Large-scale real-space electronic structure calculations

Vikram Gavini

Department of Mechanical Engineering

University of Michigan, Ann Arbor

Collaborators: Phani Motamarri (U. Mich); Bikash Kanungo (U. Mich)

Funding: TRI, ARO, NSF, DoE-BES, XSEDE
Defective Crystals

- Defects play a crucial role in influencing a variety of materials properties – mechanical, electronic, optical, chemical

- Dislocations
  - Metal Plasticity – Renders the strength of materials to 1/1000 its theoretical strength

- Vacancies/Interstitials
  - Creep, Spall, Ageing, hardening due to radiation

- Interfaces/Surfaces
  - Phase stability, Energetics, Diffusion mediation, defect sources and sinks

TEM image of dislocation partial
T.J. Balk, K.J. Hemker, Phil. Mag. A, 2001

Prismatic loops formed from vacancies,
Giess et. al, Microsc Microanal, 2005

TEM image of Ni-Al interface,
Defective crystals: The challenge

- The energetics of defects: (i) core-energy; (ii) elastic energy
- The core of a defect is governed by electronic structure – need electronic structure calculations!
- Defects result in a vast span of interacting length scales
  - Electronic structure of the core (10^{-12} m)
  - Complex rearrangements of atoms around the core (10^{-9} m)
  - Long ranged elastic effects (10^{-6} m)

Realistic defect concentration in materials is parts per million!

- Challenge: Need electronic structure calculations at macroscopic scales!
  - (i) Development of computational techniques for large-scale electronic structure calculation that can explicitly treat systems up to 10,000 atoms
  - (ii) Development of seamless coarse-graining schemes using adaptive numerical schemes

But need single physics at all length scales! - No patching, seamless description
Quantum Mechanics

- Schrödinger equation - \[ H\psi = E\psi \]

\[
H = -\frac{1}{2} \sum_{i=1}^{N} \nabla_i^2 - \frac{1}{2} \sum_{A=1}^{M} \frac{1}{M_A} \nabla_A^2 - \sum_{i=1}^{N} \sum_{A=1}^{M} \frac{Z_A}{|r_i - R_A|} \\
+ \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{1}{|r_i - r_j|} + \sum_{A=1}^{M} \sum_{B=1, B>A}^{M} \frac{Z_A Z_B}{|R_A - R_B|}
\]

\[ \psi = \psi(x_1, x_2, \ldots, x_N, R_1, R_2, \ldots, R_M) \]

- Born-Oppenheimer approximation - Classical treatment of atomic nuclei

\[ \psi = \psi(x_1, x_2, \ldots, x_N) \]

- Computational complexity - \[ \psi \in \mathbb{R}^{3N} \] !!
Density-functional theory – Kohn-Sham approach

- Ground-state energy is a function of electron-density !! (Kohn & Sham, 1964-65)

\[ \langle \psi | H | \psi \rangle \geq E_0 \quad \text{(Variational statement)} \]

\[
E_0 = \min_\psi \{ \langle \psi | T + \frac{1}{2} \sum_i \sum_j' \frac{1}{|r_i - r_j|} + V_{\text{ext}}(r_i) | \psi \rangle + E_{zz} \} 
= \min_\psi \{ \langle \psi | T + \frac{1}{2} \sum_i \sum_j' \frac{1}{|r_i - r_j|} | \psi \rangle + \int \rho(r) V_{\text{ext}}(r) \, dr + E_{zz} \}
= \min_\rho \left\{ \left( \min_{\psi \to \rho} \{ \langle \psi | T + \frac{1}{2} \sum_i \sum_j' \frac{1}{|r_i - r_j|} | \psi \rangle \} + \int \rho(r) V_{\text{ext}}(r) \, dr \right) + E_{zz} \right\}
= F(\rho)
\]

\[ F(\rho) = T_s(\rho) + E_H(\rho) + E_{xc}(\rho) \quad \text{Exchange-correlation functional: Model using LDA, GGA} \]

Kinetic energy of non-interacting electrons:
Computed from wave-functions of the resulting E-L eqn.
Kohn-Sham density-functional theory (KSDFT)

