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

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UCRL-PRES-233150
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]

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

- 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)

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

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

One eigenfunction
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
  \[ Q_i^{(k-1)} = \langle \phi_i^{(k-1)} | X | \phi_i^{(k-1)} \rangle, \quad i = 1, \ldots, N \]

- Define localization centers \( Q_i^{(k)} \) by extrapolation from 2 previous steps:
  \[ Q_i^{(k)} = 2Q_i^{(k-1)} - Q_i^{(k-2)}, \quad i = 1, \ldots, N \]

- Initialize trial orbitals by extrapolation from 2 previous steps:
  \[ \phi_i^{(k)} = 2\phi_i^{(k-1)} - \phi_i^{(k-2)}, \quad i = 1, \ldots, N \]

- Optimize localized non-orthogonal orbital for LR centered at \( Q_i^{(k)} \), \( i=1,\ldots,N \) until convergence criterion satisfied

- Move atoms according to Verlet scheme:
  \[ R_I^{(k+1)} = 2R_I^{(k)} - R_I^{(k-1)} + F_I^{(k)}(\Delta t)^2/M_I \]
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 \(O(N^3)\) calculations
  - Compute energy for small virtual displacements (with frozen electronic wave functions)
  - Compute forces (derivatives) by Finite Differences

- **2nd term:** vanishes for \(R_c \to \infty\). 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

<table>
<thead>
<tr>
<th>LR radius (Bohr)</th>
<th>Energy drift (K/ps)</th>
<th># SC iterations/MD step</th>
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<tr>
<td>8</td>
<td>-47</td>
<td>29</td>
</tr>
<tr>
<td>9</td>
<td>-22</td>
<td>23</td>
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<tr>
<td>10</td>
<td>-1&lt;…&lt;1</td>
<td>14</td>
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</tbody>
</table>
Effective linear scaling

- O(N) scaling, liquid H₂O
- Equivalent accuracy!

Equivalent cutoff for Finite Difference

\[ \rightarrow \quad 80 \text{ Ry} \sim h=0.2 \text{ Bohr} \]
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 than the MLWF associated to covalent bonds

MLWF: Maximally Localized Wannier Functions
NOLMO: Non-Orthogonal Localized Molecular Orbitals

Al256, Γ-point
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
  \[ \langle \phi_i \mid (X - \langle \phi_i \mid X \mid \phi_i \rangle)^2 \mid \phi_i \rangle^{1/2} \]
- 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 polyacetylene

$C_{12}H_{12}$: 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

**Current Funding:** Department of Energy, SciDAC

Work performed under the auspices of the U. S. Department of Energy by University of California Lawrence Livermore National Laboratory under Contract W-7405-Eng-48