Real-space finite difference method for O(N) first-principles molecular dynamics with plane waves accuracy

Jean-Luc Fattebert

Center for Applied Scientific Computing

Lawrence Livermore National Laboratory

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Outline

- O(N) approach for real-space finite differences Density Functional Theory
- Adaptive localization regions
- Accuracy
- Forces
- Molecular Dynamics
- Calculating unoccupied states
- Applications

Ab initio electronic structure calculations

2 main categories of numerical approaches

- Basis set made of atomic orbitals
  - Assume solution of general problem can be well represented in such a basis
  - Usually expended in terms of Gaussians
  - Small number of degrees of freedom/electron
  - Hard to improve accuracy by basis set expansion
- General numerical discretization
  - No a priori assumption on solution
  - Plane Waves, Finite differences, Finite Elements,…
  - No bias
  - Large number of degrees of freedom/electron

O(N) algorithm for Density Functional Theory calculations

- **DFT Energy functional formulated for general non-orthogonal orbitals [Galli and Parrinello, PRL, 1992]**

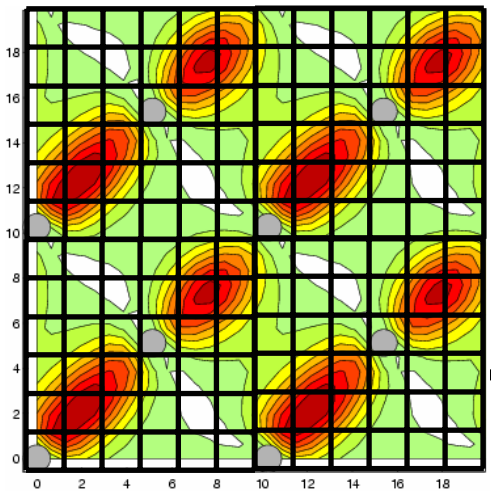
$$E_{KS} = \sum_{i,j=1}^{N} \left(S^{-1}\right)_{ij} \int_{\Omega} \phi_i(r) \Delta \phi_j(r) + F[\rho] + \sum_{i,j=1}^{N} 2\left(S^{-1}\right)_{ij} \int_{\Omega} \phi_i(r) \left(V_{ext} \phi_j\right)(r)$$

- **Real-space discretization on uniform mesh: Mehrstellen (compact) Finite Difference, O(h^4) [Briggs et al., PRB, 1996]**
- **Minimize Energy functional under localization constraints for the wave-functions: Iterative block algorithm based on steepest descent directions**
  - **Preconditioning: Multigrid [JLF and Bernholc, PRB (2000)]**
  - **Extrapolation scheme [D.G. Anderson, J. ACM 12 (1965)]**
- **Choose Localization regions large enough so that *truncation error < discretization error***

General method in picture...

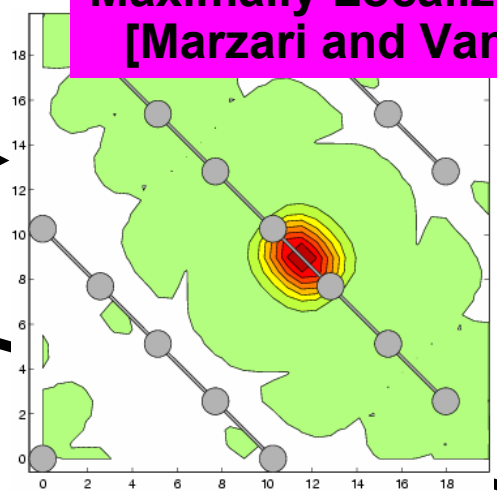
Example: silicon bulk, 64 atoms, Γ point, 128 occupied orbitals

Contour plots in 2D slice (atoms projections in grey)

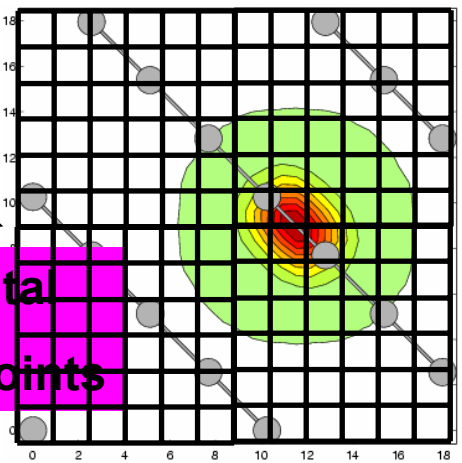


One eigenfunction

Maximally Localized Wannier function
[Marzari and Vanderbilt, PRB (1997]