- The KSDFT energy functional is given by,

$$E(\Psi, \mathbf{R}) = T_s(\Psi) + E_{xc}(\rho) + E_H(\rho) + E_{ext}(\rho, \mathbf{R}) + E_{Z\!Z}(\mathbf{R})$$

where

$$\Psi = \{\psi_1(\mathbf{r}), \psi_2(\mathbf{r}), \ldots, \psi_N(\mathbf{r})\}$$

$$\rho(\mathbf{r}) = \sum_i |\psi_i(\mathbf{r})|^2$$

$$T_s(\Psi) = \sum_i \frac{1}{2} \int |\nabla \psi_i(\mathbf{r})|^2 d\mathbf{r}$$

$$E_{xc}(\rho) = \int \epsilon_{xc}(\rho(\mathbf{r})) \rho(\mathbf{r}) d\mathbf{r}; \quad \text{Local density approximation (LDA)}$$

$$E_H(\rho) = \frac{1}{2} \int \int \frac{\rho(\mathbf{r}) \rho(\mathbf{r'})}{|\mathbf{r} - \mathbf{r'}|} d\mathbf{r} d\mathbf{r'};$$

$$E_{ext}(\rho, \mathbf{R}) = \int \rho(\mathbf{r}) V_{ext}(\mathbf{r}) d\mathbf{r}$$

$$= \sum_{I=1}^{M} \int \rho(\mathbf{r}) \frac{Z_I}{|\mathbf{r} - \mathbf{R}_I|} d\mathbf{r}$$

$$E_{Z\!Z}(\mathbf{R}) = \frac{1}{2} \sum_{I=1}^{M} \sum_{J=1, J \neq I}^{M} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|};$$

Classical electrostatic interaction energy:

Computed in Fourier-space (reciprocal-space) in almost all DFT implementations.
Electrostatic interactions can be re-written locally as,

\[ E_H(\rho) = \frac{1}{2} \int \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'; \]

\[ E_{ext}(\rho, \mathbf{R}) = \sum_{I=1}^{M} \int \int \frac{\rho(\mathbf{r})Z_I}{|\mathbf{r} - \mathbf{R}_I|} d\mathbf{r}; \]

\[ E_{zz}(\mathbf{R}) = \frac{1}{2} \sum_{I=1}^{M} \sum_{J=1, J \neq I}^{M} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|}; \]

- Electrostatic interactions can be re-written locally as,

\[ E_H(\rho) + E_{ext}(\rho, \mathbf{R}) + E_{zz}(\mathbf{R}) = \]

\[ - \inf_{\phi \in H^1(\mathbb{R}^3)} \left\{ \frac{1}{8\pi} \int |\nabla \phi(\mathbf{r})|^2 d\mathbf{r} - \int (\rho(\mathbf{r}) + b(\mathbf{r}; \mathbf{R})) \phi(\mathbf{r}) d\mathbf{r} \right\} \]

- Thus,

\[ E(\Psi, \mathbf{R}) = \sup_{\phi \in H^1(\mathbb{R}^3)} L(\Psi, \mathbf{R}, \phi) \]

(Regularized nuclear charges)

\[ L(\Psi, \mathbf{R}, \phi) = \sum_i \frac{1}{2} \int |\nabla \psi_i(\mathbf{r})|^2 d\mathbf{r} + \int \epsilon_{xc}(\rho(\mathbf{r})) \rho(\mathbf{r}) d\mathbf{r} \]

\[ - \frac{1}{8\pi} \int |\nabla \phi(\mathbf{r})|^2 d\mathbf{r} + \int (\rho(\mathbf{r}) + b(\mathbf{r})) \phi(\mathbf{r}) d\mathbf{r} \]
The saddle-point problem is given by,

\[
\inf_{\mathbf{R} \in \mathbb{R}^{3M}} \inf_{\Psi \in X} \sup_{\phi \in H^1(\mathbb{R}^3)} L(\Psi, \mathbf{R}, \phi)
\]

\[
L(\Psi, \mathbf{R}, \phi) = \sum_i \frac{1}{2} \int |\nabla \psi_i(\mathbf{r})|^2 d\mathbf{r} + \int \epsilon_{xc}(\rho(\mathbf{r}))\rho(\mathbf{r}) d\mathbf{r} - \frac{1}{8\pi} \int |\nabla \phi(\mathbf{r})|^2 d\mathbf{r} + \int (\rho(\mathbf{r}) + b(\mathbf{r}))\phi(\mathbf{r}) d\mathbf{r}
\]

- Define, \( X = \{ \Psi | \Psi \in (H^1_0(\Omega))^N, \langle \psi_i, \psi_j \rangle = \delta_{ij} \} \)

- Theorem: \( E(\Psi) \) has a minimum in \( X \).

