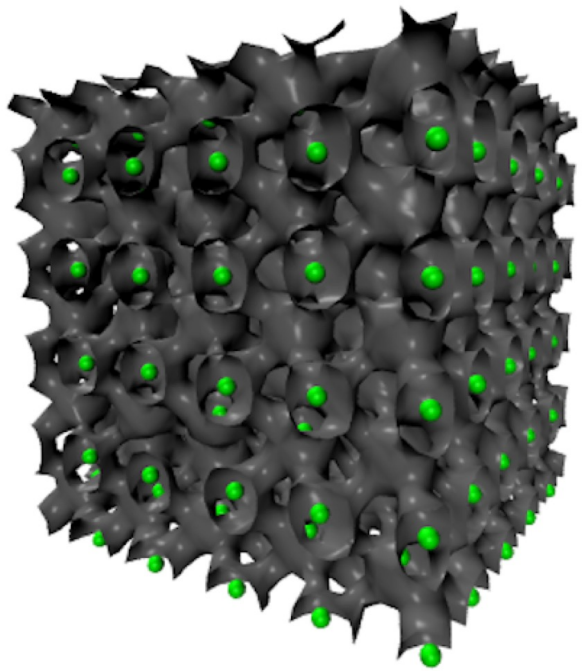
$$\mathbf{s}^* \longrightarrow m_i \ddot{\mathbf{R}}_i = -\nabla_{\mathbf{R}_i} V(\mathbf{R}_i, \mathbf{s}^*)$$

Move R with force computed with s at the solution set

First principles MD: Electrons (ground state) and nuclei

Ground state energy as a functional of the electronic density

$$E[n;\boldsymbol{R}] = E_{\mathrm{K}}[n] + E_{\mathrm{PS}}[n;\boldsymbol{R}] + E_{\mathrm{ES}}[n;\boldsymbol{R}] + E_{\mathrm{XC}}[n]$$



Plane waves representation of electronic density

$$n(\boldsymbol{r}) = \sum_{\boldsymbol{G}} \tilde{n}_{\boldsymbol{G}} e^{i\boldsymbol{G}\cdot\boldsymbol{r}},$$

Electronic state adapts instantaeously to nuclear positions: Born-Oppenheimer approximation

$$\frac{\partial E(\boldsymbol{R}, \tilde{\boldsymbol{n}}, \tilde{n}_{\boldsymbol{G}_0})}{\partial \tilde{n}^{\star}_{\boldsymbol{G}_\alpha}} = 0$$

$$\frac{\partial E(\boldsymbol{R}, \tilde{\boldsymbol{n}}, \tilde{n}_{\boldsymbol{G}_0})}{\partial \tilde{n}_{\boldsymbol{G}_\alpha}} = 0$$

$$M_I \ddot{\boldsymbol{R}}_I = -\nabla_{\boldsymbol{R}_I} E(\boldsymbol{R}, \tilde{\boldsymbol{n}}),$$

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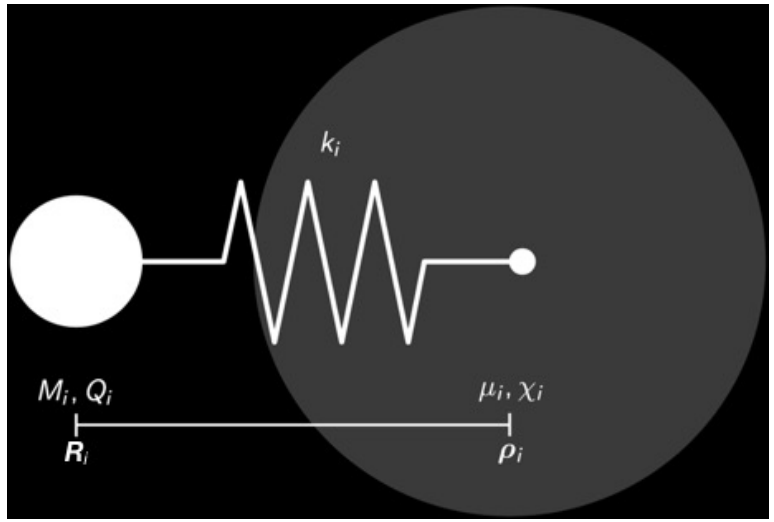
Polarizable force fields

General idea: mimic changes in the electronic density by introducing auxiliary dofs that embody different effects.

Shell model: dipole polarization. Total charge is shared between a core (representing the nucleus) and a massless shell (representing the electronic charge density).



$$\mathcal{V}(\mathbf{r}, \rho)$$

Shells adapt instantaneously to the positions of the cores and satisfy

$$\boldsymbol{\nabla}_{\boldsymbol{\rho}_h} \mathcal{V}(\boldsymbol{r}, \boldsymbol{\rho}) = 0 \quad h = 1 \ldots N$$

Solve for shells positions

$$\boldsymbol{\rho}^* \equiv \{\boldsymbol{\rho}_h(\boldsymbol{r})\}_{h=1}^{N}$$

Ions (cores) move according to

$$m_i \ddot{\mathbf{r}}_i = -\nabla_{\mathbf{r}_i} \mathcal{V}(\mathbf{r}, \rho)|_{\rho=\rho^*}$$

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Direct minimization: Born Oppenheimer dynamics for dummies

$$\frac{\partial V(\boldsymbol{R}, s)}{\partial s_\alpha} = 0 \qquad \alpha = 1, \ldots, M$$

Solve by (non-linear) minimization methods, e.g. non-linear conjugate gradient

$\mathbf{S}^*$ Use these as input in potential

$$m_i \ddot{\mathbf{R}}_i = -\nabla_{\mathbf{R}_i} V(\mathbf{R}_i, \mathbf{s}^*)$$

Use, e.g. velocity Verlet, to solve numerically This of equations for R (only!)

Born-Oppenheimer dynamics: pros and cons

correct dynamics and samping if minimization fully converged

typically non-linear problem expensive to converge

incomplete convergence results in pathologies for the dynamics

- lack of time-reversibility
- bad energy conservation

Car-Parrinello for Dummies:
Extend system to include “fast” variables and let the dynamics realise adiabatic separation

Lagrangian mechanics provides a convenient framework

$$L_{\mathrm{CP}}^{\mathrm{4Dummy}}(\mathbf{R},\dot{\mathbf{R}},\mathbf{s},\dot{\mathbf{s}}) = \frac{1}{2}\sum_{i=1}^{N} m_i\dot{\mathbf{R}}^2 + \frac{1}{2}\sum_{\alpha=1}^{M}\mu\dot{\mathbf{s}}^2 - V(\mathbf{R},\mathbf{s})$$

Evolution equations are obtained from

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\partial L}{\partial \dot{q}_k}\right) - \frac{\partial L}{\partial q_k} = 0$$

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Car-Parrinello for Dummies:
Extend system to include “fast” variables and let the dynamics realise adiabatic separation

$$m_i \ddot{\mathbf{R}}_i = -\nabla_{\mathbf{R}_i} V(\mathbf{R}, \mathbf{s})$$

$$\mu \ddot{s}_\alpha = -\frac{\partial V(\mathbf{R}, \mathbf{s})}{\partial s_\alpha}$$

Use algorithm, e.g. velocity Verlet, to solve numerically this coupled set of equations