$$\phi_i = \sum_{j=1}^{N} c_{ij}\psi_j$$

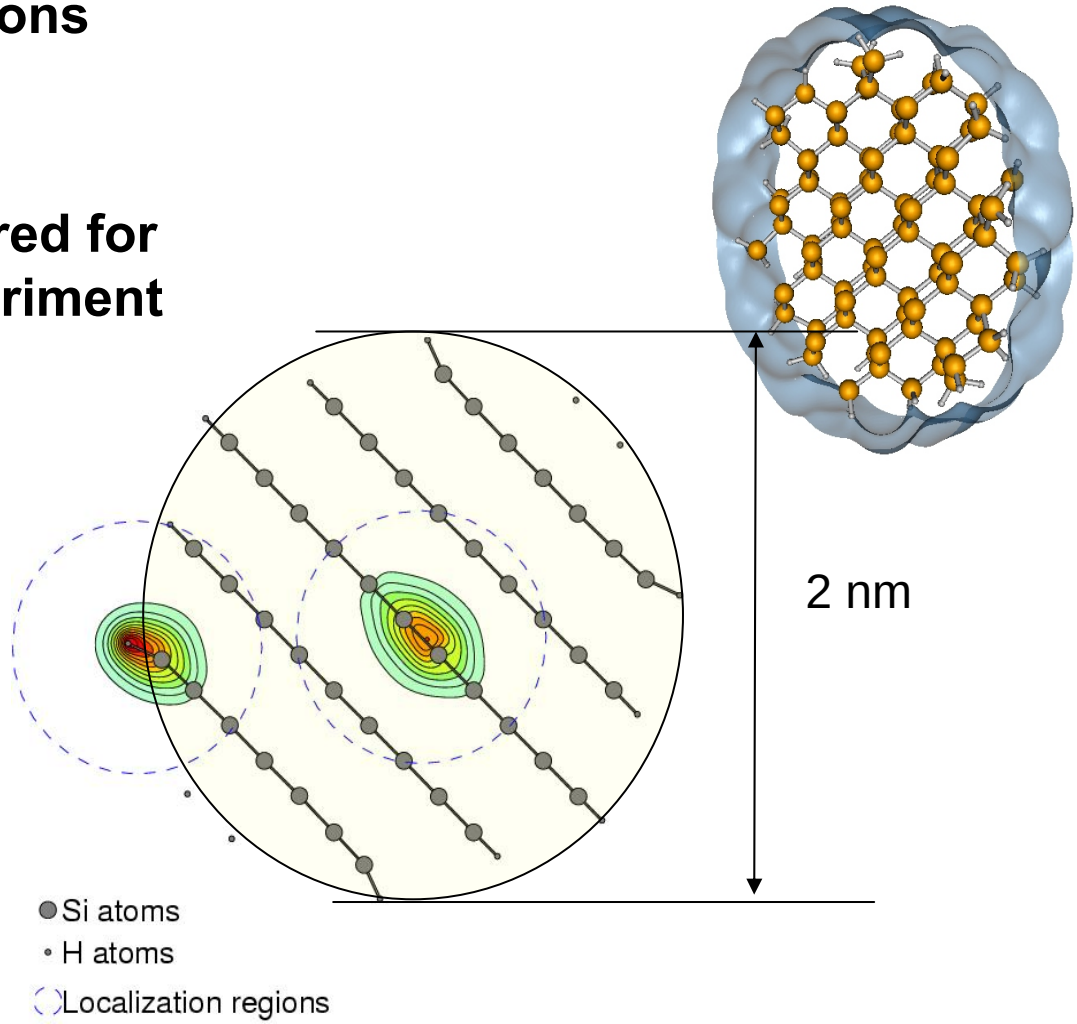


Strictly localized orbital

Non-zero at O(1) grid points

Application: Silicon nanowires

- **Plane Waves calculations “possible” up to 3 nm diameter only**
- **Larger diameter required for comparison with experiment**

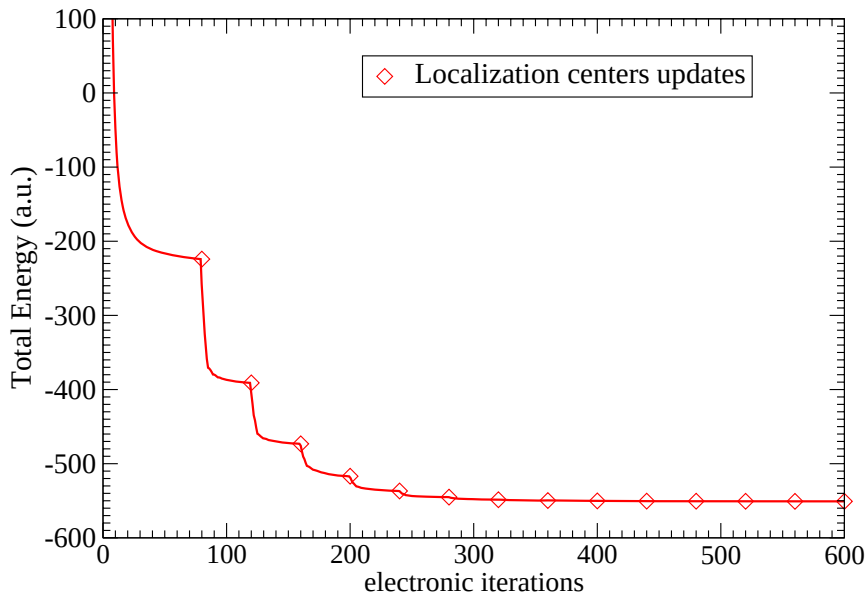


Adaptive Localization regions

- How to define localization regions?
  - Usual approach: a few orbitals centered on each atom
- Adaptive Localization Centers (ALC) to enhance accuracy and enable energy conserving microcanonical Molecular Dynamics
  - Localization regions are re-centered at charge center after every MD step
  - References: [JLF & F. Gygi, CPC 162 (2004), PRB (2006)]
- Adapting Localization Region sizes to get accurate unoccupied/partially occupied states