Proof: Sobolev embeddings; Poincaré inequality \( \) (Direct Method)
Consider the E-L equation corresponding to the variational problem:

\[
\left(-\frac{1}{2} \nabla^2 + V_{\text{eff}}\right) \psi_i = \epsilon_i \psi_i
\]

\[
\rho = \sum_i f_i |\psi_i|^2, \quad V_{\text{eff}}(r) = V_H(\rho(r)) + V_{xc}(\rho(r)) + V_{\text{ext}}(R)
\]

\[
T_s(\Psi) = \frac{1}{2} \sum_i f_i \int |\nabla \psi_i(r)|^2 dr \quad E_0(\Psi) = T_s(\Psi) + E_{xc}(\rho) + E_H(\rho) + E_{\text{ext}}(\rho) + E_{zz}
\]

To avoid charge-sloshing:

\[
f_i = f(\varepsilon_i, \mu) = \frac{1}{1 + e^{(\varepsilon_i - \mu) k_B T}} \sum_i f_i = N
\]
State of the art

Solutions to Kohn-Sham Equations

Fourier Space Formulations

Real Space Formulations (LCAO, FDM, FEM)

Key Features (plane-waves)
- Very efficient for periodic calculations
- Restrictive to periodic domains
- Provide only uniform spatial resolution
- Suitable only when the solution fields are smooth.

Key Features (LCAO)
- Suitable for isolated systems
- Can handle both pseudopotential and all electron calculations
- Systematic convergence can not be ascertained
- Parallel scalability is a concern

WCPM/CSC, U. Warwick, 2018
Use finite-element basis for computing –

\[ \psi_k^h(r) = \sum_i \psi_{ki} N_i(r) \quad k = 1, \ldots, N, \quad \phi^h(r) = \sum_i \phi_i N_i(r) \]

\( \psi_{ki}, \phi_i \ldots \) – Nodal values
\( N_i(r) \) – Shape functions

Features of finite-element basis:

1. Unstructured coarse-graining
2. Complex geometries can be represented, and arbitrary boundary conditions can be imposed.
3. Systematic convergence
4. Ease of parallel implementation

By changing the positioning of the nodes the spatial resolution of basis can be changed/adapted
KSDFT – FE discretization

Main Limitations:

- Previous attempts showed that the number of FE basis functions (linear) needed to obtain chemical accuracy is very large ~ 100,000-1,000,000 basis functions per atom.

- The finite-element discretization leads to a generalized eigenvalue problem, which is more challenging to solve than a standard eigenvalue problem.

Present Work:

- We demonstrate an efficient, scalable computational approach using adaptive higher-order finite-element discretization.

- We propose a linear scaling algorithm (in number of electrons) which treats both insulating and metallic systems on an equal footing.
KSDFT – FE discretization

- Discrete eigenvalue problem:
  \[ H\hat{\psi}_k = \varepsilon_k^h M\hat{\psi}_k \]

  \[ H_{ij} = \frac{1}{2} \int_{\Omega} \nabla N_i(r) \cdot \nabla N_j(r) \, dr + \int_{\Omega} V_{eff}(r, R) N_i(r) N_j(r) \, dr \]

  \[ M_{ij} = \int_{\Omega} N_i(r) N_j(r) \, dr \]

- Transformation to a standard eigenvalue problem:
  \[ \tilde{H}\tilde{\psi}_k = \varepsilon_k^h \tilde{\psi}_k \quad \text{where} \quad \tilde{H} = M^{-1/2}HM^{-1/2} \quad \text{and} \quad \tilde{\psi}_k = M^{1/2}\hat{\psi}_k \]

- Remark: \( \tilde{H} \) denotes the projection of the Hamiltonian operator into a space spanned by Löwden orthonormalized finite-element basis
Can higher-order finite-elements do any better?

Here, we investigate the viability and computational efficiency afforded by higher-order finite-element discretization in electronic structure calculations using density functional theory to answer the following questions:

- What is the numerical convergence rate for various orders of finite-element approximations in electronic structure calculations using DFT?

- What is the computational advantage derived by using higher-order finite element discretization in terms of the CPU time?

