Asymptotics-based Sub-linear Scaling Algorithms for the Study of the Electronic Structure of Materials

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Outline

1. Quantum Mechanical Models of Solids:
   - Thomas-Fermi-type models.
   - Kohn-Sham model.
2. Sub-linear scaling algorithms.
3. Crystalline solids: Band structure and localization.
4. Asymptotics-based sub-linear scaling algorithms.
5. Embedded Kohn-Sham DFT.
6. Linear scaling methods for Density Functional Theory (DFT): Localized Subspace Iteration.
7. Numerical examples.

Why Quantum Mechanics?

A number of problems require a description at the level of Quantum Mechanics:

1. Quantum Mechanics is a *first principles* approach.
2. Defects in solids: A crack propagates by breaking the chemical bonds within the crystalline lattice.

Quantum Mechanical description of solids

All properties of solids can be understood from the interaction between its constituent electrons and nuclei.

1. Born-Oppenheimer approximation: Nuclei are treated classically.
2. Relativistic effects not considered in what follows.
3. The state of N electrons is given by the **wave function** $\Psi(x_1, \ldots, x_N, s_1, \ldots, s_N)$, $x_i \in \mathbb{R}^3$, and $s_i \in \{-\frac{1}{2}, \frac{1}{2}\}$.

Quantum Mechanics

Ground state (Minimum energy):

$$\mathcal{H}\Psi = E\Psi.$$

Hamiltonian:

$$\mathcal{H} = -\frac{1}{2}\sum_{j=1}^{N}\Delta_{x_i} + \sum_{j=1}^{N} V(x_j) + \sum_{i<j}\frac{1}{|x_i - x_j|}.$$

Given N_a nuclei with Z_k protons each located at R_k for $k = 1, \ldots, N_a$:

$$V(x) = -\sum_{k=1}^{N_a}\frac{Z_k}{|x - R_k|}.$$

Even for small systems the dimension of the problem becomes too large to be manageable.

Thomas-Fermi Model (1920)

Electronic structure of solids can be fully understood in terms of the electron density, ρ:

$$E[\rho] = C_{TF} \int \rho^{5/3} + \int V(x)\rho(x)\,dx + \frac{1}{2}\int\int \frac{\rho(x)\rho(y)}{|x-y|}\,dx\,dy \qquad (1)$$

Ground State:

$$\min_{\rho\in\mathcal{A}} E[\rho],$$

$$\mathcal{A} = \left\{\rho \in L^{5/3}(\mathbb{R}^3) \cap L^1(\mathbb{R}^3), \rho \geq 0, \int \rho = N\right\}$$

Density Functional Theory

Formalizes the idea of Thomas and Fermi:

Theorem (Hohenberg-Kohn '64)

There exists a universal functional $F[\rho]$ such that the ground state associated to an external potential V can be obtained by minimizing

$$E[\rho] = F[\rho] + \int V(x)\rho(x)\,dx.$$

1. Reduces the problem from $\mathbb{R}^{3N}$ to $\mathbb{R}^3$.
2. However, $F[\rho]$ is **unknown**.
3. Extensions by J.K. Percus (1978), M. Levy (1979), and E. Lieb (1982), among others.

Kohn-Sham Approach (1965)

Approximation scheme:

$$\begin{aligned} E[\rho] &= 2\sum_{i=1}^{N} \int \psi_i \left(-\frac{1}{2}\Delta\psi_i\right) + \frac{1}{2}\int\int \frac{(\rho - m)(x)(\rho - m)(y)}{|x-y|}\, dx\, dy \\ &\quad + F_{XC}[\rho] + \int V(x)\rho(x)\, dx, \end{aligned}$$

where

$$\rho = 2\sum_{i=1}^{N} |\psi_i|^2, \qquad \int \psi_i^* \psi_j = \delta_{ij}, \qquad m(x) = \sum_{i=1}^{N} m_a(x - R_i),$$

- V and m provide a description of the underlying atomic lattice.
- Pauli exclusion principle: orthogonality constraint.

Exchange and Correlation energy

1. Local Density Approximation (LDA):

$$F_{xc}[\rho] = \int f(\rho).$$

2. Generalized Gradient approximations (GGA):

$$F_{xc}[\rho] = \int f(\rho, \nabla\rho).$$

Kohn-Sham DFT

The Euler-Lagrange equations for the Kohn-Sham energy functional are

$$-\frac{1}{2}\Delta\psi_i + W(\rho; x)\psi_i = \sum_j \epsilon_{ij}\psi_j, \quad i = 1, \ldots, N,$$

where

$$\rho = 2\sum_{i=1}^{N} |\psi_i|^2, \qquad \int \psi_i\psi_j = \delta_{ij}.$$

This is a nonlinear eigenvalue problem, and is usually solved using a self-consistent iteration:

1. Give a potential W, the wave functions are determined by diagonalization and orthogonalization.
2. Give the wave functions, the density is updated, and a new potential is computed.

Sub-linear scaling algorithms for solids

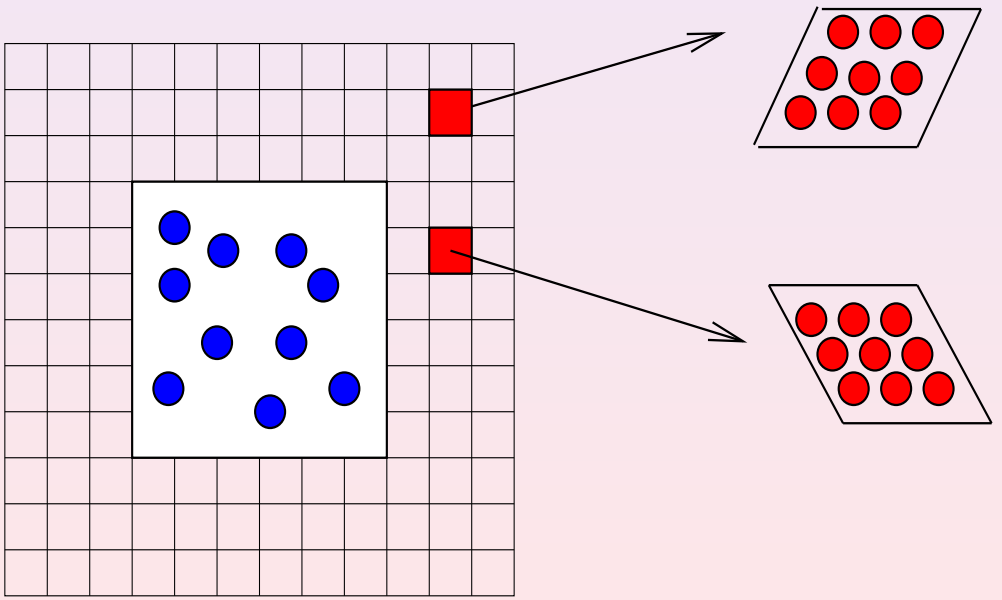
- A complete description of all the atoms in a crystalline solid at the level of Quantum Mechanics is impractical: Linear scaling is too expensive.
- **Goal:** Sub-linear algorithms: Algorithms whose computational cost scales sub-linearly with the size of the system.

Examples:

- Quasicontinuum Method (empirical potentials): Tadmor, Ortiz, and Phillips ('96), E, Lu, Yang ('06), Dobson and Luskin ('07).
- OF-DFT extension: E, Lu, Kaxiras ('06), Hayes, Ho, Ortiz, and Carter ('06), Gavini, Bhattacharya and Ortiz ('07), Peng, Zhang, Hung, Carter, Lu ('08),
- Non-perturbative embedding approach: Cancès, Deleurence and Lewin ('08)

An example of sub-linear scaling: Quasicontinuum method

- Consider a material sample with a defect, e.g., a crack, vacancy, dislocation, etc.
- Decompose the domain into a **nonlocal** region containing the defect, and a **local** region, containing the rest.
- In the nonlocal region, we deal directly with the atoms.
- In the local region, we use a coarse-grained description.