ALC algorithm convergence

- **Disordered Deuterium, 992 atoms**
- **Start with LR centered on atoms**
- **Recenter Localization regions at charge center every 40 steps**



Born-Oppenheimer molecular dynamics with ALC

- Evaluate center of charge of each localized orbital

$$Q_i^{(k-1)} =< \phi_i^{(k-1)} | X | \phi_i^{(k-1)} >,\ i = 1, \ldots, N$$

- Define localization centers $Q_i^{(k)}$ by extrapolation from 2 previous steps:

$$Q_i^{(k)} = 2Q_i^{(k-1)} - Q_i^{(k-2)},\ i = 1, \ldots, N$$

- Initialize trial orbitals by extrapolation from 2 previous steps:

$$\phi_i^{(k)} = 2\phi_i^{(k-1)} - \phi_i^{(k-2)},\ i = 1, \ldots, N$$

- Optimize localized non-orthogonal orbital for LR centered at $Q_i^{(k)}$, i=1,…,N until convergence criterion satisfied
- Move atoms according to Verlet scheme:

$$R_I^{(k+1)} = 2R_I^{(k)} - R_I^{(k-1)} + F_I^{(k)}(\triangle t)^2/M_I$$

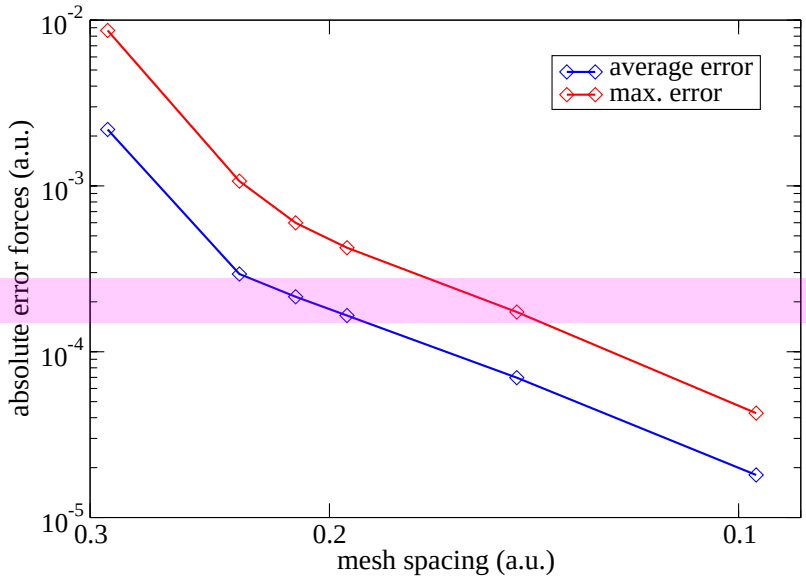
Forces computation

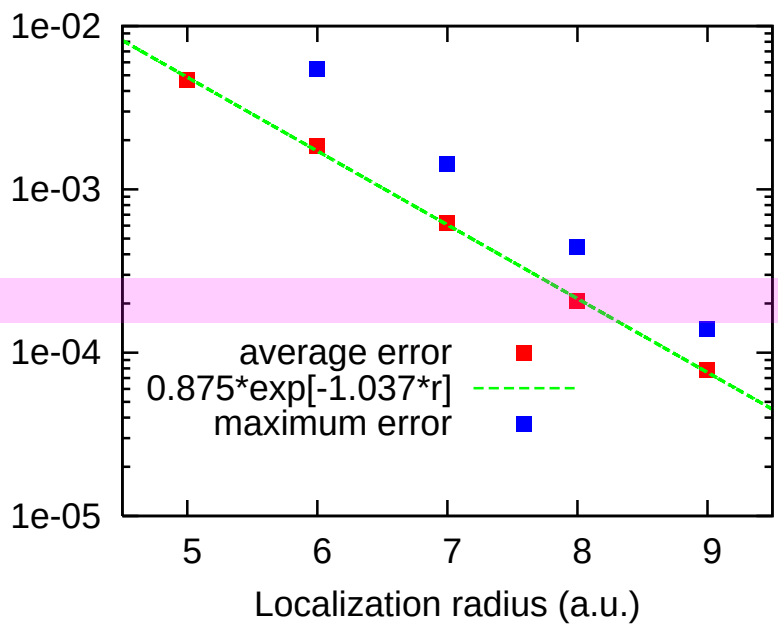
$$\frac{dE}{dR_{k,\alpha}} = \frac{\partial E}{\partial R_{k,\alpha}} + \sum_{j=1}^{N} \frac{\delta E}{\delta \phi_j} \frac{d\phi_j}{dR_{k,\alpha}} + \sum_{k=1}^{N} \sum_{\beta=1}^{3} \frac{\delta E}{\delta Q_{k,\beta}} \frac{dQ_{k,\beta}}{dR_{k,\alpha}}$$