Pros and cons

extended dynamical system brings several nice properties

time-reversible

small mass associated to fast variables

small time step necessary

incomplete adiabatic separation

incorrect physical dofs sampling

bias in dynamical properties

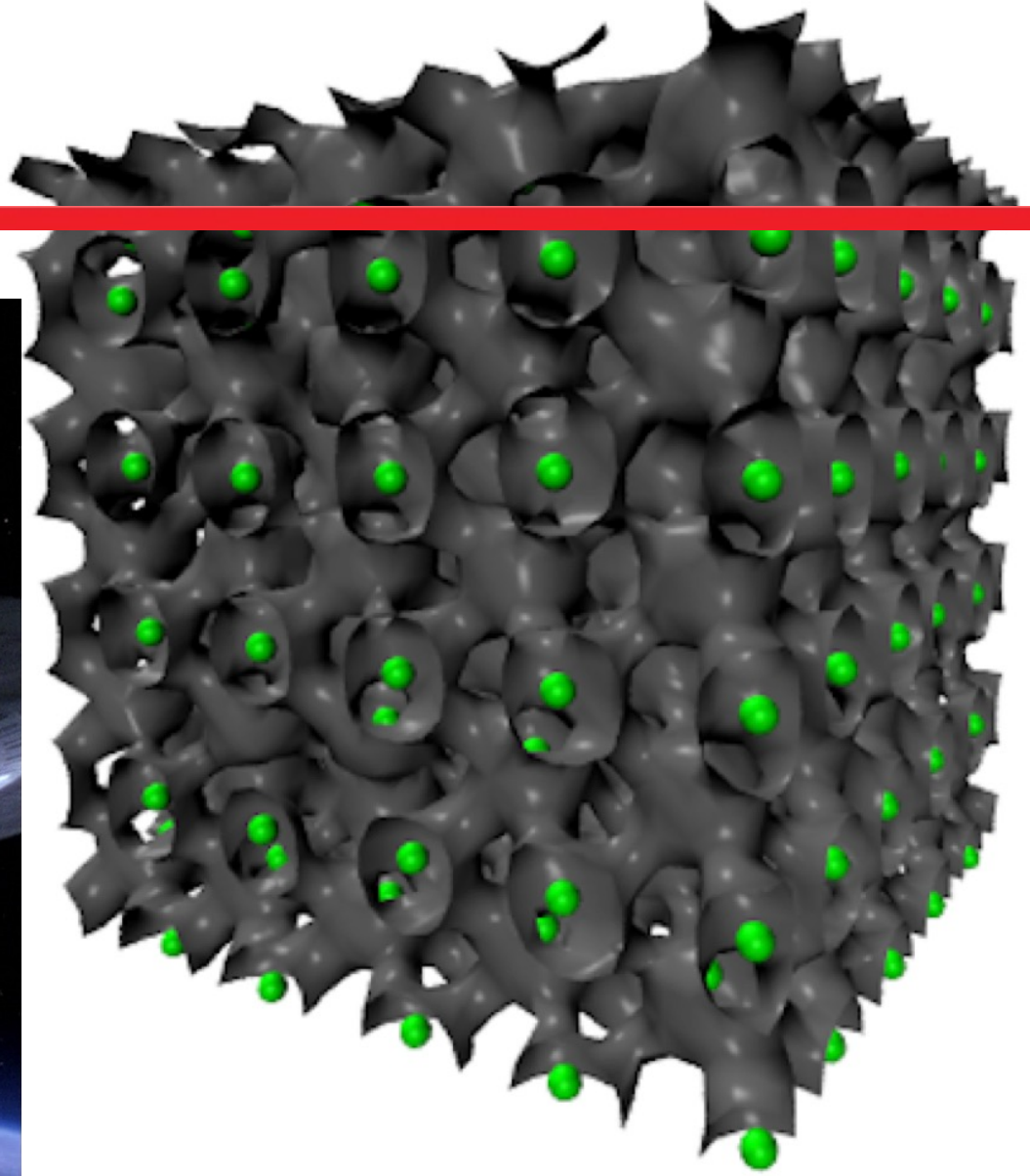
MaZe: “Best of both worlds” (?)

Algorithm

Two applications

First priciple MD

Polarizable



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Extend system to include “fast” variables and interpret minimum condition as a set of holonomic constraints

Lagrangian mechanics provides again a convenient framework

$$L(\boldsymbol{R}, \dot{\boldsymbol{R}}, s, \dot{s}) = \frac{1}{2}\sum_{i=1}^{N} m_i \dot{\boldsymbol{R}}_i^2 + \frac{1}{2}\sum_{\alpha=1}^{M} \mu \dot{s}_\alpha^2 - V(\boldsymbol{R}, s)$$

$$\sigma_\alpha(\boldsymbol{R}, s) \equiv \frac{\partial V(\boldsymbol{R}, s)}{\partial s_\alpha} = 0 \qquad \alpha = 1, \ldots, M$$

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\partial L}{\partial \dot{q}_k}\right) - \frac{\partial L}{\partial q_k} = G_k$$

$$G_k = -\sum_{\alpha=1}^{M} \lambda_\alpha \frac{\partial \sigma_\alpha}{\partial q_k}$$

*A. Coretti, S. Bonella, and G. Ciccotti J. Chem. Phys. Comm., **149**, 191102 (2018)*

*J.P. Ryckaert, A. Bellemans, and G. Ciccotti Mol. Phys, **44**, 979 (1986)*

Into the MaZe: Evolution equations for the full system

$$m_i \ddot{\boldsymbol{R}}_i = -\boldsymbol{\nabla}_{\boldsymbol{R}_i} V(\boldsymbol{R}, s) - \sum_{\beta=1}^{M} \lambda_\beta \boldsymbol{\nabla}_{\boldsymbol{R}_i} \sigma_\beta(\boldsymbol{R}, s)$$

$$\mu \ddot{s}_\alpha = -\frac{\partial V(\boldsymbol{R}, s)}{\partial s_\alpha} - \sum_{\beta=1}^{M} \lambda_\beta \frac{\partial \sigma_\beta(\boldsymbol{R}, s)}{\partial s_\alpha}$$

$$m_i \ddot{\boldsymbol{R}}_i = -\boldsymbol{\nabla}_{\boldsymbol{R}_i} V(\boldsymbol{R}, s) - \sum_{\beta=1}^{M} \lambda_\beta \boldsymbol{\nabla}_{\boldsymbol{R}_i} \sigma_\beta(\boldsymbol{R}, s)$$

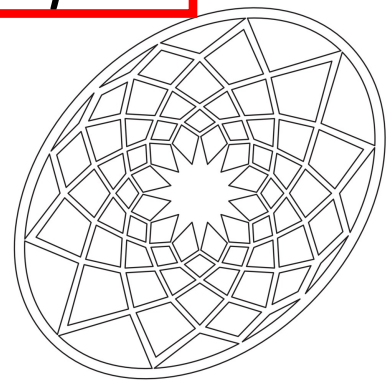
$$\ddot{s}_\alpha = -\sum_{\beta=1}^{M} \frac{\lambda_\beta}{\mu} \frac{\partial \sigma_\beta(\boldsymbol{R}, s)}{\partial s_\alpha}$$

$$\mu \to 0 \qquad \text{and} \qquad \lambda_\beta \propto \mu \longrightarrow \gamma_\beta = \lim_{\mu \to 0} \frac{\lambda_\beta}{\mu}$$

Mass-Zero (MaZe!) limit for auxiliary variables

$$m_i \ddot{\boldsymbol{R}}_i = -\boldsymbol{\nabla}_{\boldsymbol{R}_i} V(\boldsymbol{R}, s)$$

$$\ddot{s}_\alpha = -\sum_{\beta=1}^{M} \gamma_\beta \frac{\partial \sigma_\beta(\boldsymbol{R}, s)}{\partial s_\alpha}$$



*A. Coretti, S. Bonella, and G. Ciccotti J. Chem. Phys. Comm., **149**, 191102 (2018)*