Floquet-Bloch theory

- Consider a Hamiltonian with a periodic potential in a crystalline solid:

$$\mathbf{H} = -\frac{1}{2}\Delta + V(x). \tag{2}$$

- Floquet-Bloch theorem: The eigenfunctions can be chosen in the form

$$\psi_{n,k}(x) = e^{ik\cdot x} u_{n,k}(x), \tag{3}$$

  where $u_{n,k}$ has the periodicity of V, and k belongs to the first Brouillon zone.

- $\psi_{n,k}$ is the Bloch function associated to wave vector k and band index n.

Undeformed crystal: Floquet-Bloch theory

To illustrate the previous definitions, consider the following one-dimensional model:

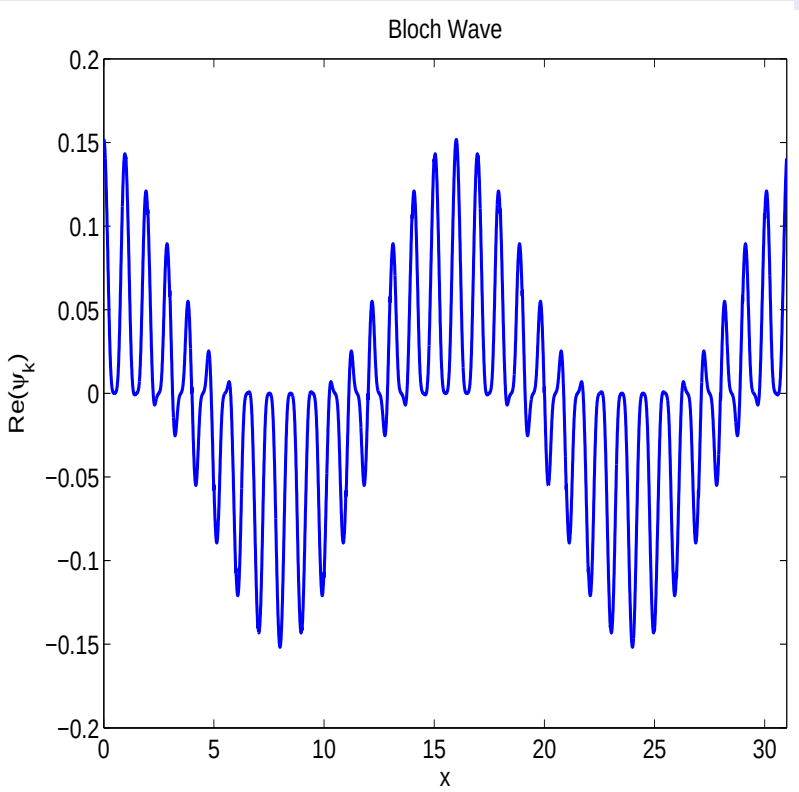
$$\mathbf{H} = -\frac{1}{2}\frac{d^2}{dx^2} + V(x), \tag{4}$$

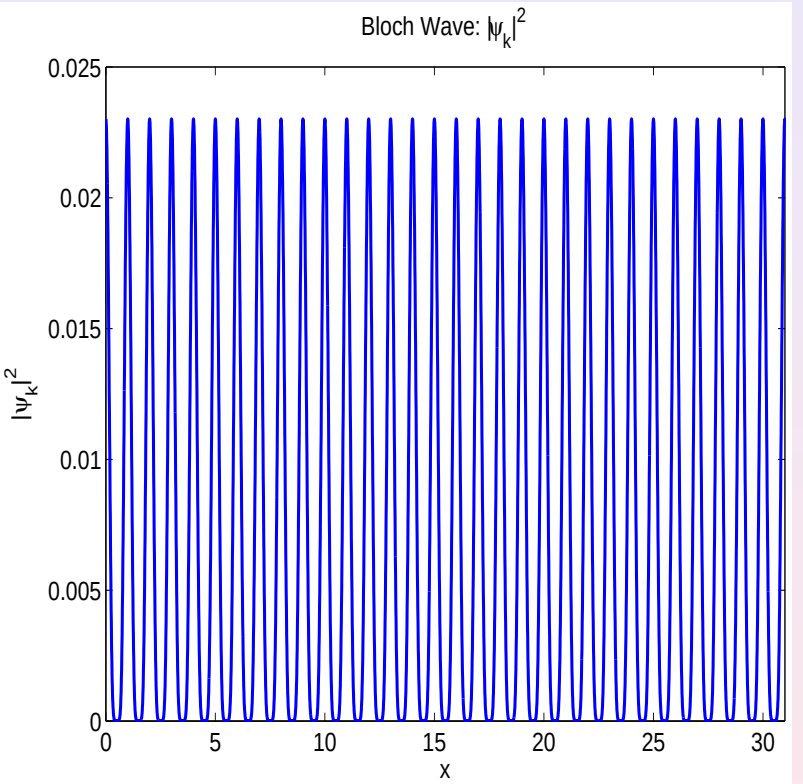
where

$$V(x) = -a \sum_{i=-\infty}^{\infty} \frac{1}{\sqrt{2\pi\sigma^2}} e^{-(x-i)^2/(2\sigma^2)}. \tag{5}$$

- The parameter a represents the strength of the potential.
- The parameter σ represents the width of the potential.

Bloch waves


Bloch Wave
Re(ψ_k)
x
0.2
0.15
0.1
0.05
0
−0.05
−0.1
−0.15
−0.2
0
5
10
15
20
25
30


Bloch Wave: $|\psi_k|^2$
$|\psi_k|^2$
x
0.025
0.02
0.015
0.01
0.005
0
0
5
10
15
20
25
30

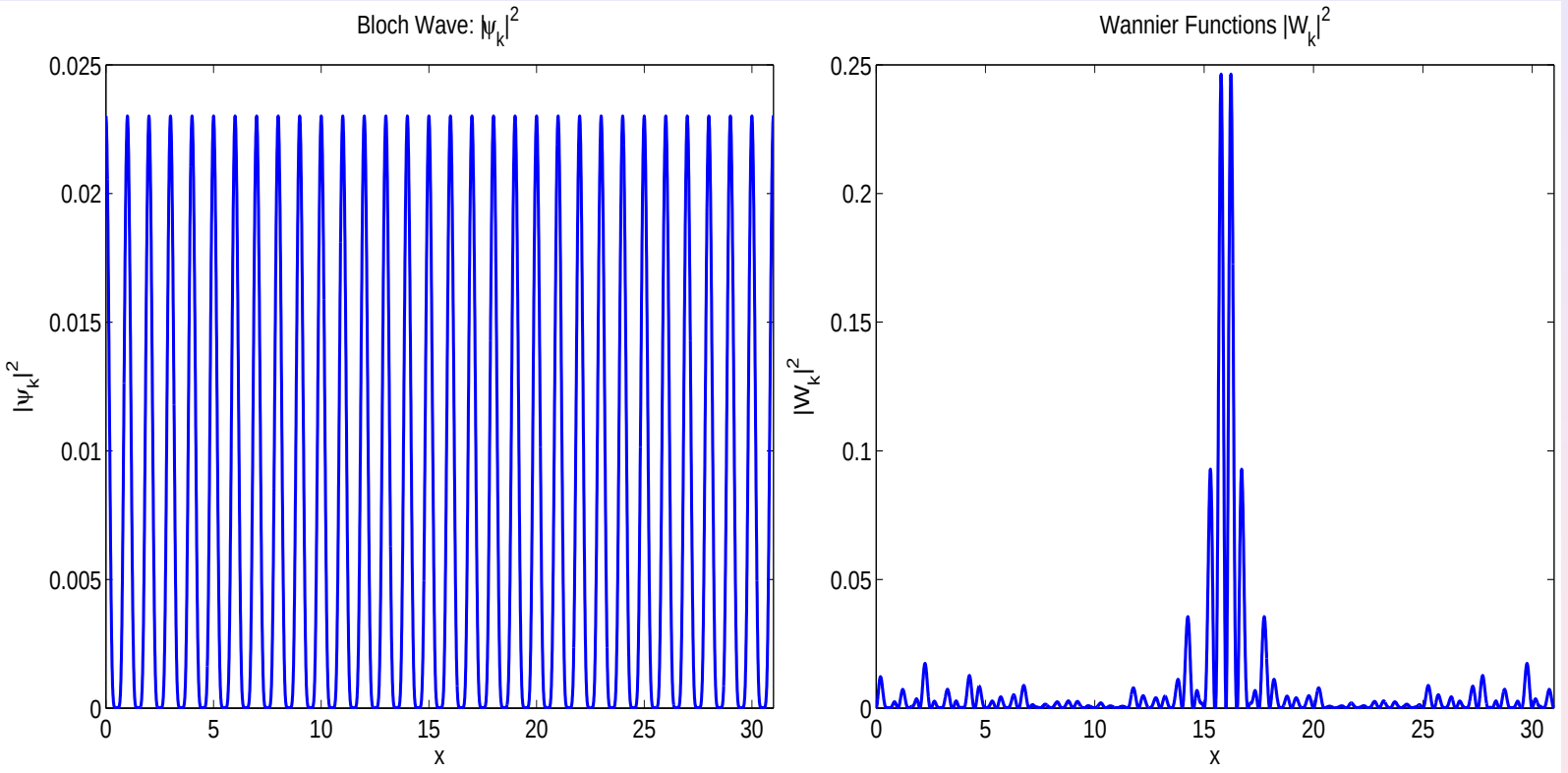
Localization in Quantum-Mechanics: Wannier Functions