First studies which demonstrate the computational efficiency afforded by higher-order elements for Kohn-Sham DFT calculations.
The study has been carried out by a suite of higher order elements:

- **TET 10** (TETRAHEDRAL QUADRATIC ELEMENT)
- **HEX 27** (TRI QUADRATIC HEXAHEDRAL ELEMENT)
- **HEX 64** (TRI CUBIC HEXAHEDRAL ELEMENT)
- **HEX 125** (TRI QUARTIC HEXAHEDRAL ELEMENT)
- **HEX 64 SPECTRAL**, **HEX 125 SPECTRAL** … upto 10th order
  (Lagrange Polynomials are constructed on Gauss-Lobatto Legendre Points for spectral elements)

Elements have been tested against three types of problems: (a) CH₄ (b) Barium Cluster (35 atoms)

(a) CH₄ : An all electron calculation
(b) Barium Cluster: Pseudopotential calculation
Convergence rates

Optimal rate of convergence!
Computational efficiency of higher-order FE discretization

Two Key questions:

- How do higher-order FE discretizations compare to lower order elements in computational efficiency?
- How do higher-order FE discretizations compare against plane-wave basis and Gaussian basis?

Key ideas in improving computational efficiency:

- Developed a priori mesh adaption techniques
- Use of Gauss-Legendre-Lobatto quadrature rules for the overlap matrix in conjunction with Spectral FE discretization
- Developed a Chebyschev acceleration technique to directly compute the eigenspace
Error Estimate:

\[ |E - E_h| \leq C \left( \sum_i ||\psi_i - \psi^h_i||_{1,\Omega}^2 + ||\phi - \phi^h||_{1,\Omega}^2 + \sum_i ||\psi_i - \psi^h_i||_{0,\Omega}||\phi - \phi^h||_{1,\Omega} \right) \]

\[ |E - E_h| \leq C \sum_{e=1}^{N_e} \int_{\Omega_e} \left( h_e^{2k} \left[ \sum_i |D^{k+1} \psi_i(r)|^2 + |D^{k+1} \phi(r)|^2 \right] dr \right) \]

\leq C' \int_{\Omega} \left( h^{2k}(r) \left[ \sum_i |D^{k+1} \psi_i(r)|^2 + |D^{k+1} \phi(r)|^2 \right] dr \right) \]

Optimal mesh distribution:

\[ \min_h |E - E_h| \quad \text{subject to:} \quad \int_{\Omega} \frac{dr}{h^3(r)} = N_e \]
Spectral FE and Gauss-Lobatto-Legendre quadrature

**Spectral-element basis functions:**

- Constructed from Lagrange polynomials interpolated through nodes corresponding to the roots of the derivatives of the Legendre polynomials and boundary nodes (GLL points)
- Upon using a Gauss-Lobatto-Legendre quadrature rule, the quadrature points coincide with the FE nodes

\[ M_{ij} = \int_{\Omega_e} N_i(r) N_j(r) dr = C_i \delta_{ij} \]

**Remarks:**

- Transformation to standard eigenvalue problem is trivial
- The reduced order quadrature rule is only employed for the computation of the overlap matrix, and the full Gauss quadrature is employed to compute the Hamiltonian matrix.
Eigen-space computation: Chebyshev acceleration

\[ \bar{H} = c_1 \tilde{H} + c_2 \]
### Eigen-space computation: Chebyshev acceleration

#### Table 1: Comparison of Generalized vs Standard eigenvalue problems.

<table>
<thead>
<tr>
<th>Element Type</th>
<th>DOFs</th>
<th>Problem Type</th>
<th>$N$</th>
<th>Time (GHEP)</th>
<th>Time (SHEP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HEX125SPECT</td>
<td>1,368,801</td>
<td>graphene</td>
<td>96</td>
<td>1786 CPU-hrs</td>
<td>150 CPU-hrs</td>
</tr>
<tr>
<td>HEX343SPECT</td>
<td>2,808,385</td>
<td>Al 3 × 3 × 3 cluster</td>
<td>516</td>
<td>2084 CPU-hrs</td>
<td>80 CPU-hrs</td>
</tr>
</tbody>
</table>

#### Table 2: Comparison of Standard eigenvalue problem vs Chebyshev filtered subspace iteration (ChFSI).

<table>
<thead>
<tr>
<th>Element Type</th>
<th>DOFs</th>
<th>Problem Type</th>
<th>$N$</th>
<th>Time (SHEP)</th>
<th>Time (ChFSI)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HEX125SPECT</td>
<td>1,368,801</td>
<td>graphene</td>
<td>96</td>
<td>150 CPU-hrs</td>
<td>12.5 CPU-hrs</td>
</tr>
<tr>
<td>HEX343SPECT</td>
<td>2,808,385</td>
<td>Al 3 × 3 × 3 cluster</td>
<td>512</td>
<td>80 CPU-hrs</td>
<td>13 CPU-hrs</td>
</tr>
</tbody>
</table>
Numerical algorithm