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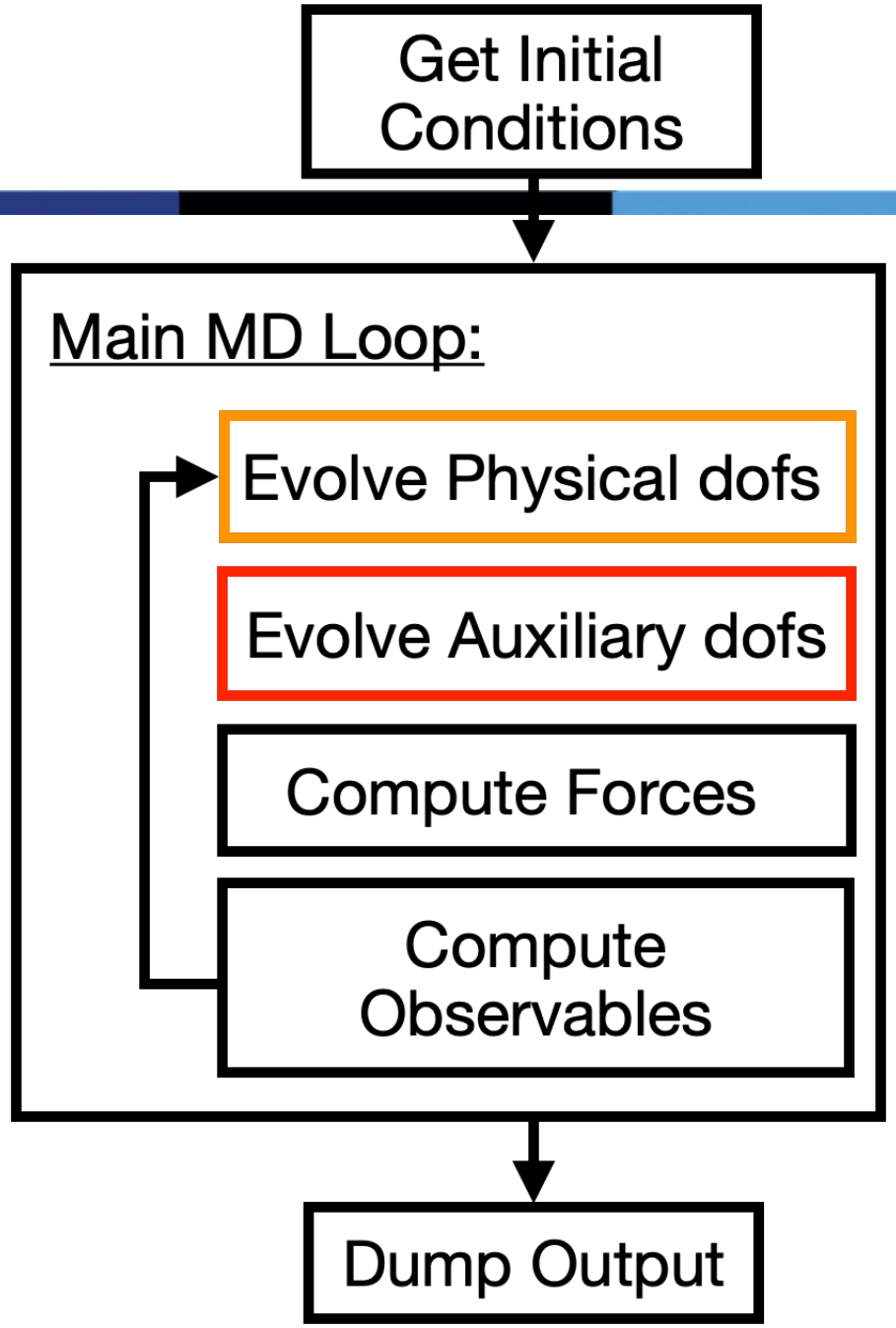
The algorithm



Standard integration algorithm, e.g. Verlet

$$\boldsymbol{R}_i(t+\Delta t) = 2\boldsymbol{R}_i(t) - \boldsymbol{R}_i(t-\Delta t) + \frac{\Delta t^2}{m_i}\boldsymbol{F}_i\big(\boldsymbol{R}(t), s(t)\big)$$

$$s_\alpha(t+\Delta t) = 2s_\alpha(t) - s_\alpha(t-\Delta t) + \Delta t^2 \sum_{\beta=1}^{M} \gamma_\beta \frac{\partial \sigma_\beta\big(\boldsymbol{R}(t), s(t)\big)}{\partial s_\alpha}$$

+ SHAKE to determine the Lagrange multipliers

SHAKE*: $\sigma\big(\boldsymbol{R}(t+\Delta t), s(t+\Delta t)\big) = 0 \Rightarrow \gamma$

Solve by (adapted) Newton-Raphson

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MaZe properties

$$m_i \ddot{\boldsymbol{R}}_i = -\boldsymbol{\nabla}_{\boldsymbol{R}_i} V(\boldsymbol{R}, s)$$

$$\ddot{s}_\alpha = -\sum_{\beta=1}^{M} \gamma_\beta \frac{\partial \sigma_\beta(\boldsymbol{R}, s)}{\partial s_\alpha}$$

Explicit evolution equations for slow and fast variables from a consistent dynamical framework

Full adiabatic separation → **Exact sampling of Born-Oppenheimer probability for the physical degrees of freedom**

Symplectic algorithm :

SHAKE enables to satisfy the constraint “exactly” at an affordable cost,
fully time-reversible,
no reduction of cores time-step,
extremely stable for very long times

Involves the hessian of the potential…but always applied to something!

$$\boldsymbol{G}_i(t) = \sum_{h=1}^{3N} \gamma_h(t) \nabla_{\boldsymbol{\rho_i}} \sigma_h(\boldsymbol{r}(t), \boldsymbol{\rho}(t))$$

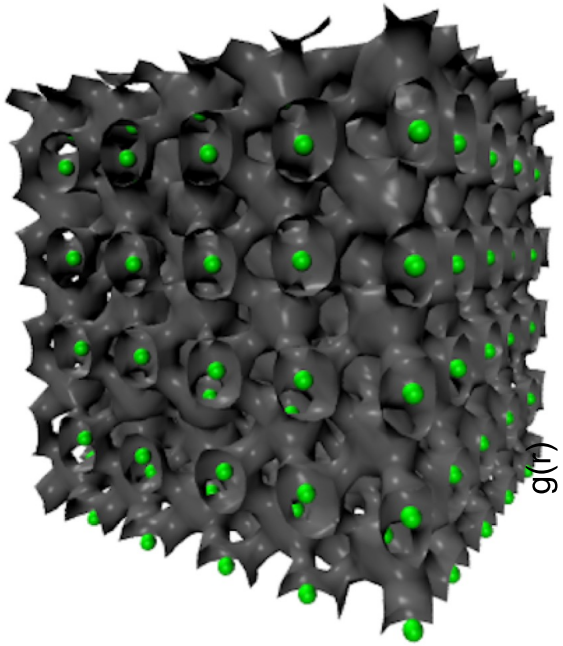
$$\boldsymbol{\sigma}_h \equiv \boldsymbol{\nabla}_{\boldsymbol{\rho}_h} V(\boldsymbol{r}, \boldsymbol{\rho}) = 0 \quad h = 1 \ldots N$$