- Related to *Nearsightedness:* A small disturbance in a molecule only has a local effect in the electron density (W. Kohn, '96).
- From the Bloch functions, we construct the Wannier function for the n-th band as:

$$W_n(x, R) = \frac{V}{(2\pi)^3} \int_{BZ} e^{-ikR} \psi_{k,n}(x)\, dk. \tag{6}$$

  - Wannier functions are not unique: The Bloch functions can be multiplied by an arbitrary phase.
  - Wannier functions are translation invariant: $W_n(x, R) = W_n(x - R)$.
  - With this definition, they form an orthonormal basis.

Bloch waves and Wannier functions



Wannier Functions and Localization

- Wannier functions have good localization properties (W. Kohn '59, des Cloizeaux '63-'64, E. Prodan & W. Kohn '05, G. Panati '06-'07, Jianfeng Lu '08).
- Wannier functions have been used for numerical computations, e.g., *Maximally* Localized Wannier Functions (Marzari and Vanderbilt, '97).
- In general, localized wave functions have been used to design $O(N)$ methods, typically
  - As basis sets,
  - Via truncation,
  - Or both.
- For the study of solids, the definition must be extended to non-orthogonal wave functions, and non-periodic systems.
- Localized Wannier functions can be constructed for elastically deformed solids (Jianfeng Lu, '08).

Asymptotics in the Kohn-Sham framework

Euler-Lagrange equations:
$\varepsilon =$ Lattice Constant/Diameter of the domain.

$$\begin{aligned} -\frac{\varepsilon^2}{2}\Delta\psi_k + V_{XC}(\varepsilon^3\rho)\psi_k - \phi\psi_k &= \lambda_k\psi_k; \\ -\Delta\phi &= 4\pi\varepsilon(m-\rho), \end{aligned}$$

$$\rho(x) = 2\sum_{j=1}^{N} |\psi_j(x)|^2. \tag{7}$$

Asymptotic expansion for $\varepsilon \ll 1$:

$$\begin{aligned} \psi_\alpha\left(y, \frac{x}{\varepsilon}\right) &= \frac{1}{\varepsilon^{3/2}}\psi_{\alpha,0}\left(y, \frac{x}{\varepsilon}\right) + \frac{1}{\varepsilon^{1/2}}\psi_{\alpha,1}\left(y, \frac{x}{\varepsilon}\right) + \varepsilon^{1/2}\psi_{\alpha,2}\left(y, \frac{x}{\varepsilon}\right) + \cdots \\ \rho\left(y, \frac{x}{\varepsilon}\right) &= \frac{1}{\varepsilon^3}\rho_0\left(y, \frac{x}{\varepsilon}\right) + \frac{1}{\varepsilon^2}\rho_1\left(y, \frac{x}{\varepsilon}\right) + \frac{1}{\varepsilon^1}\rho_2\left(y, \frac{x}{\varepsilon}\right) + \cdots \\ \phi\left(y, \frac{x}{\varepsilon}\right) &= \phi_0\left(y, \frac{x}{\varepsilon}\right) + \varepsilon\phi_1\left(y, \frac{x}{\varepsilon}\right) + \varepsilon^2\phi_2\left(y, \frac{x}{\varepsilon}\right) + \cdots. \end{aligned}$$

Asymptotics in the Kohn-Sham framework[1]

Leading order:

$$\rho_0(y,z) = 2\sum_{\alpha}\sum_{z_j\in L}|\psi_{\alpha,0}(y,z-z_j)|^2.$$

$$\int_{\mathbb{R}^3}\psi^*_{\alpha,0}(y,z-z_i)\psi_{\alpha',0}(y,z-z_j)\,dz = \delta_{\alpha\alpha'}\delta_{ij}/\det(\nabla\varphi(x)).$$

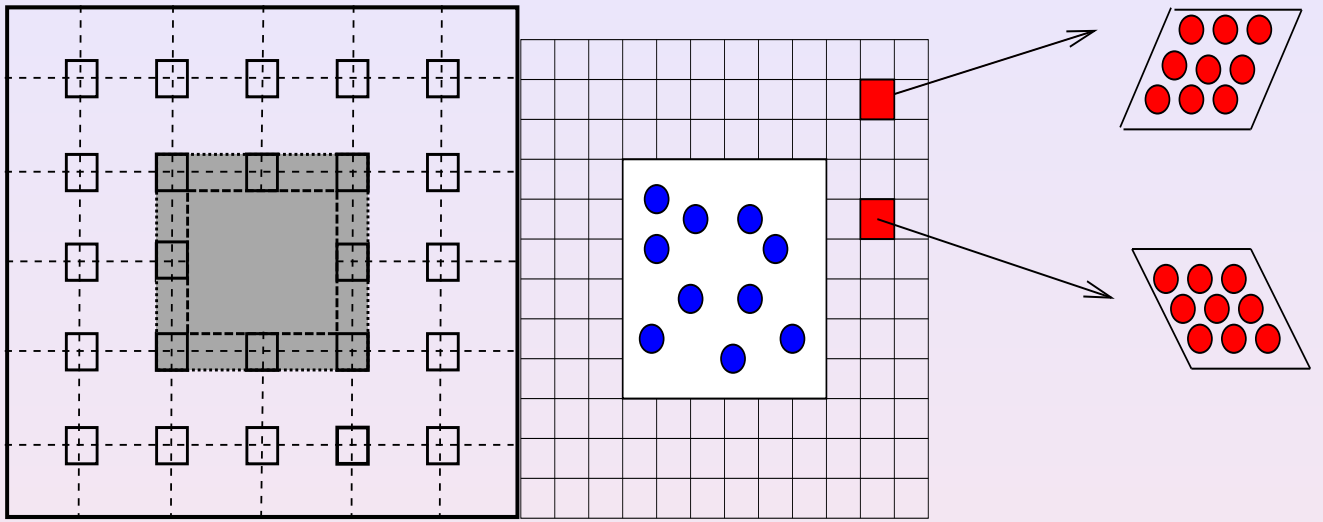
$$-\frac{1}{2}\Delta_2^x\psi_{\alpha,0}(y,z) + V_{XC}(\rho_0)\psi_{\alpha,0}(y,z) - \phi_0(y,z)\psi_{\alpha,0}(y,z) + \sum_{\alpha',z_j\in L}\lambda_{\alpha\alpha',z_j0}\psi_{\alpha',0}(y,z-z_j) = 0;$$

$$-\Delta_2^x\phi_0(y,z) = 4\pi(m_0-\rho_0)(y,z).$$

These are the Euler-Lagrange equations for the *periodic* problem, on the deformed cell: Cauchy-Born rule.