1. Start with initial guess for electron density \( \rho_{in}^h(\mathbf{r}) = \rho_0(\mathbf{r}) \) and the initial wavefunctions \( \Psi = \{ \tilde{\psi}_1 \ldots \tilde{\psi}_N \} \)

2. Compute the discrete Hamiltonian \( \overline{H} \) using the input electron density \( \rho_{in}^h \)

3. Compute the Chebyshev filtered basis : \( \Phi = T_m(\overline{H})\Psi \)

4. Orthonormalize the basis \( \Phi \) and compute \( \overline{H}^\Phi = \Phi^T\overline{H}\Phi \), the projected Hamiltonian into the subspace spanned by \( \Phi \)

5. Compute the Fermi-energy and the output electron density by diagonalizing projected Hamiltonian and using the following equation

\[
\rho_{out}^h(\mathbf{r}) = \sum_i f(\varepsilon_i, \mu) |\psi_i^h(\mathbf{r})| \quad \text{where} \quad f(\varepsilon_i, \mu) = \frac{1}{1 + e^{(\varepsilon_i - \mu)/k_B T}}
\]

6. If \( \| \rho_{out}^h(\mathbf{r}) - \rho_{in}^h(\mathbf{r}) \| < tol \), EXIT; else, compute new \( \rho_{in}^h \) using a mixing scheme and go to (2).
Computational efficiency

Barium Cluster

![Graph showing computational efficiency for Barium Cluster](image)

Methane Molecule

![Graph showing computational efficiency for Methane Molecule](image)
Aluminum clusters

<table>
<thead>
<tr>
<th>Type of basis set</th>
<th>Energy per atom (eV)</th>
<th>Abs. error (meV/atom)</th>
<th>CPU Hrs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plane-waves (20 Ha; 60 a.u.; 461, 165 basis)</td>
<td>-56.69289</td>
<td>3.8</td>
<td>910</td>
</tr>
<tr>
<td>FE basis (5th order; 1, 107, 471 nodes)</td>
<td>-56.69497</td>
<td>2.0</td>
<td>147</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Type of basis set</th>
<th>Energy per atom (eV)</th>
<th>Abs. error (meV/atom)</th>
<th>CPU Hrs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plane-waves (20 Ha; 80 a.u.; 1, 093, 421 basis)</td>
<td>-56.87392</td>
<td>4.3</td>
<td>8640</td>
</tr>
<tr>
<td>FE basis (5th order; 4, 363, 621 nodes)</td>
<td>-56.87652</td>
<td>2.1</td>
<td>1132</td>
</tr>
</tbody>
</table>
Scalability

![Graph showing scalability](image)

- Ideal Speedup
- Observed Speedup

Relative Speedup vs. Number of Processors
All-electron calculations

100 atom Graphene sheet

<table>
<thead>
<tr>
<th>Type of basis set</th>
<th>Relative error</th>
<th>Time (CPU-hrs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pc2 (Gaussian, 3,000 basis functions)</td>
<td>$1.06 \times 10^{-4}$</td>
<td>666</td>
</tr>
<tr>
<td>FE basis (HEX125SPECT, 8,004,003 nodes)</td>
<td>$1.2 \times 10^{-4}$</td>
<td>7461</td>
</tr>
</tbody>
</table>
Additional functions appended to the ‘Classical’ FE basis

\[ \psi^h(x) = \sum_j N_j^C(x)\psi_j^C + \sum_k N_k^E(x)\psi_j^E \]

Enriched functions: Radial part computed using 1D radial Kohn-Sham solve, and multiplied by spherical harmonics

Compact support for the enriched functions is obtained by multiplying with a mollifier

Integrals computed using an adaptive quadrature (Mousavi et al. (2012))

Key advantages of enrichment:
- Reduced degrees of freedom
- Reduced spectral width of the discrete Hamiltonian
Enriched FE basis

\[
M = \begin{bmatrix}
M_{11} & M_{21}^T \\
M_{21} & M_{22}
\end{bmatrix}
\quad M^{-1} = \begin{bmatrix}
M_{11}^{-1} + L^T S^{-1} L & -L^T S^{-1} \\
-S^{-1} L & S^{-1}
\end{bmatrix}
\]

\[
L = M_{21} M_{11}^{-1} \quad S = M_{22} - M_{21} M_{11}^{-1} M_{21}^T
\]

- $M_{11}$ is diagonal when spectral FE are used along with Guass-Lobatto quadrature.