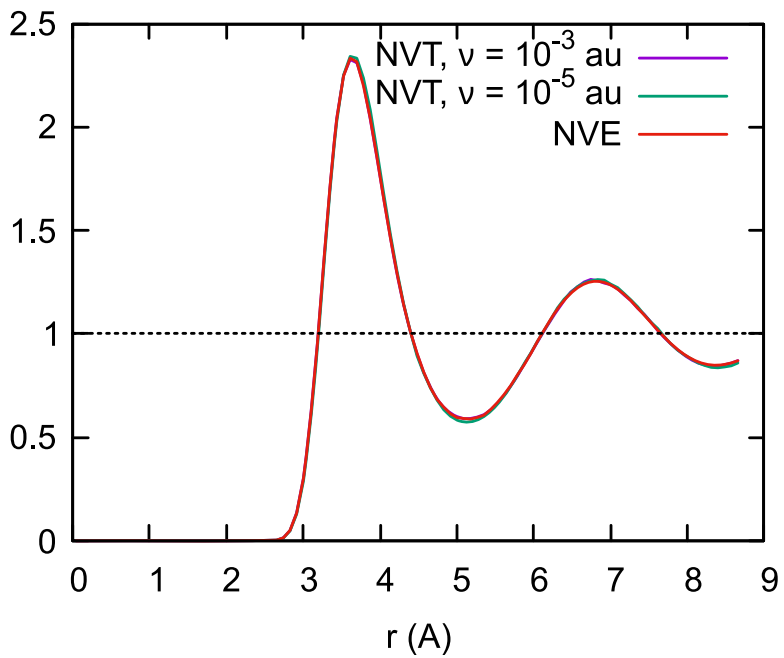
First-Principles MD

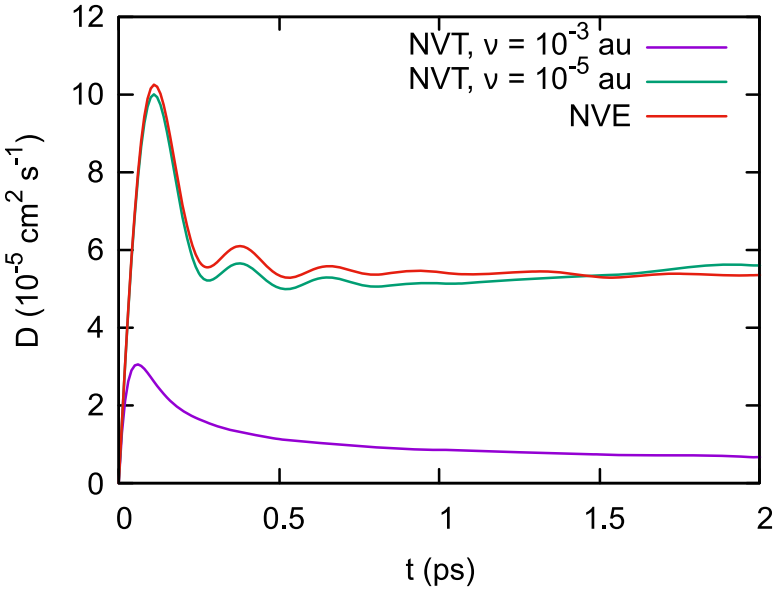
Static and dynamical properties of Na (typical test system)

$$E[n;\boldsymbol{R}] = E_{\mathrm{K}}[n] + E_{\mathrm{PS}}[n;\boldsymbol{R}] + E_{\mathrm{ES}}[n;\boldsymbol{R}] + E_{\mathrm{XC}}[n]$$

Up to 2000 ions and 100000 auxiliary variables







*S. Bonella, A. Coretti, R. Vuilleumier & G. Ciccotti, Phys. Chem. Chem. Phys., **22**, 10775 (2020)*

*A. Coretti, T. Baird, R. Vuilleumier & S. Bonella, J. Chem. Phys., **157**, 214110 (2022)*

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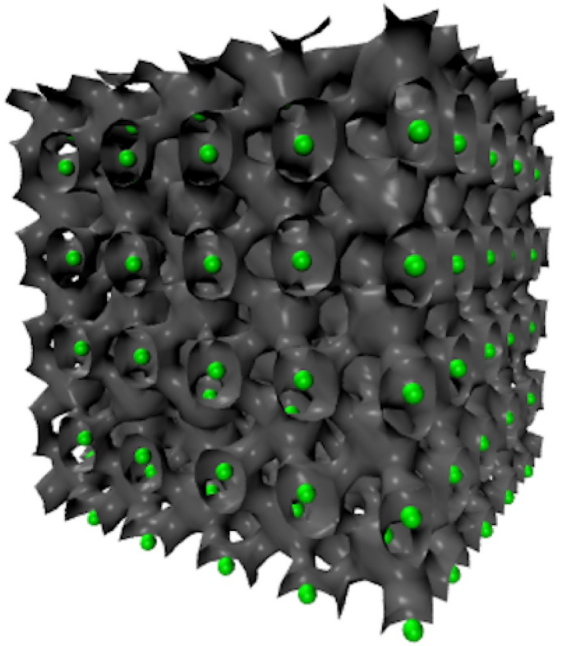
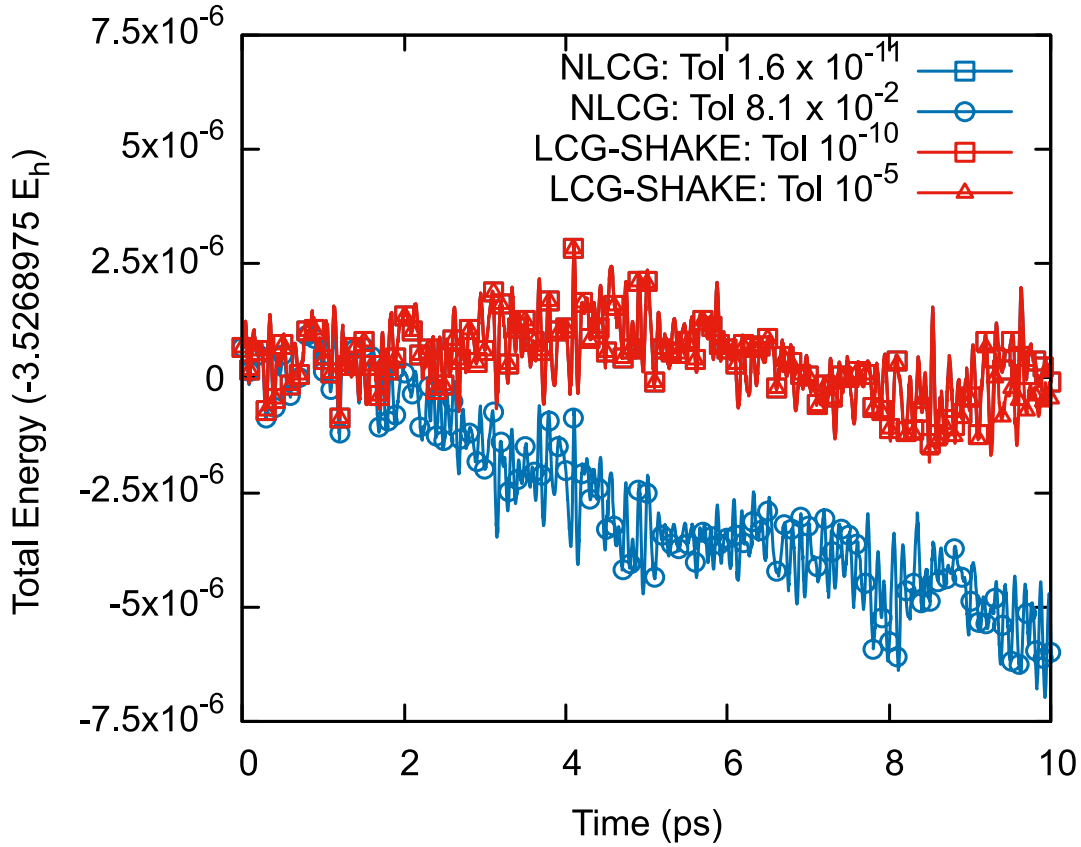
First principles MD: Orbital Free DFT properties of Na