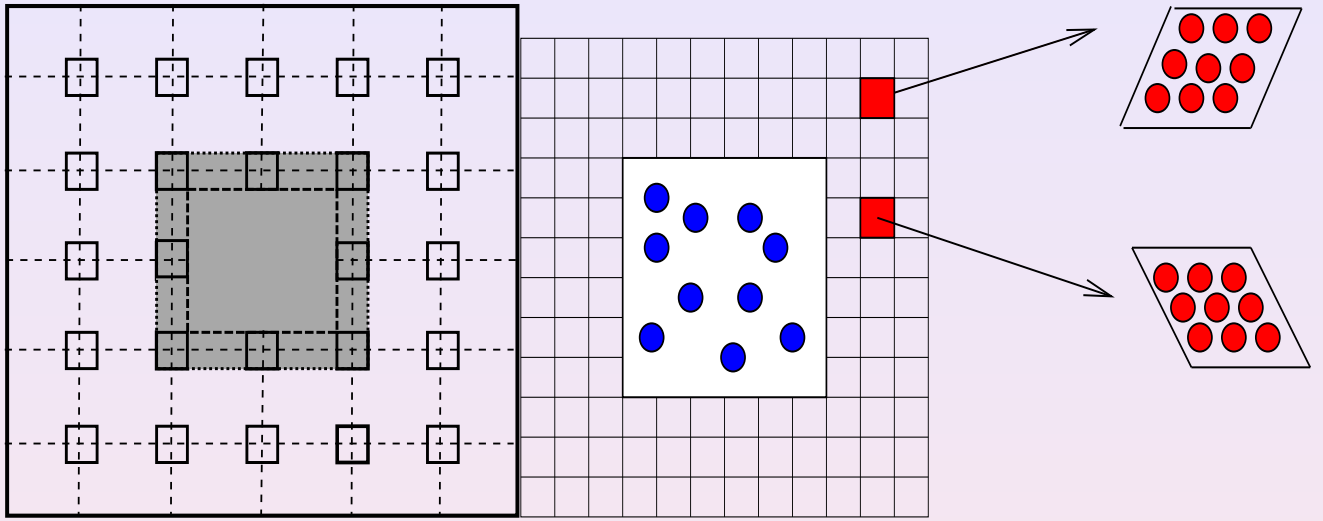
[1] E, Lu, *Comm. Math. Sci.*, 2007

Embedded Kohn-Sham DFT



- In the original formalism, the orbitals must be kept orthogonal to each other: Domain decomposition difficult.
- Orbitals overlap within each region, and with the orbitals from other regions.
- Non-smooth region: Boundary conditions are complicated due to the overlap of the wave functions in the smooth and non-smooth regions.

Embedded Kohn-Sham DFT



- Orthogonality can be avoided: Non-orthogonal formulation of Kohn-Sham.
- Kohn-Sham embedding: We define an *environment* region around the non-smooth region.
- Localization determines the size of the environment.

Non-Orthonormal Formulation of Kohn-Sham DFT[1]

Given N linearly independent wave functions, $\{\psi_j\}$, define the overlap matrix:

$$\mathbf{S}_{jk} = \int \psi_j \psi_k .$$

Then,

$$E_{KS}[\{\psi_j\}] = 2 \sum_{j,k} \left(-\frac{1}{2}\right) (\mathbf{S}^{-1})_{jk} \int \psi_j \left(\Delta \psi_k\right) \, dx + F_{XC}[\rho]$$

$$+\frac{1}{2} \int \int \frac{(\rho - m)(x)(\rho - m)(y)}{|x - y|} \, dx \, dy + \int \int \psi_i(x) V(x, y) \psi_i(y) \, dx \, dy,$$

where

$$\rho(x) = 2 \sum_{jk} \psi_j(x) (\mathbf{S}^{-1})_{jk} \psi_k(x).$$

[1] Mauri, Galli, Car '93

Advantages of the Non-Orthogonal formulation

- $\{\psi_j\}$ not orthogonal.
- Invariant under nonsingular linear transformations: Let $\widetilde{\Psi} = \Psi R$, with $R \in \mathbb{R}^{N\times N}$, invertible. Then,

$$E_{KS}[\widetilde{\Psi}] = E_{KS}[\Psi].$$

- The emphasis is therefore on the subspace spanned by $\{\psi_j\}$.
- Nonorthogonal wave functions have better localization properties.

Embedded Kohn-Sham DFT: Environment region

- Let K, K_s and K_{ns} denote the collection of indices for the wave functions associated with the whole domain, atoms in the smooth region and atoms in the non-smooth region, respectively.
- Note that $K = K_s \cup K_{ns}$, and $K_s \cap K_{ns} = \emptyset$.
- Non-smooth region:

$$\inf_{\{\psi_k\}_{k \in K_{ns}}} \frac{1}{2} \sum_{k \in K} \sum_{j \in K} \left(\int_{\mathbb{R}^3} (\nabla \psi_k)^{\mathrm{T}} (\boldsymbol{S}^{-1})_{kj} \nabla \psi_j \, \mathrm{d}y + \int_{\mathbb{R}^3} \epsilon_{\mathrm{xc}}(\rho) \rho(y) \, \mathrm{d}y \right.$$
$$\left. + \frac{1}{2} \iint_{\mathbb{R}^3 \times \mathbb{R}^3} \frac{\rho(y)\rho(y')}{|y - y'|} \, \mathrm{d}y \, \mathrm{d}y' \right)$$

- We define an environment region, with indices $K_{env} \subset K_s$. This environment region contains the indices of the wave functions that overlap with the non-smooth region.

Embedded Kohn-Sham DFT: Computation of the density

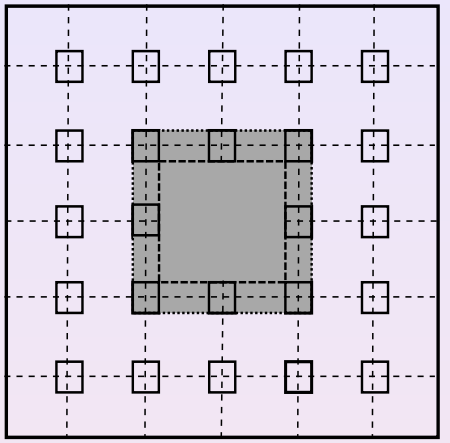
The density can be written as

$$\rho(y) = 2 \sum_{i \in K_{ns} \cup K_{env}} \sum_{j \in K_{ns} \cup K_{env}} \psi_i (S^{-1})_{ij} \psi_j(y) + 4 \sum_{i \in K_{ns} \cup K_{env}} \sum_{j \in K_s \setminus K_{env}} \psi_i (S^{-1})_{ij} \psi_j(y) + 2 \sum_{i \in K_s \setminus K_{env}} \sum_{j \in K_s \setminus K_{env}} \psi_i (S^{-1})_{ij} \psi_j(y). \tag{8}$$

- This decomposition is exact.
- If $y \in \Omega_{ns}$, only the first term in (8) is not zero:

$$\rho(y) = 2 \sum_{i,j \in K_{ns} \cup K_{env}} \psi_i (S^{-1})_{ij} \psi_j(y), \quad y \in \Omega_{ns}.$$

Asymptotic-based sub-linear-scaling algorithms: General strategy[1]



1. Decompose the domain into a smooth and non-smooth region.
2. Lay down a coarse grid in the smooth region, and fine grid in the non-smooth region.
3. At each grid point, solve the electronic structure problem on the unit cell, with uniform local deformation.
4. Compute interacting potential.
5. Solve the electronic structure problem in non-smooth region.

Note that each grid point represents a large number of atoms.