- **1st term: Same algorithm used for O(N³) calculations**
  - **Compute energy for small virtual displacements (with frozen electronic wave functions)**
  - **Compute forces (derivatives) by Finite Differences**
- **2nd term: vanishes for Rc→∞. Neglected and included in error**
- **3rd term: "Pulay-like", Q_k=localization center, not very sensitive to position: very flat energy surface. Neglected and included in error.**

Discretization vs. truncation (localization)

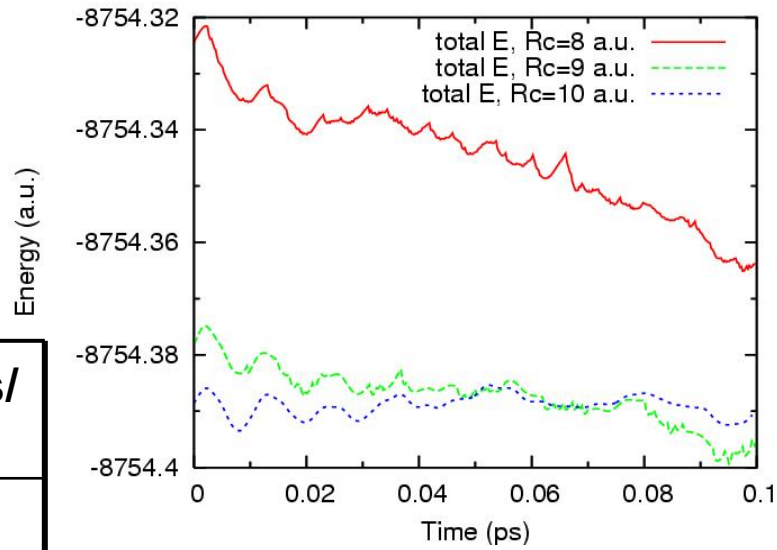
- **Liquid water sample, 54 molecules**





Molecular dynamics: liquid water, 512 molecules

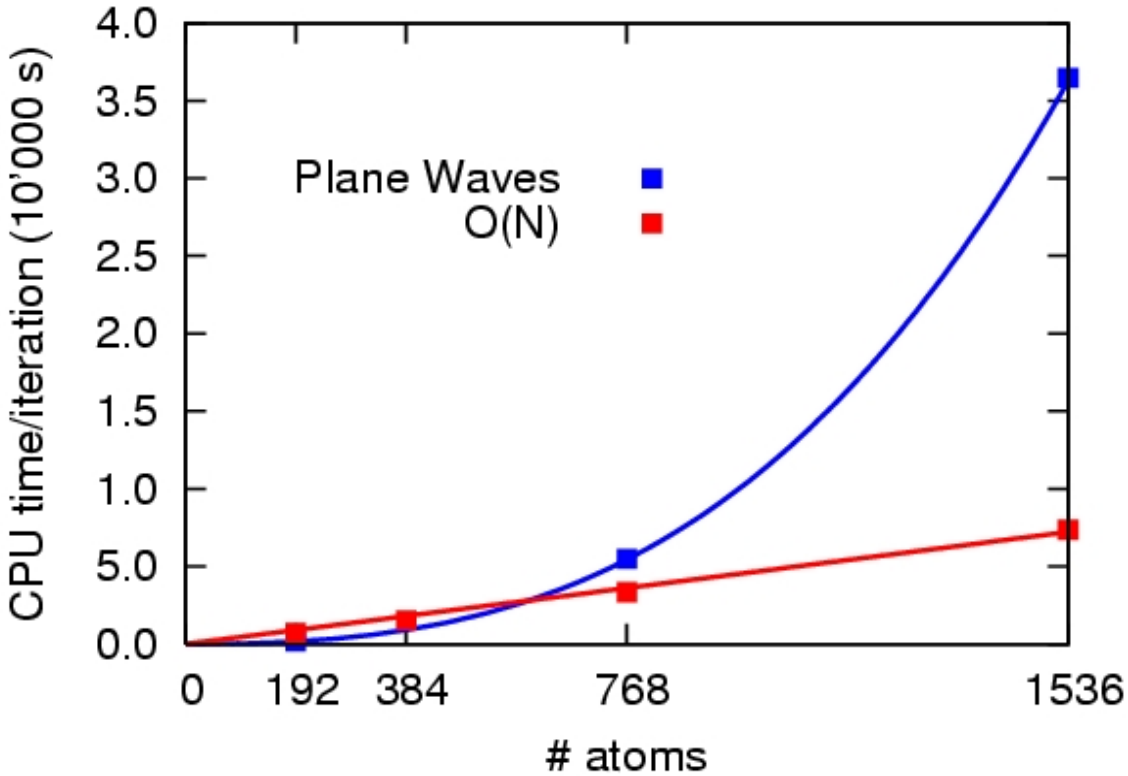
- Adaptive localization regions follow the dynamics: adapt localization center at each MD step
- Energy conservation is critical to avoid any bias due to numerical approximation