Comparison with conjugate gradient minimization



LCG-SHAKE Wall time 10^-2/10^-1

NLCG Wall time 1

NLCG Wall time 10^-1

S. Bonella, A. Coretti, R. Vuilleumier & G. Ciccotti, Phys. Chem. Chem. Phys., ***22****, 10775 (2020)*

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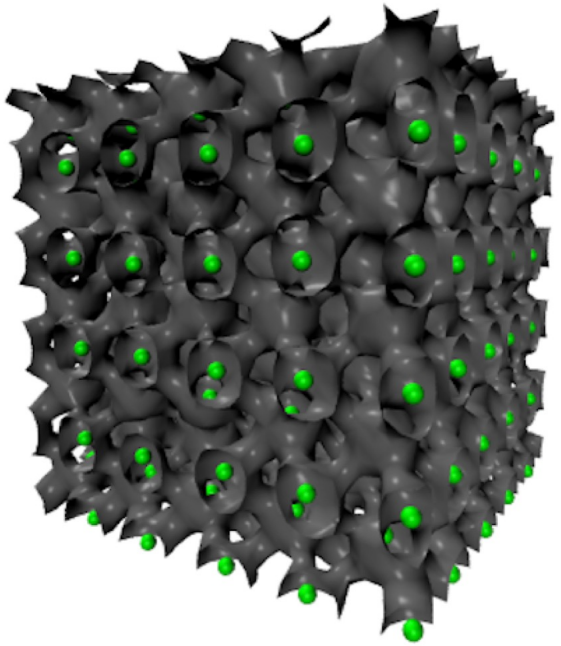
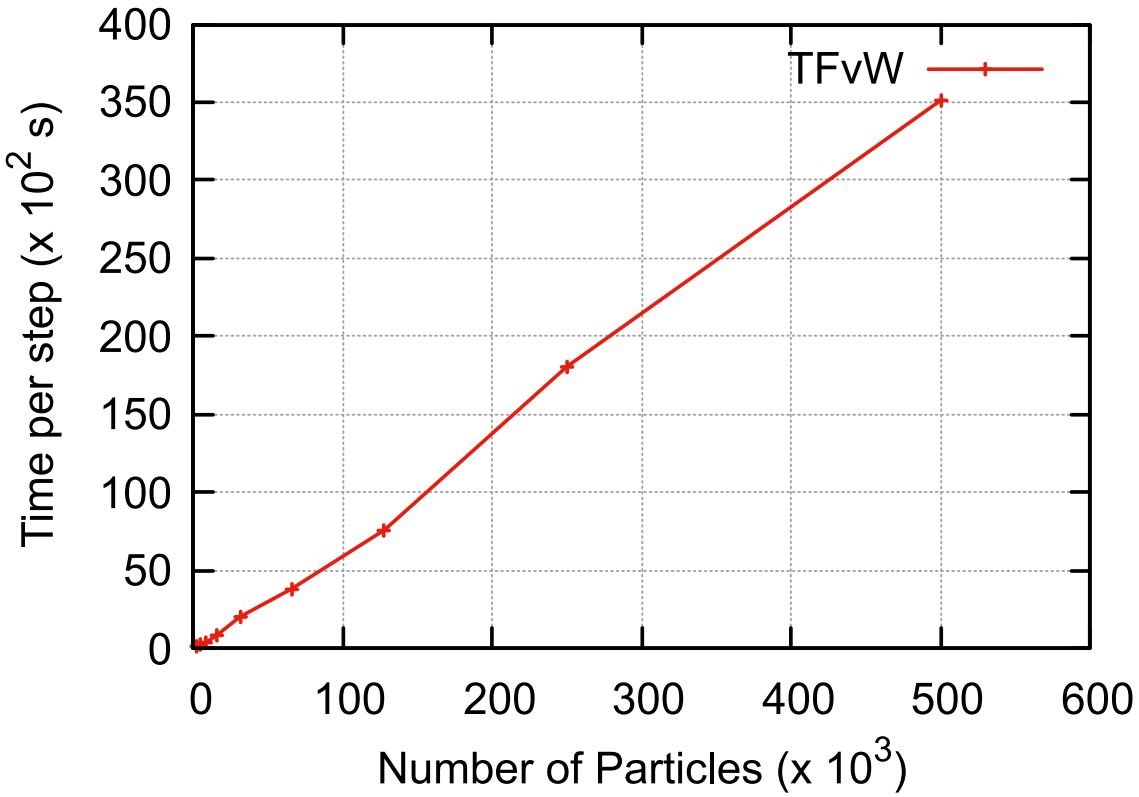
Orbital Free DFT Na: scaling with system size





S. Bonella, A. Coretti, R. Vuilleumier & G. Ciccotti, Phys. Chem. Chem. Phys., ***22****, 10775 (2020)*

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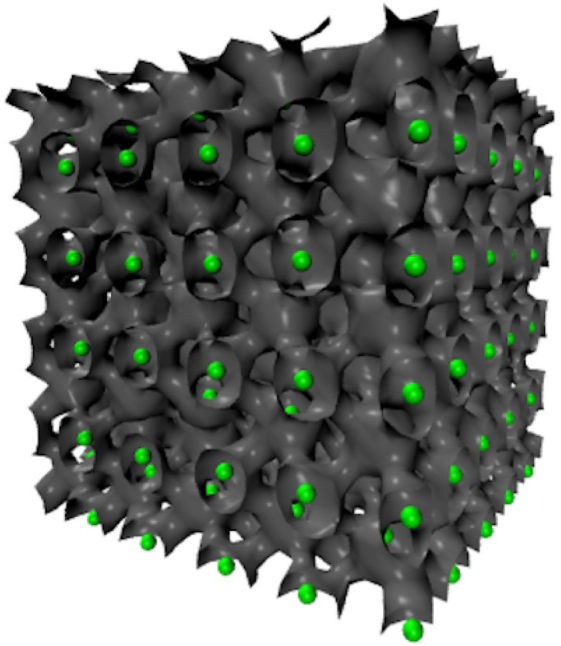
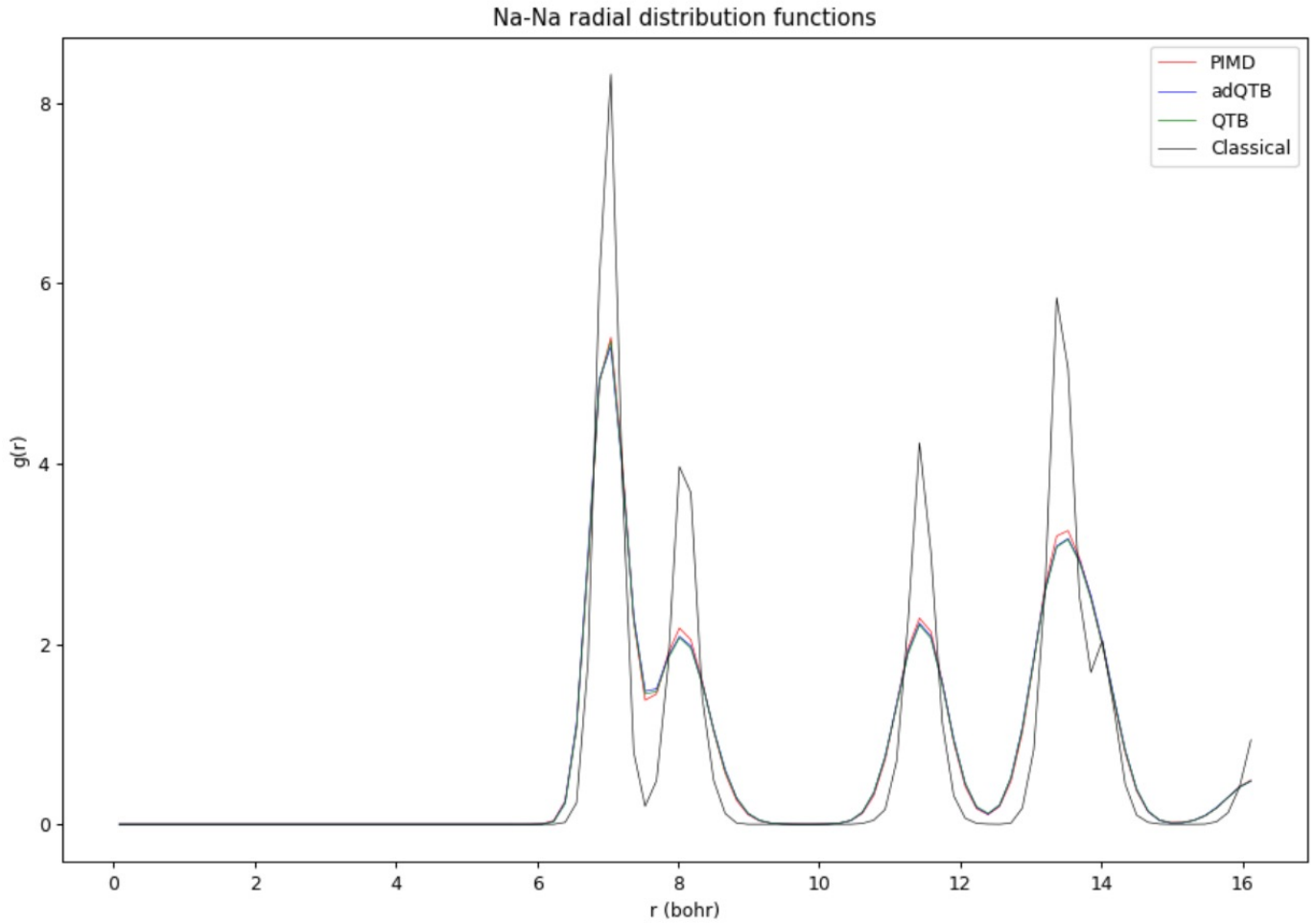
Orbital Free DFT Na : quantum nuclear effects