[1] CJGC, Jianfeng Lu, and Weinan E, *Comm. Math. Sci.*, 5(4), pp.999-1026, (2007)

Algorithmic details

1. Coupling smooth and non-smooth regions:
   - 1.1 Long-range interaction.
   - 1.2 Continuity of the electronic density: Environment region.
2. Long range interactions can be efficiently evaluated using a combination of techniques:
   - 2.1 Lattice Sum (Huang '99).
   - 2.2 Potential Theory.
   - 2.3 Fast Multipole Method (Greengard, Rokhlin '87, Greengard '97), Tree Code (Barnes, Hut '86, Krasny '01).
3. The elastic deformation is obtained by minimizing the energy using Conjugate Gradient, or BFGS.

How do we obtain the Kohn-Sham density?:Linear scaling.

Linear scaling methods for Kohn-Sham DFT

A number of linear scaling methods have appeared in the literature (Goedecker '99):

1. Orbital Minimization (Mauri, Galli, Car '93, W. Yang '97, C. Yang, J.C. Meza and L.W. Wang '06, Burger and Yang '07, W. Gao and W. E '08).
2. Density Matrix Minimization (Li, Nunes, Vanderbilt, '93).
3. Fermi Operator Expansion (Goedecker '94).
4. Divide and Conquer (Yang '91, L.W. Wang, Z. Zhao, J. Meza '06, Barrault, Cancès, Hager, Le Bris '07).

An interesting $O(N^3)$ algorithm:

- **Subspace Iteration** (Zhou, Saad, Tiago, Chelikowsky '06).
- New algorithm: Similar to the subspace iteration method of Zhou, Saad, Tiago, and Chelikowsky '06, **but**, we avoid diagonalization and orthogonalization (which is $O(N^3)$) (CJGC, Lu, E, '07, CJGC, Lu, Xuan, E '08).

Linear scaling methods for Kohn-Sham DFT

Guiding principles:

- In the non-orthogonal formulation, the emphasis is on the **subspace generated by the wave functions**.
- We want to generate the optimal eigenspace of the self-consistent Hamiltonian: **Filtering out the high end of the spectrum**.
- Localization is key for linear scaling: **We choose a localized basis for this subspace**.
- We use finite differences, and **real-space formulation**.

We **avoid**:

- Diagonalization and orthogonalization.
- Using a basis set.
- Using plane waves.
- Using a *supercell* for non-periodic problems.

Optimally localized wave functions[1]

Given $\{\psi_j\}$, define

$$V = span\{\psi_j\}.$$

The optimally localized wave function, or generalized non-orthogonal Wannier function, ϕ^*, is the minimizer of

$$\inf_{\phi \in V, \|\phi\|_2 = 1} \int w(x)|\phi(x)|^2 \, dx.$$

- Generalizes the Maximally Localized Wannier Functions of Marzari and Vanderbilt (1997).
- An alternative procedure is the *Frobenius Localization* (Weiguo Gao and Weinan E '08).

[1] Weinan E, Tiejun Li, and Jianfeng Lu, '07

Optimally localized wave functions[1]

Theorem (Insulator)

Suppose p is the index of the first nonzero term in $\{w^{(2p)}(0)\}$, $p \geq 1$, then the generalized non-orthogonal Wannier function for an insulator decays as $|\boldsymbol{x} - \boldsymbol{x}_c|^{-2p} \exp(-h|\boldsymbol{x} - \boldsymbol{x}_c|)$.

The *best* weight function: $w(x) = |x - c|^{2p}$.

[1] Jianfeng Lu, '08

Algorithm for Localization[1]

1. Given a set of wave functions, $\{\psi_j\}_{j=1}^N$, centered at the locations $\{b_j\}_{j=1}^N$, respectively.
2. We obtain an optimally localized basis by minimizing

$$F[\phi] = \frac{\int_{\mathbb{R}^3} |x - b_j|^{2p} |\phi(x)|^2 \, dx}{\int_{\mathbb{R}^3} |\phi(x)|^2 \, dx},$$

   among functions ϕ of the form

$$\phi(y) = \sum_{k=1}^{r} \alpha_k \psi_k(x).$$

3. Minimization leads to

$$\mathbf{W}a = \lambda \mathbf{S}a.$$

- **Only a fixed number r of functions involved, so this is $O(N)$**
- The localized functions span the same space.

[1] Weinan E, Tiejun Li, Jianfeng Lu, '07; CJGC, Jianfeng Lu, Weinan E, '07; CJGC, Jianfeng Lu, Yulin Xuan, Weinan E, '08

Filtering Step

Goal: To improve the subspace by removing components in the high end of the spectrum of the Hamiltonian

$$H = -\frac{1}{2}\Delta + V_{\mathit{eff}}[\rho].$$

Power Method

The simplest filter is probably the Power Method (Parlett, '98):

1. Given an initial vector $\mathbf{v}^0$.
2. For $k \geq 0$, define
   2.1
   $$\mathbf{v}^{k+1} = \frac{\mathbf{H}\mathbf{v}^k}{\|\mathbf{H}\mathbf{v}^k\|}, \tag{9}$$
   2.2 $\mu^{k+1} = (\mathbf{v}^{k+1})^T \cdot \mathbf{H}\mathbf{v}^{k+1}$.
3. Repeat until $|\mu^{k+1} - \mu^k| \leq \text{Tolerance}$.

Convergence: If $\mathbf{H}\psi_i = \lambda_i\psi_i$, and $|\lambda_1| \leq |\lambda_2| \leq \cdots \leq |\lambda_N|$, then

$$\frac{1}{\|\mathbf{H}\mathbf{v}\|}\mathbf{H}\mathbf{v} = \psi_N + O\left(\left|\frac{\lambda_{N-1}}{\lambda_N}\right|\right). \tag{10}$$

- Note that when applied to a subspace, the space collapses to a one-dimensional space.

Subspace Iteration

The Subspace Iteration generalizes the Power Method to a subspace (Parlett, '98):

1. Given an initial space V_0 of dimension $M < N$, for each $k \geq 1$:
   - 1.1 Calculate $W_k = \mathbf{H} V_k$.
   - 1.2 Orthogonalize the basis (QR decomposition, for example): $W_k = Q_k R_k$.
   - 1.3 Let $V_k = Q_k$.
2. Repeat until convergence.

- The orthogonalization step is necessary in order to ensure the linear independence of the vectors in the new space.
- If $\mathbf{H}\psi_i = \lambda_i \psi_i$, and $|\lambda_1| \leq |\lambda_2| \leq \cdots \leq |\lambda_N|$, then the subspace iteration converges with rate of convergence

$$\tau = \frac{\lambda_M}{\lambda_{M+1}} < 1. \tag{11}$$

Polynomial Filtering

- Filtering improves the rate of convergence of the subspace iteration.
- If the polynomial P splits the spectrum of $\mathbf{H}$, in the sense that

$$P(\lambda_i) \leq P(\lambda_M), \quad i = 1, \ldots, M, \tag{12}$$
$$P(\lambda_j) \geq P(\lambda_{M+1}), \quad j = M+2, \ldots, M, \tag{13}$$

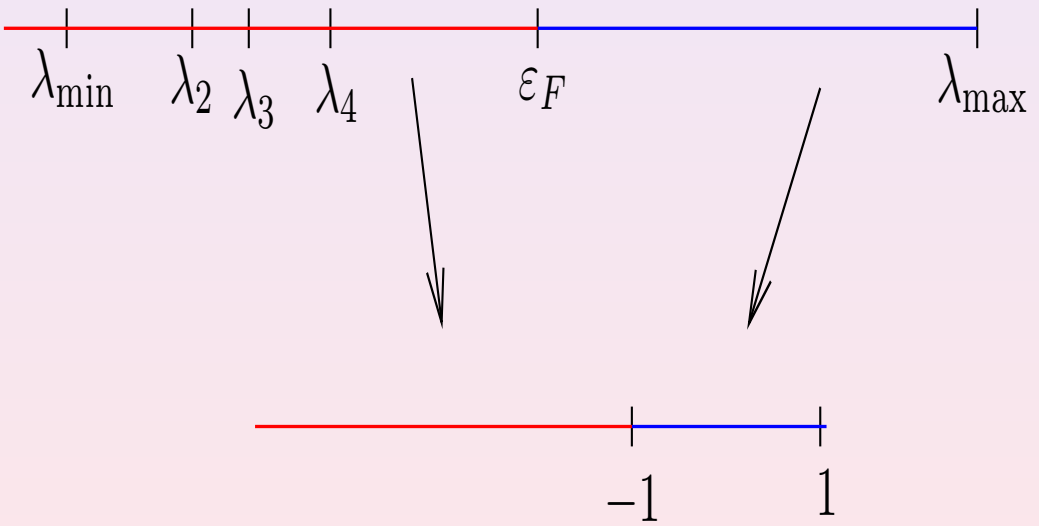
  the rate of convergence of the polynomial filtered subspace iteration is