LR radius (Bohr)	Energy drift (K/ps)	# SC iterations/ MD step
8	-47	29
9	-22	23
10	-1<…<1	14

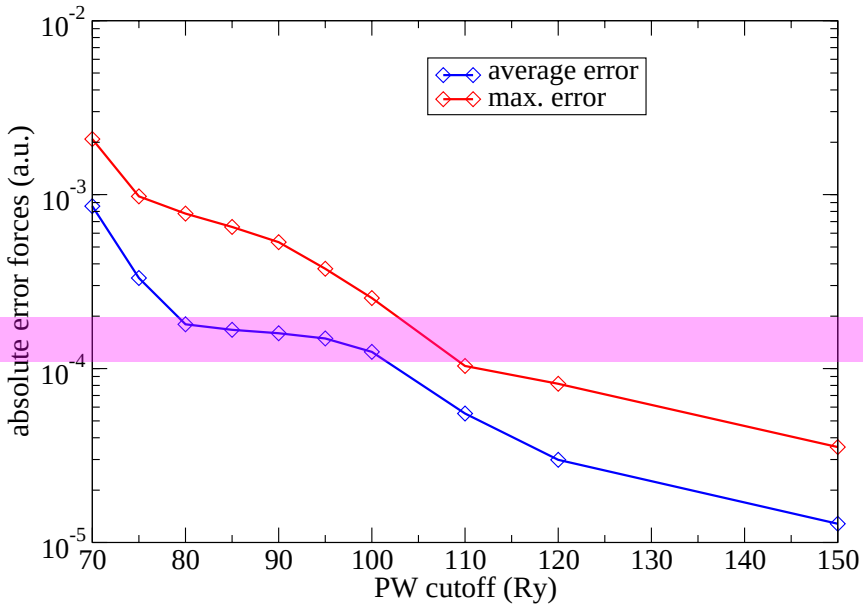
Effective linear scaling

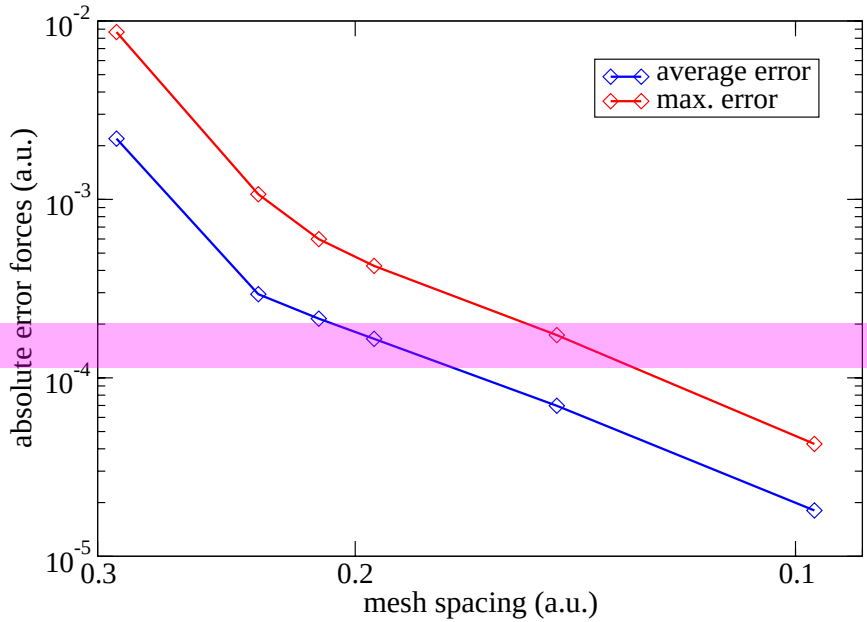
- O(N) scaling, liquid H_2O
- Equivalent accuracy!



JLF & F. Gygi, Phys Rev B (2006)