128 ions
32 beads for Path Integrals

10000 electronic coefficients

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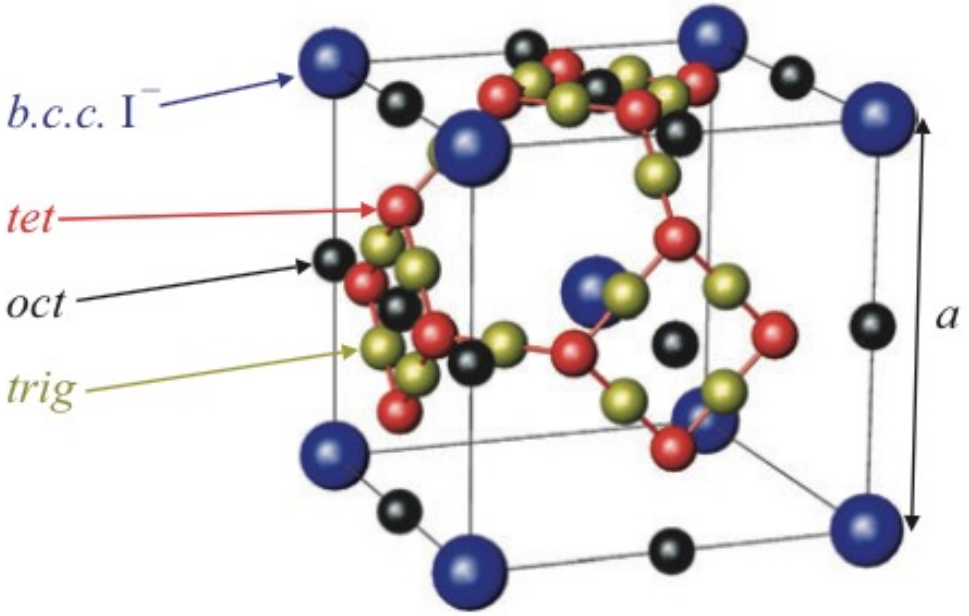
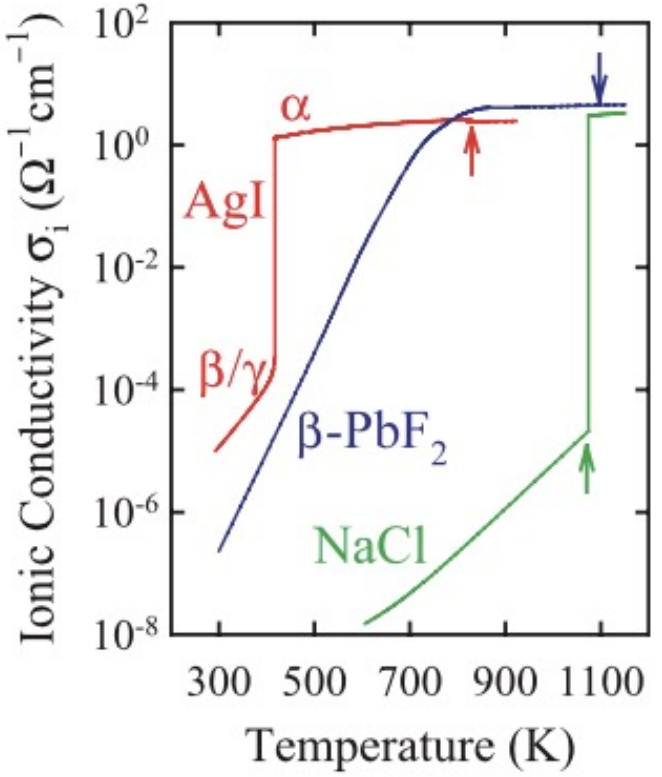
Polarizable models

Charge transport properties in superionic conductors….



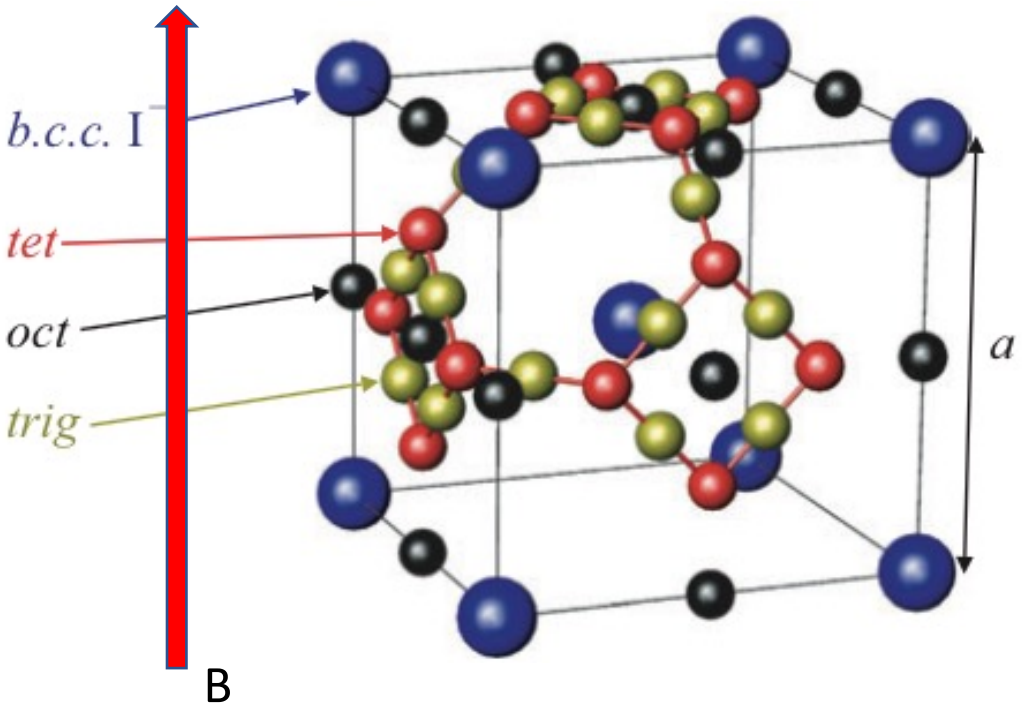
$$\sigma_{\alpha\beta} = \frac{1}{k_B T \Omega} \lim_{\mathcal{T}\to\infty} \int_0^{\mathcal{T}} d\tau < J_\alpha(\tau) J_\beta(0) >$$