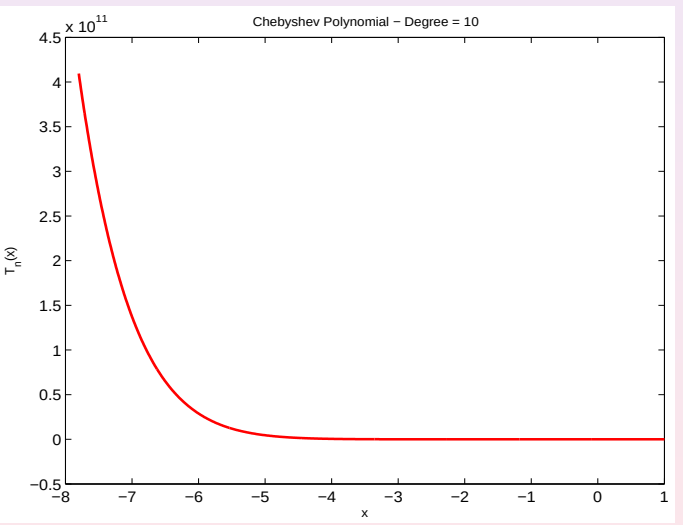
$$\kappa = \left| \frac{P(\lambda_M)}{P(\lambda_{M+1})} \right|. \tag{14}$$

- No diagonalization necessary.

Chebyshev Filter

- Optimal choice: Chebyshev polynomial. $T_n(H)$.
  - Recursive: $T_{n+1}(x) = 2xT_n(x) - T_{n-1}(x)$.
  - $$T_n(x) = \begin{cases} \cos(n \cos^{-1} x) & if\ |x| \leq 1, \\ (-1)^n \cosh(n \cosh^{-1} |x|) & if\ |x| \geq 1, \end{cases}$$





Chebyshev Filter

- In the context of electronic structure analysis, subspace iteration has been used by Zhou, Saad, Tiago, and Chelikowsky, '06.
- The orthogonalization step leads to an $O(N^3)$ method.
- We replace the orthogonalization step with a localization step, achieving $O(N)$.
- The Fermi energy must be estimated (no diagonalization is used).

Estimation of the Fermi energy

- Given the wave functions Ψ, we know that $\Phi = \Psi \mathbf{S}^{-1/2}$ are orthogonal (*Löwdin transformation*).
- The Ritz matrix is

$$\mathbf{R} = \Phi^T \mathbf{H} \Phi = \mathbf{S}^{-1/2} \psi^T \mathbf{H} \Psi \mathbf{S}^{-1/2}$$

- We estimate the Fermi energy by the maximum eigenvalue of the Ritz matrix.
- The eigenvalues of $\mathbf{R}$ are the same as the eigenvalues of $\mathbf{S}^{1/2} \mathbf{R} \mathbf{S}^{-1/2} = \psi^T \mathbf{H} \Psi \mathbf{S}^{-1}$.
- We can use the Power method.
- Note that we do not need $\mathbf{S}^{-1}$, only $\mathbf{w} = \mathbf{S}^{-1} \mathbf{v}$, which can be obtained by solving

$$\mathbf{S} \mathbf{w} = \mathbf{v}.$$

- $\mathbf{S}$ is sparse and localized, and $\Psi^T \mathbf{H} \Psi$ is sparse: The Fermi energy can be estimated in $O(N)$.

Computation of the Electronic Density

$$\rho(x) = 2 \sum_{jk} \psi_j(x) (\mathbf{S}^{-1})_{jk} \psi_k(x)$$

- Computing $\mathbf{S}^{-1}$ directly is $O(N^3)$.
- Instead, we use the Newton-Schultz iteration to solve

$$\mathbf{DSD} - \mathbf{D} = 0.$$

- $\mathbf{S}$ and $\mathbf{S}^{-1}$ are localized near the diagonal.
- Exploiting sparsity, computation is $O(N)$ (Jansik, Host, Jorgensen, Olsen, and Helgaker '07, Rubensson and Salek '05).
- Alternatively, a pseudoinverse can be used (W. Yang '97).

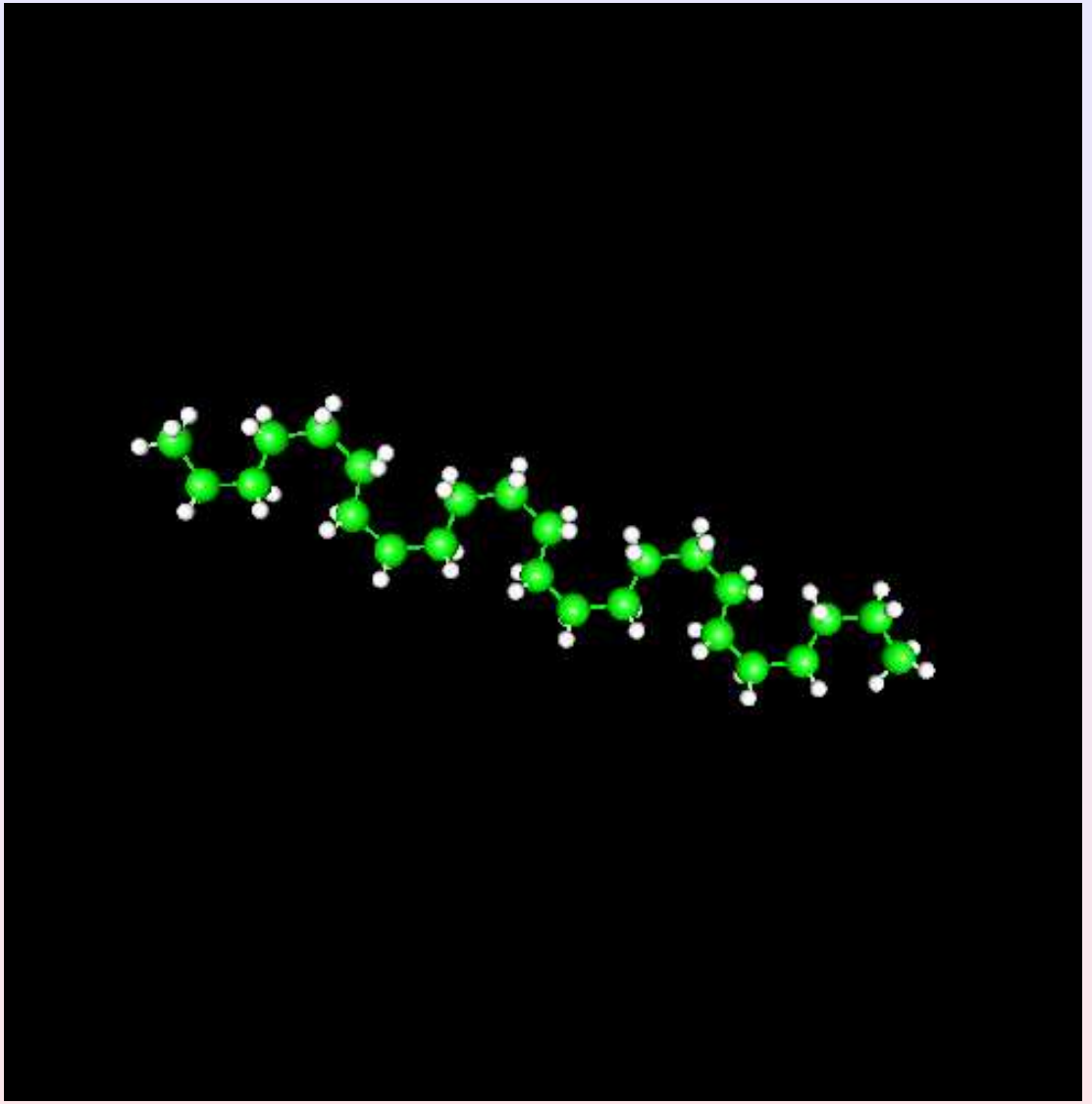
Linear Scaling Algorithm for Kohn-Sham[1]