- $S$ is a small matrix of size $N_{el} \times N_{el}$ and can be easily inverted using direct solvers.
## Enriched FE basis v/s Classical FE basis

### Silicon 1x1x1: 18 atoms (252 electrons)

<table>
<thead>
<tr>
<th>FE Type</th>
<th>Energy per atom (Ha)</th>
<th># Basis functions per atom</th>
<th>Chebyshev Degree</th>
<th>CPU Hrs</th>
</tr>
</thead>
<tbody>
<tr>
<td>EFEM</td>
<td>−288.31935809</td>
<td>27261</td>
<td>80</td>
<td>42.60</td>
</tr>
<tr>
<td>CFEM</td>
<td>−288.32003559</td>
<td>402112</td>
<td></td>
<td>1599.15</td>
</tr>
</tbody>
</table>

### Silicon 2x1x1: 31 atoms (434 electrons)

<table>
<thead>
<tr>
<th>FE Type</th>
<th>Energy per atom (Ha)</th>
<th># Basis functions per atom</th>
<th>Chebyshev Degree</th>
<th>CPU Hrs</th>
</tr>
</thead>
<tbody>
<tr>
<td>EFEM</td>
<td>−288.33338251</td>
<td>25368</td>
<td>80</td>
<td>139.97</td>
</tr>
<tr>
<td>CFEM</td>
<td>−288.33412399</td>
<td>386205</td>
<td></td>
<td>16441.43</td>
</tr>
</tbody>
</table>

### Silicon 2x2x2: 95 atoms (1330 electrons)

<table>
<thead>
<tr>
<th>FE Type</th>
<th>Energy per atom (Ha)</th>
<th># Basis functions per atom</th>
<th>Chebyshev Degree</th>
<th>CPU Hrs</th>
</tr>
</thead>
<tbody>
<tr>
<td>EFEM</td>
<td>−288.35939776</td>
<td>20074</td>
<td>80</td>
<td>1076.46</td>
</tr>
<tr>
<td>CFEM</td>
<td>−288.35945954</td>
<td>360467</td>
<td>1500</td>
<td>75936.4</td>
</tr>
</tbody>
</table>
Enriched FE basis v/s pc basis (NWChem)

### Silicon 1x1x1: 18 atoms (252 electrons)

<table>
<thead>
<tr>
<th>Basis</th>
<th>Energy per atom (Ha)</th>
<th>CPU Hrs</th>
</tr>
</thead>
<tbody>
<tr>
<td>EFEM</td>
<td>−288.3193580</td>
<td>42.60</td>
</tr>
<tr>
<td>pc-3</td>
<td>−288.31899656</td>
<td>12.21</td>
</tr>
<tr>
<td>pc-4</td>
<td>−288.31944856</td>
<td>98.88</td>
</tr>
</tbody>
</table>

### Silicon 2x1x1: 31 atoms (434 electrons)

<table>
<thead>
<tr>
<th>Basis</th>
<th>Energy per atom (Ha)</th>
<th>CPU Hrs</th>
</tr>
</thead>
<tbody>
<tr>
<td>EFEM</td>
<td>−288.333382</td>
<td>139.97</td>
</tr>
<tr>
<td>pc-3</td>
<td>−288.3334470</td>
<td>261.69</td>
</tr>
<tr>
<td>pc-4</td>
<td>−288.3338987</td>
<td>3580.08</td>
</tr>
</tbody>
</table>

### Silicon 2x2x2: 95 atoms (1330 electrons)

<table>
<thead>
<tr>
<th>Basis</th>
<th>Energy per atom (Ha)</th>
<th>CPU Hrs</th>
</tr>
</thead>
<tbody>
<tr>
<td>EFEM</td>
<td>−288.3593977</td>
<td>1076.46</td>
</tr>
<tr>
<td>pc-3</td>
<td>−288.36004547</td>
<td>4097.29</td>
</tr>
<tr>
<td>pc-4</td>
<td>Didn’t Converge</td>
<td>N/A</td>
</tr>
</tbody>
</table>
### Silicon 3x3x3: 280 atoms (3920 electrons)

<table>
<thead>
<tr>
<th>Basis</th>
<th>Energy per atom (H\text{a})</th>
<th>CPU Hrs</th>
</tr>
</thead>
<tbody>
<tr>
<td>EFEM</td>
<td>$-288.37247084$</td>
<td>10052.78</td>
</tr>
<tr>
<td>pc-3</td>
<td>Didn’t Converge</td>
<td>N/A</td>
</tr>
<tr>
<td>pc-4</td>
<td>Didn’t Converge</td>
<td>N/A</td>
</tr>
</tbody>
</table>