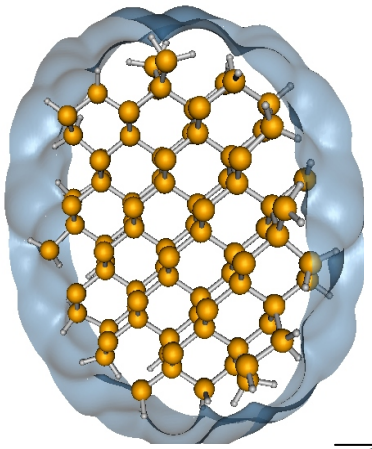
Equivalent cutoff for Finite Difference

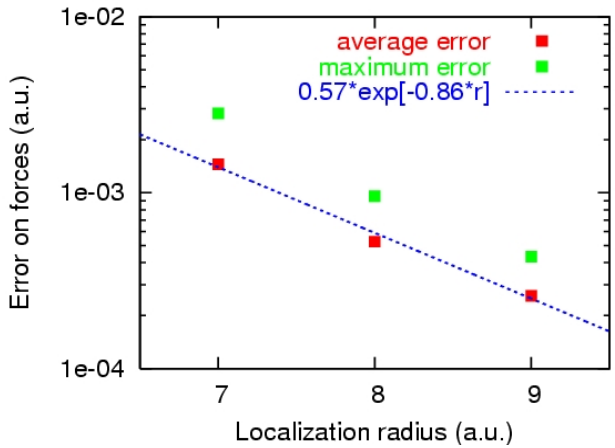




→ **80 Ry ~ h=0.2 Bohr**

Application: Silicon nanowires



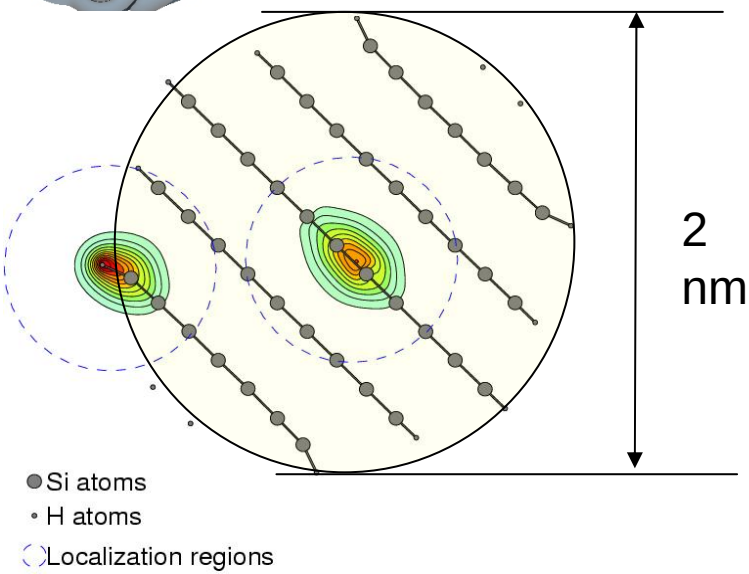


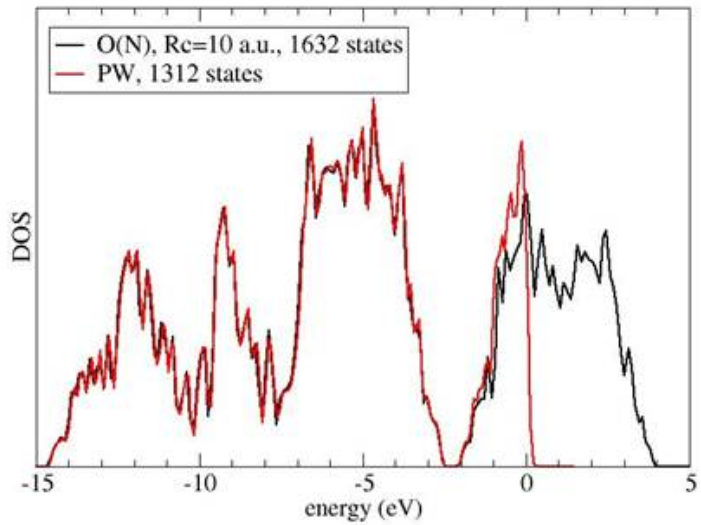
520 Si + 144 H

localization radius 10 a.u.