1: Given (localized) wave functions Ψ_0.
2: **repeat** {(*Self-Consistency Loop (SCF)*)}
3: Compute electronic density: ρ
4: Compute effective potential: $V_{\text{eff}}[\rho]$.
5: **repeat** {(*Localized Subspace Iteration*)}
6: Estimate Fermi energy.
7: Filtering Step: $\Phi = T_n(H)\Psi$.
8: Localization Step: Localize ψ_r for $r = 1, \cdots, k$.
9: Truncation beyond cut-off radius.
10: **until** Convergence of LINEAR iteration
11: Update electronic density (mixing).
12: **until** $\|\rho_{k+1} - \rho_k\|_2 \leq Tol$.

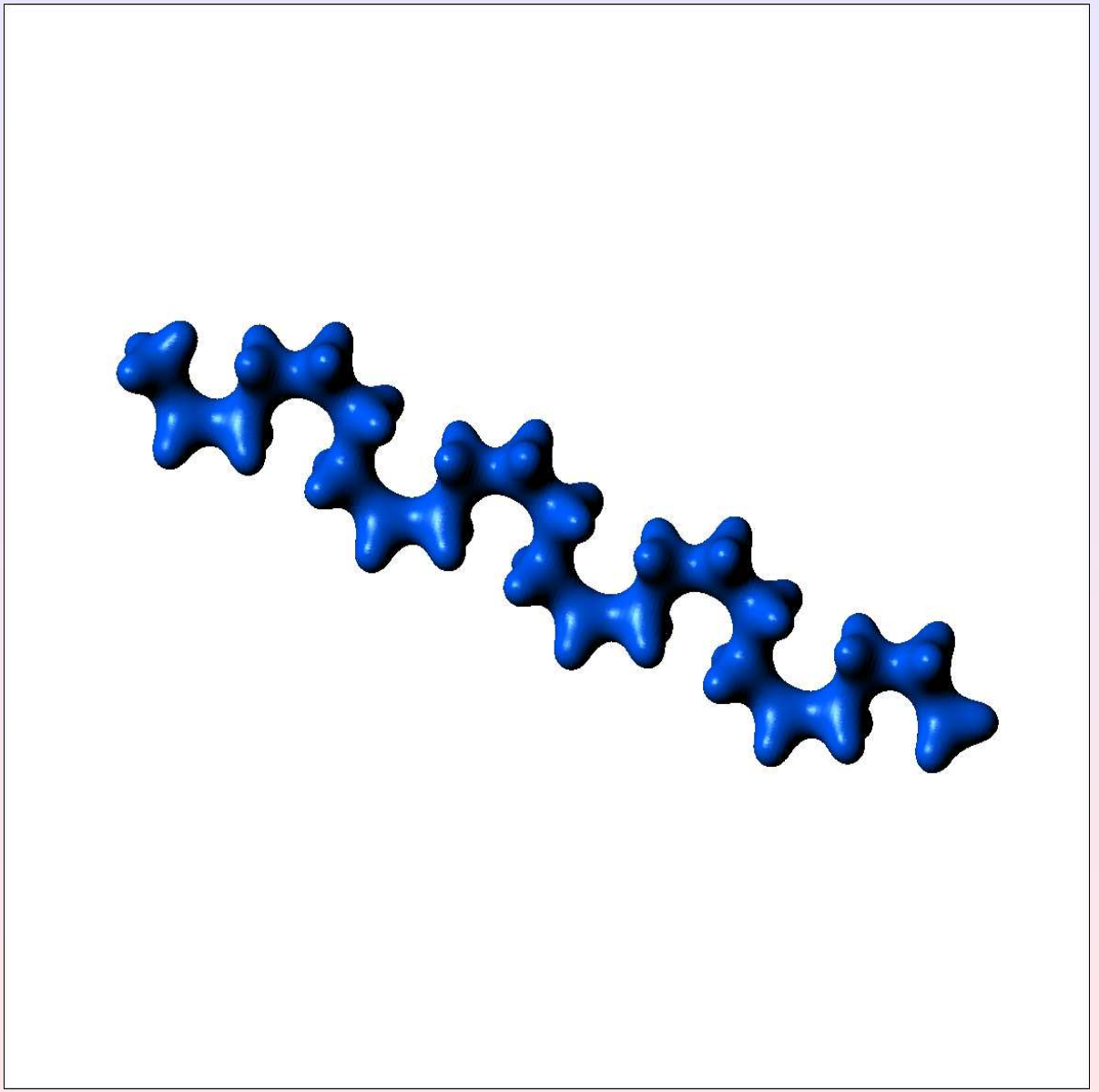
- Similar to the subspace iteration method of Zhou, Saad, Tiago, and Chelikowsky '06, **but**, we avoid diagonalization and orthogonalization (which is $O(N^3)$).
- In practice, only one filtering step is performed.

[1] CJGC, Jianfeng Lu, Weinan E '07; CJGC, Jianfeng Lu, Yulin Xuan, Weinan E, '08

Example: Alkane - $CH_3(CH_2)_{22}CH_3$ (74 atoms)