### Silicon 4x4x4: 621 atoms (8694 electrons)

<table>
<thead>
<tr>
<th>Basis</th>
<th>Energy per atom (H\text{a})</th>
<th>CPU Hrs</th>
</tr>
</thead>
<tbody>
<tr>
<td>EFEM</td>
<td>$-288.38224514$</td>
<td>92816.16</td>
</tr>
<tr>
<td>pc-3</td>
<td>Didn’t Converge</td>
<td>N/A</td>
</tr>
<tr>
<td>pc-4</td>
<td>Didn’t Converge</td>
<td>N/A</td>
</tr>
</tbody>
</table>
Computational complexity

*Complexity in each SCF iteration:*

- $M$: Number of degrees of freedom
- $N$: Number of electrons ($M \propto N$)

- Chebyshev filtering procedure: $O(MN)$
- Orthonormalization of Chebyshev filtered vectors: $O(MN^2)$
- Diagonalization of the projected Hamiltonian: $O(N^3)$

Cubic Scaling in $N!$
Key features of the proposed method:

- Chebyshev filtering to generate the approximate occupied subspace

- Construct non-orthogonal localized basis functions that span the same space & truncate these localized functions beyond a prescribed tolerance
  - Subsequently localized basis functions have a compact support
  - Use an adaptive tolerance for the truncation: truncation tolerance tied to the error in the SCF iteration; ensures strict control on accuracy

- Project Hamiltonian into the occupied subspace expressed in the non-orthogonal basis

- Fermi-operator expansion of the projected Hamiltonian to estimate Fermi-energy and compute the electron density
  - Avoids diagonalization of the Hamiltonian to compute orbital occupancies
  - Applicable for both metallic and insulating systems
  - Applicable for both pseudopotential and all-electron calculations
Subspace projection approach: Key ideas

\[ \Phi = \{\psi_1, \psi_2, \psi_3, \ldots, \psi_N\} \quad \rightarrow \quad \text{Eigen-space from Chebyshev filtering} \]

\[
\inf_{\psi' \in \Phi} \int w_I(\mathbf{x})|\psi'(\mathbf{x})|^2 d\mathbf{x} \quad \rightarrow \quad \Phi = \{\psi'_1, \psi'_2, \psi'_3, \ldots, \psi'_N\} 
\]

Localized basis spanning eigen-space (Garcia-Cervera et al.)

- Project Hamiltonian in the localized basis:

\[
\hat{H}^\Phi = S^{-1}\Phi_L^T\hat{H}\Phi_L \quad S = \Phi_L^T\Phi_L
\]

- Remarks:
  - Locality of \( \Phi_L \) \( \rightarrow \) \( S \) is sparse and can be computed in \( O(N) \) complexity
  - \( S^{-1} \) can be computed using Newton-Schultz algorithm which has \( O(N) \) complexity
  - Finally, \( \hat{H}^\Phi \) can be computed in \( O(N) \), if \( S^{-1} \) is sparse.
Subspace projection approach: Key ideas

- **Computation of electron density**

  Recall: \[ \rho = \sum_i f_i |\psi_i|^2, \quad f_i = f(\varepsilon_i, \mu) = \frac{1}{1 + e^{\frac{\varepsilon_i - \mu}{k_B T}}} \]

  No diagonalization \[\rightarrow\] No knowledge of eigenvalues and eigenvectors

- **Compute density matrix instead:** \[ \Gamma = f(\tilde{H} - \mu I) \]
  - The electron density is the diagonal of the density matrix

- Fermi-operator expansion techniques can be employed to compute the density matrix:
  \[ f(\tilde{H} - \mu I) \approx \sum_{n=1}^{P} c_n T_n(\tilde{H}) \]

- Challenge: \[ P \sim O(\frac{\varepsilon_{\text{max}} - \varepsilon_{\text{min}}}{k_B T}) \]; spectral width of the discrete Hamiltonian is about \( 10^3 - 10^6 \)!