510 empty states

Comparison with Plane Waves



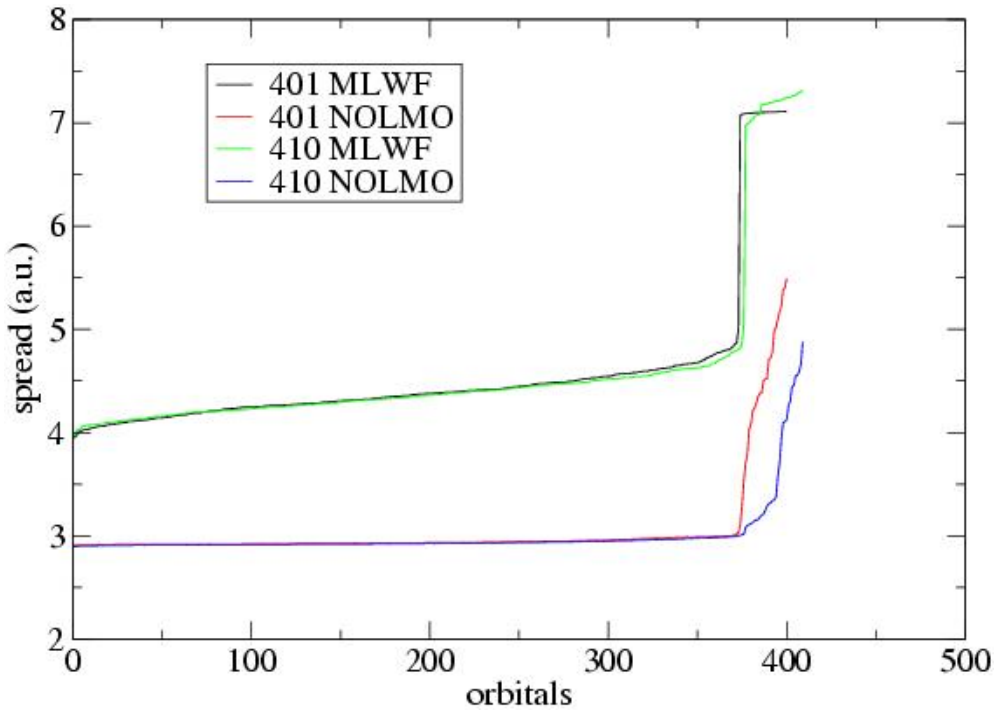


O(N) successes

- O(N) works well when the system has a relatively large band gap
- A nice and well defined electronic structure representation in terms of Maximally Localized Wannier functions is available — We have a one-to-one mapping between Localization Regions and Maximally Localized Wannier functions
- Unoccupied Orbitals sometimes added to avoid local minimas or enhance accuracy (more degrees of freedom!)

Computing unoccupied states accurately

- Sometimes we need information about unoccupied or partially occupied states
  - metals…
- They are likely to be less localized then the MLWF associated to covalent bonds