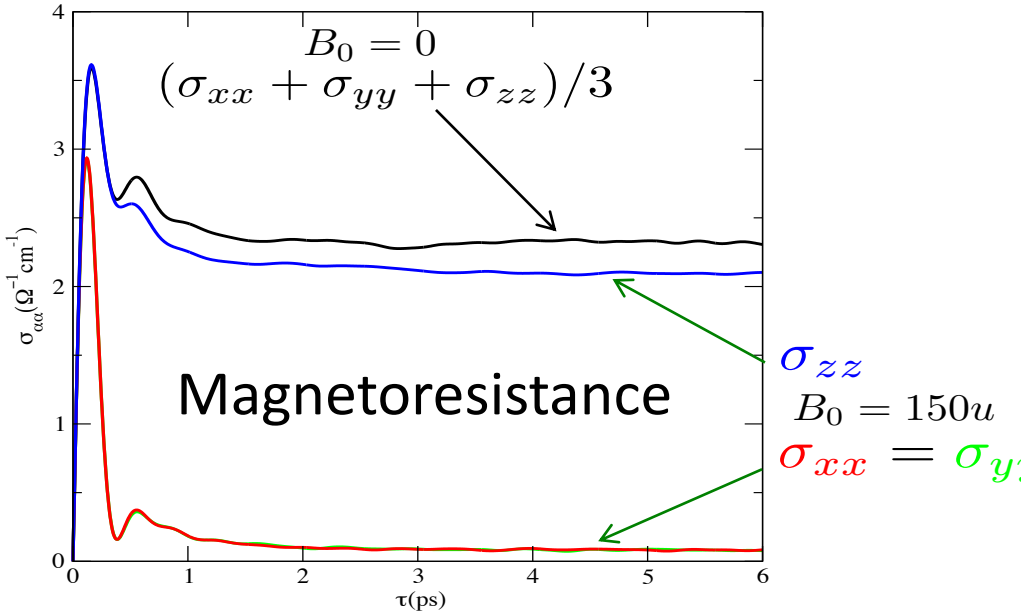


Collective properties, difficult statistical convergence, very long trajectories needed

….In the presence of an external magnetic field

MD and statistical properties not trivial due to Lorentz force





Accurate modelling of interactions needed for more subtle effects such as ionic Hall effect

Polarizable force fields

*F. Mouhat, S. Bonella, and C. Pierleoni, Molecular Physics **111**, 3651 (2013)*

*L. Gagliardi, S. Bonella Phys. Rev. B **94**, 1344 (2016)*

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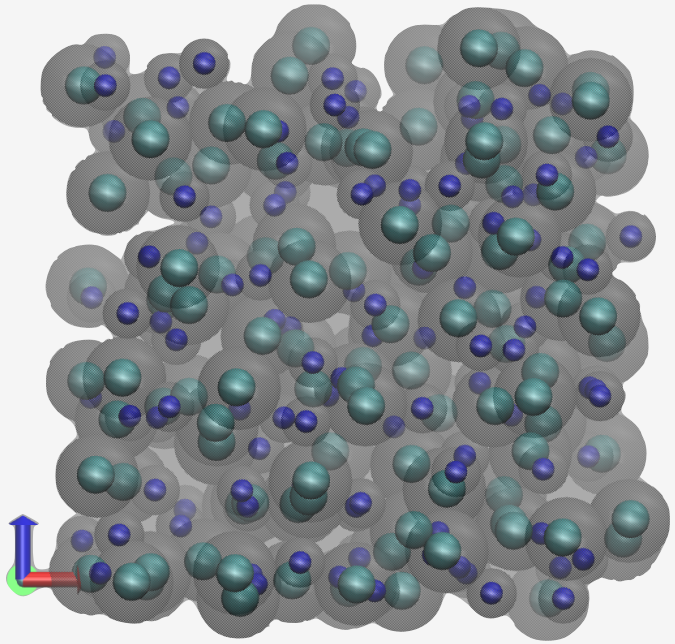
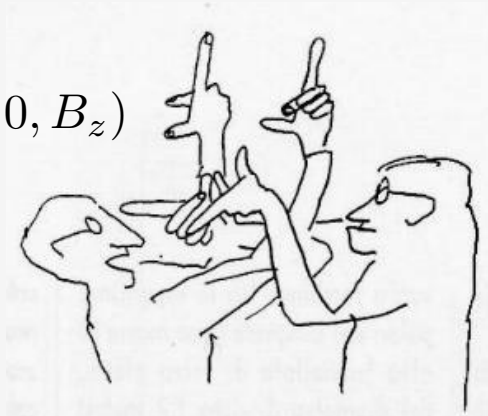
Shell model NaCl in external magnetic field



$$\boldsymbol{B} = (0, 0, B_z)$$



$$m_i \ddot{R}_i^h = -\frac{\partial V(\boldsymbol{R}, \boldsymbol{S})}{\partial R_i^h} + Q_i (\dot{\boldsymbol{R}}_i \times \boldsymbol{B})_h$$

$$\ddot{s}_\alpha^h = -\sum_{\beta=1}^{N} \sum_{l=x,y} \gamma_\beta^l \frac{\partial \sigma_\beta^l}{\partial \dot{s}_\alpha^h} - \sum_{\beta=1}^{N} \gamma_\beta^z \frac{\partial \sigma_\beta^z}{\partial s_\alpha^h}$$

Non-standard SHAKE

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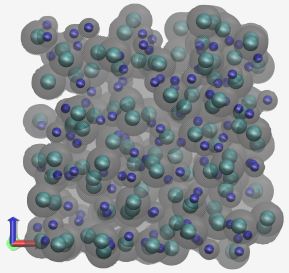
Shell model NaCl in external magnetic field



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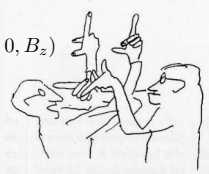
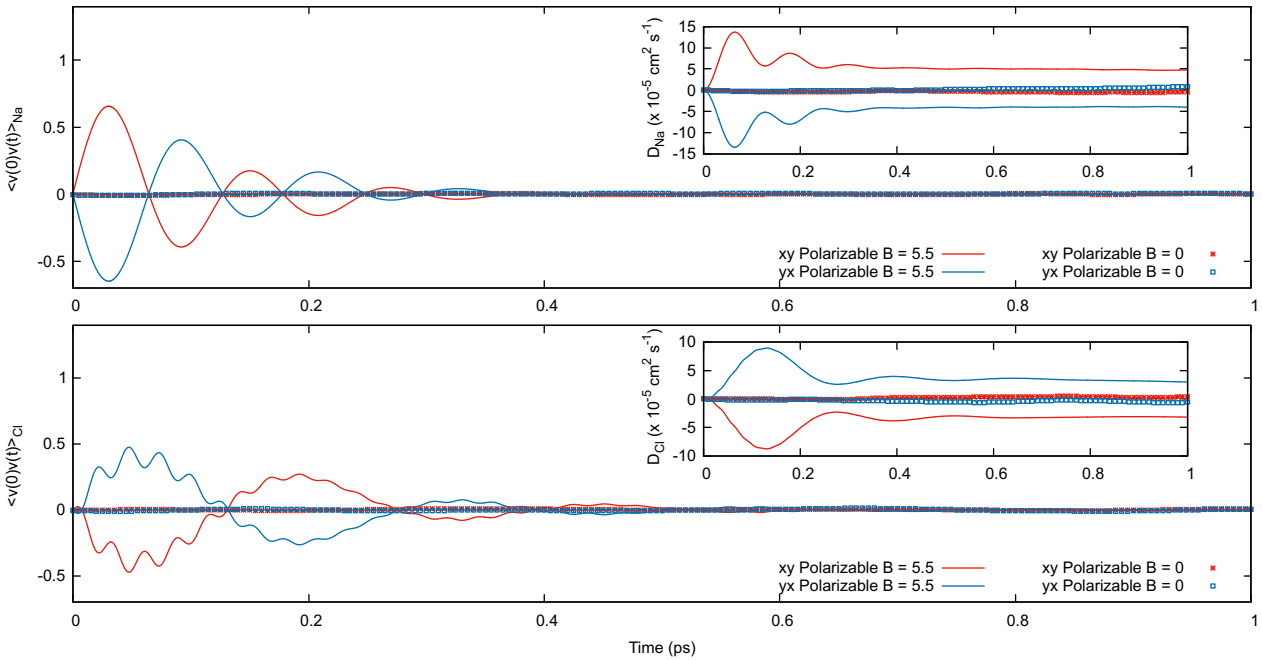
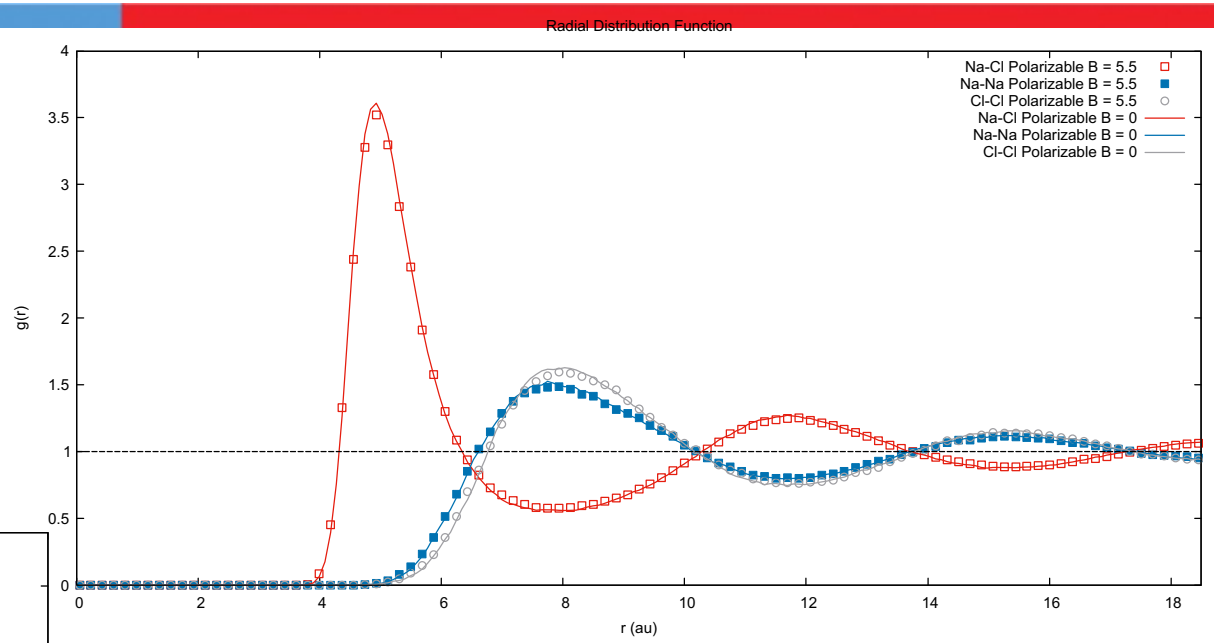