WCPM/CSC, U. Warwick, 2018
Subspace projection approach: Key ideas

Fermi-operator expansion of the projected Hamiltonian:

- Compute the density matrix using the projected Hamiltonian in the non-orthogonal localized basis

$$\Gamma = \Phi_L f (\tilde{\mathcal{H}}^\Phi - \mu I) S^{-1} \Phi_L^T$$

- The spectral width of the projected Hamiltonian is $\sim O(10)$ and thus can efficiently employ the Fermi-operator expansion
  
  - This approach treats both insulating and metallic systems on equal footing
  - This approach is applicable for both pseudopotential calculations and all-electron calculations
Case study: Al nano-clusters (3x3x3 – 9x9x9)  
Pseudopotential calculations

Total computational time
Subspace projection scaling: $O(N^{1.46})$

Electron density contours on the mid-plane of the 9x9x9 nano-cluster

Accuracy of subspace projection method commensurate with chemical accuracy
Case study: Alkane chains (C_{33}H_{68} – C_{2350}H_{4702})

Pseudopotential calculations

Numerical accuracy

<table>
<thead>
<tr>
<th>Alkane Chain</th>
<th>DoF</th>
<th>Proposed Method</th>
<th>ChFSI-FE</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_{33}H_{68}</td>
<td>870,656</td>
<td>−61.438671</td>
<td>−61.438680</td>
</tr>
<tr>
<td>C_{100}H_{202}</td>
<td>2,491,616</td>
<td>−62.041530</td>
<td>−62.041532</td>
</tr>
<tr>
<td>C_{300}H_{602}</td>
<td>7,354,496</td>
<td>−62.240148</td>
<td>−62.240277</td>
</tr>
<tr>
<td>C_{900}H_{1802}</td>
<td>21,943,138</td>
<td>−62.303101</td>
<td>−62.303608</td>
</tr>
</tbody>
</table>

Total computational time

Subspace projection scaling: O(N^{1.18})
Case study: Si nano-clusters (1x1x1 – 3x3x3)
All-electron calculations

Electron density contours on the mid-plane of the 3x3x3 Si nano-cluster

Total computational time
Subspace projection scaling: $O(N^{1.85})$

Accuracy of subspace projection method commensurate with chemical accuracy
The spectral width of subspace projected Hamiltonian grows as $O(Z^2)$

Split the eigenspectrum of $\tilde{H}^\phi$ into core and valence parts

$$\Gamma = \Gamma_{\text{core}} + \Gamma_{\text{val}}$$

$$\Gamma_{\text{core}} = \mathcal{P}_{\text{core}}^\phi$$

$$\Gamma_{\text{val}} = f \left( (\mathcal{I} - \mathcal{P}_{\text{core}}^\phi) \mathcal{H}^\phi (\mathcal{I} - \mathcal{P}_{\text{core}}^\phi) \right)$$
Spectrum Splitting

**Case study: Silicon 18 atoms**
(1x1x1 nanocluster (252 electrons))

**Case study: Silicon 31 atoms**
(2x1x1 nanocluster (434 electrons))
Case study: Silicon 95 atoms
(2x2x2 nanocluster (1330 electrons))

Spectrum Splitting
Spectrum Splitting

Case study: Gold Atom
(Single atom (79 electrons))

Case study: Gold 6 Atoms
(Nano-cluster (474 electrons))
Ongoing/future work

Real-space DFT-FE:

- Incorporate more advanced exchange-correlation functionals (beyond LDA, GGA)
- Exploring tensor structured techniques and low rank approximations in conjunction with real-space formulation
  
- Extend algorithms to time dependent DFT

Coarse-graining KSDFT:

Localization of the wavefunctions is key for extending the coarse-graining ideas

- \(O(N)\) formulations: Non-orthogonal localized orbitals
- QC-KSDFT: localization \(\rightarrow\) predictor-corrector approach \(\rightarrow\) QC
- Electronic structure calculations at macroscopic scales with Kohn-Sham DFT will enable a quantum-mechanically accurate study of defects in materials
Concluding remarks

- Developed real-space formulation for Kohn-Sham DFT
  - Reformulation of electrostatics as a local variational problem
  - Mathematical analysis

- Finite-element discretization of Kohn-Sham DFT & Numerical algorithms
  - Optimal rates of convergence
  - Spectral elements in conjunction with GLL quadratures (for overlap matrix)
  - Chebyshev filtering to directly compute the eigenspace
  - Large-scale calculations possible
  - Algorithms exhibit good scalability

- Development of a linear-scaling algorithm
  - Localized basis spanning the Chebyshev filtered subspace
  - Project of Hamiltonian into subspace
  - Use Fermi-operator expansion on the projected Hamiltonian
THANK YOU!