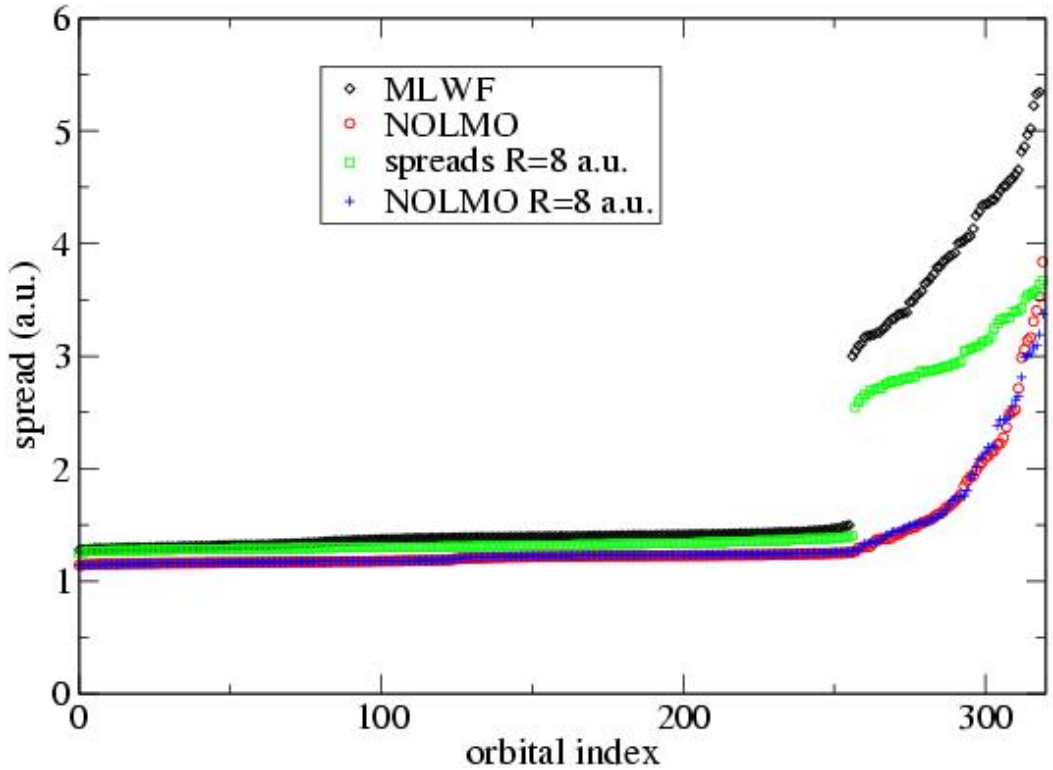


Al256, Γ-point

MLWF: Maximally Localized Wannier Functions

NOLMO: Non-Orthogonal Localized Molecular Orbitals

Orbitals Spreads: $(H_2O)_{64}$



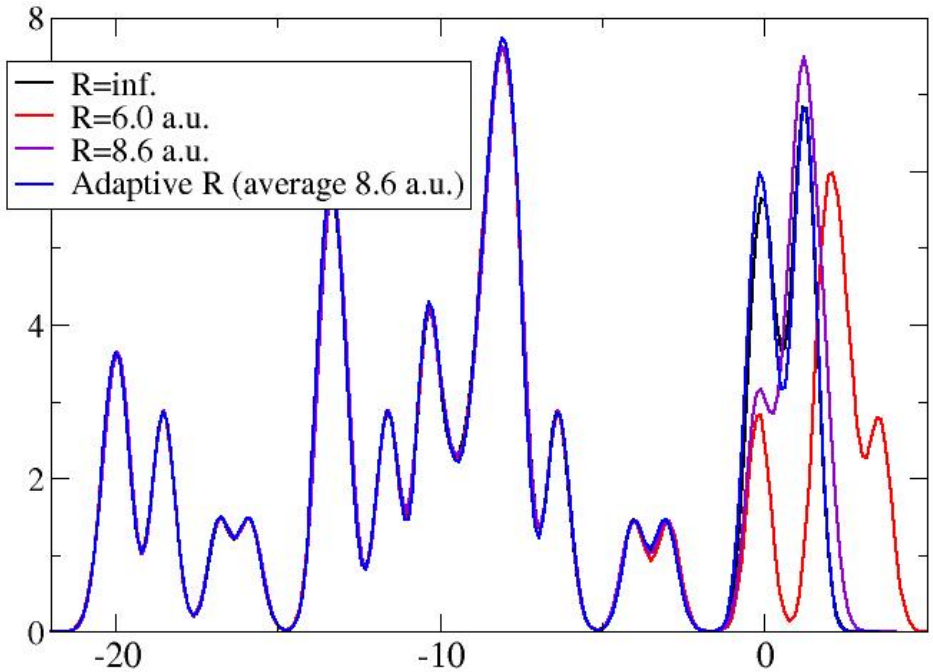
Algorithm for fully adaptive Localization Regions

- Start with a uniform localization radius
- Run a few iterations to get a reasonable ground state
- Evaluate individual spreads

$$\left\langle \phi_i \left| \left(X - \left\langle \phi_i \left| X \right| \phi_i \right\rangle \right)^2 \right| \phi_i \right\rangle^{1/2}$$

- Rescale localization region radii s.t.
  - The radius of each region is proportional to the spread of each orbital
  - The total volume of all the localization regions is a fixed value V_0
  - We use the spreads of the Nonorthogonal Localized orbitals — linear combination of non-orthogonal orbitals that minimizes the total spread without orthogonality or localization constraint — to define V_0

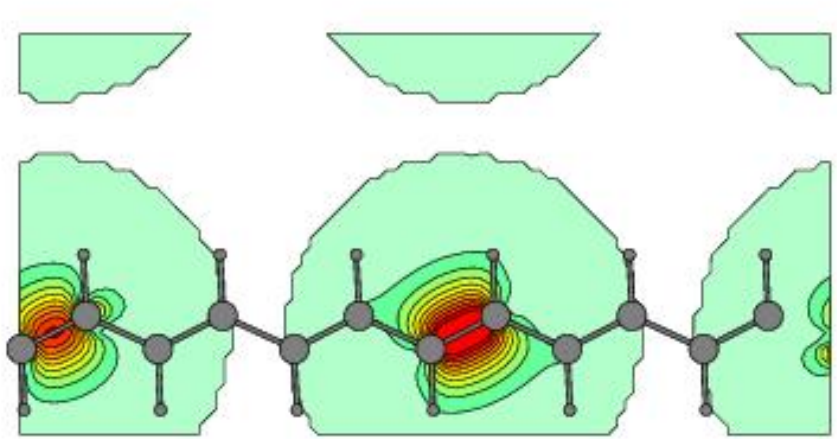
Density of States: example of polyacethylene



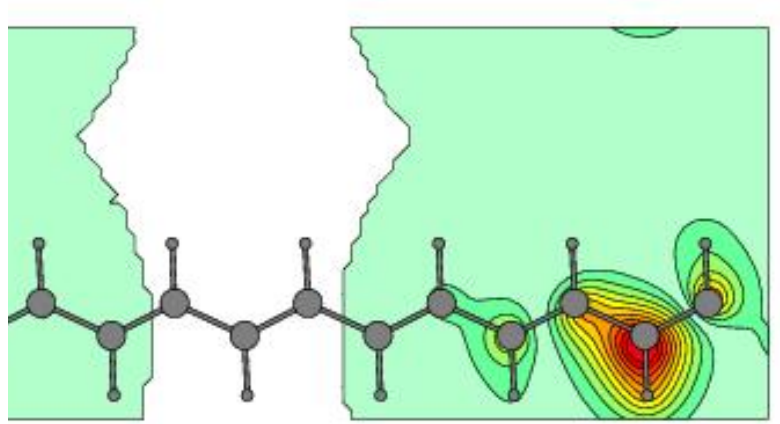
$C_{12}H_{12}$: 30 occupied states + 12 unoccupied states

Localized orbitals

2 localized orbitals with radius 6 a.u.



1 orbital with radius 10.6 a.u.



Concluding remarks

- **Finite Difference approach provides appropriate framework to achieve Plane waves accuracy and linear scaling using localized orbitals**
- **Flexible adaptive localization regions enables**
  - **Higher accuracy**
  - **Molecular dynamics**
  - **Calculation of excited states**

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