$$m_i \ddot{R}_i^h = -\frac{\partial V(\boldsymbol{R}, \boldsymbol{S})}{\partial R_i^h} + Q_i(\dot{\boldsymbol{R}}_i \times \boldsymbol{B})_h$$

$$\ddot{s}_\alpha^h = -\sum_{\beta=1}^{N} \sum_{l=x,y} \gamma_\beta^l \frac{\partial \sigma_\beta^l}{\partial \dot{s}_\alpha^h} - \sum_{\beta=1}^{N} \gamma_\beta^z \frac{\partial \sigma_\beta^z}{\partial s_\alpha^h}$$





Non-null off-diagonal diffusion in the plane orthogonal to the magnetic field

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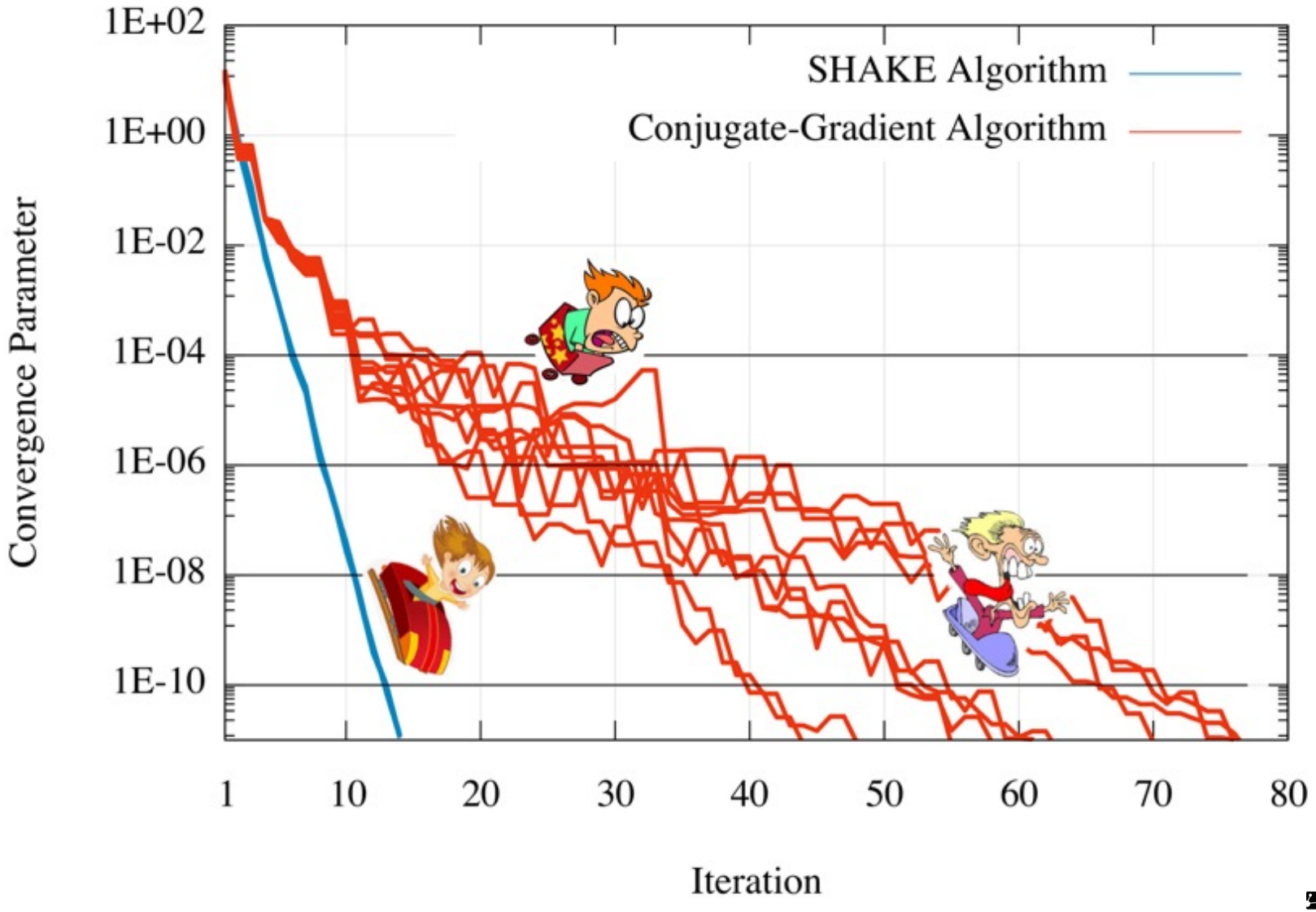
NaCl polarizable force field (no B)



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Back to Calvino

1. **Lightness:** Mass scale separation enables adiabatic approximation MaZe takes the full limit

2. **Quickness:** Method seems faster (more efficient) than alternatives

3. **Exactitude:** Formal properties of the algorithm translate in more stable numerical evolution and efficiency

4. **Visibility:** Papers, code, talks…happy to share!

5. **Multiplicity:** General idea can be applied to different problems
    1. First principles MD
    2. Polarizable models (with or without B)
    3. Solution of the Poisson-Boltzmann equation
    4. …
6. **Consistency ….**

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Visibility

Code

Classical polarizable models Implemented in MetalWalls

OF-DFT implemented in in house code

Implementation of Khon-Sham DFT in Quantum Espresso and SIRIUS on its way

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