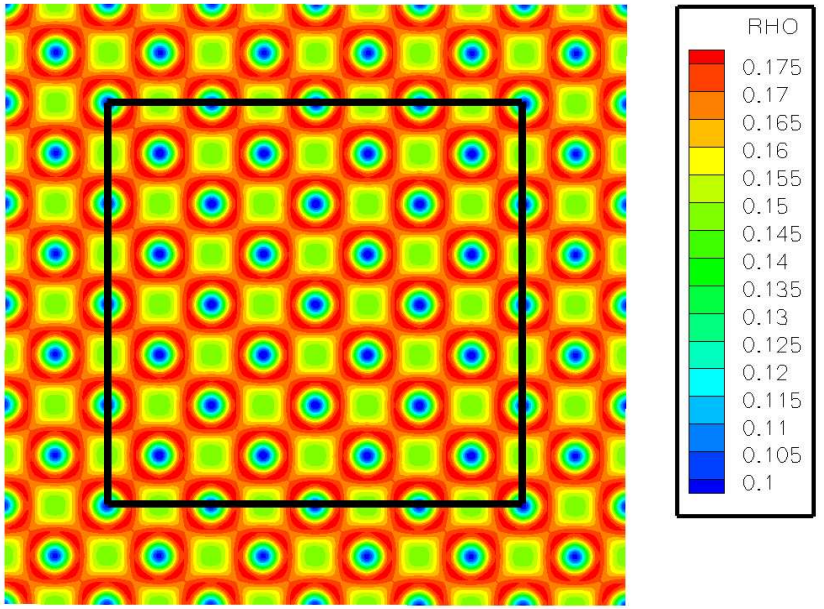


Example: Alkane - $CH_3(CH_2)_{22}CH_3$ - Density



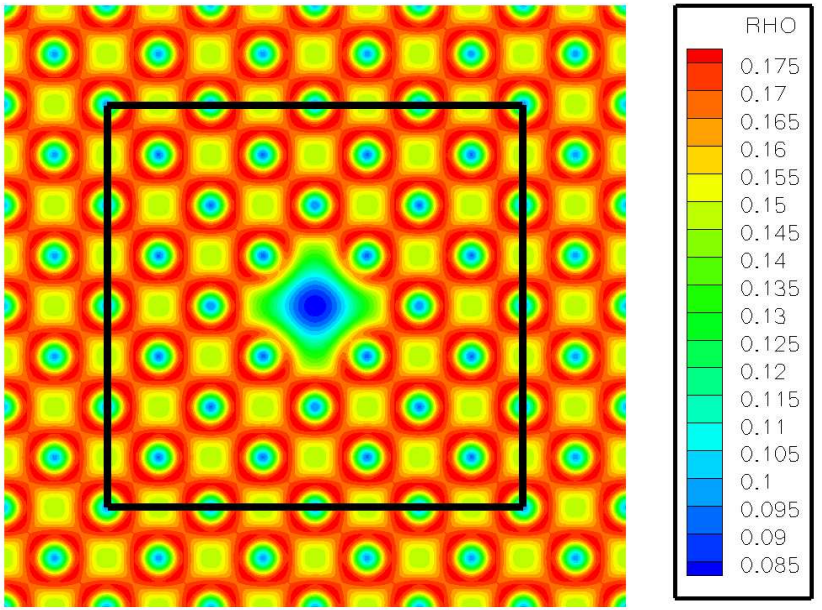
Numerical Examples: Perfect Aluminium Crystal

- Aluminium FCC crystal.
- Orbital-Free DFT (Thomas-Fermi-von Weizsacker).

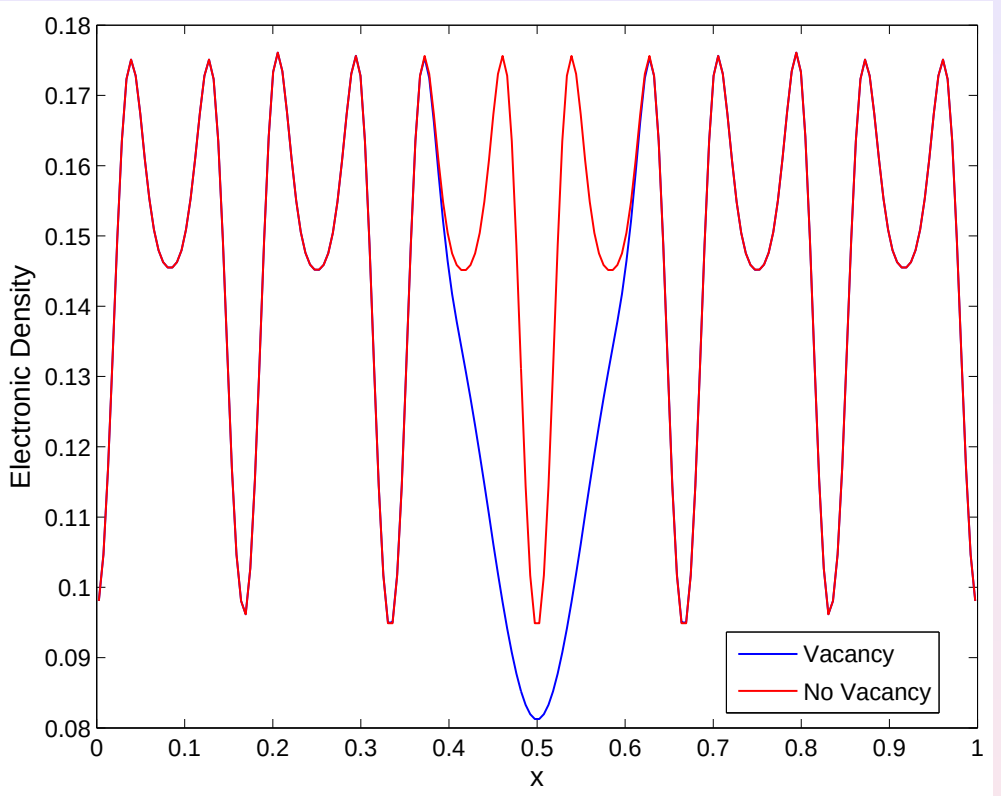


Numerical Examples: Vacancy Formation

- Aluminium FCC crystal.
- One atom has been removed.
- Orbital-Free DFT (Thomas-Fermi-von Weizsacker).



Density Profile



1. The coupling is seamless.
2. Effect of vacancy is localized.

Numerical Examples - Carbon Chain

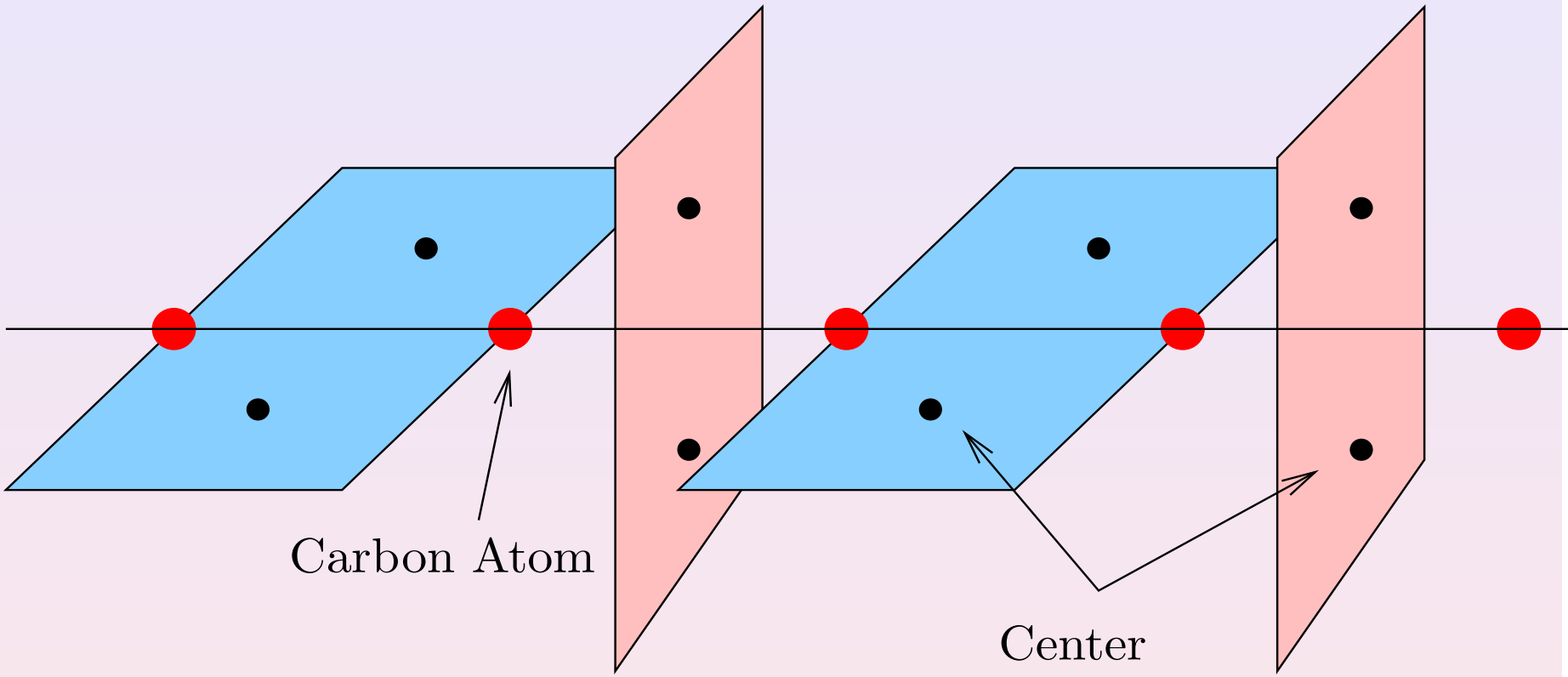


Figure: Carbon Chain. In red, the location of the atoms. The wave functions have centers on alternating orthogonal planes.

Numerical Examples - Carbon Chain

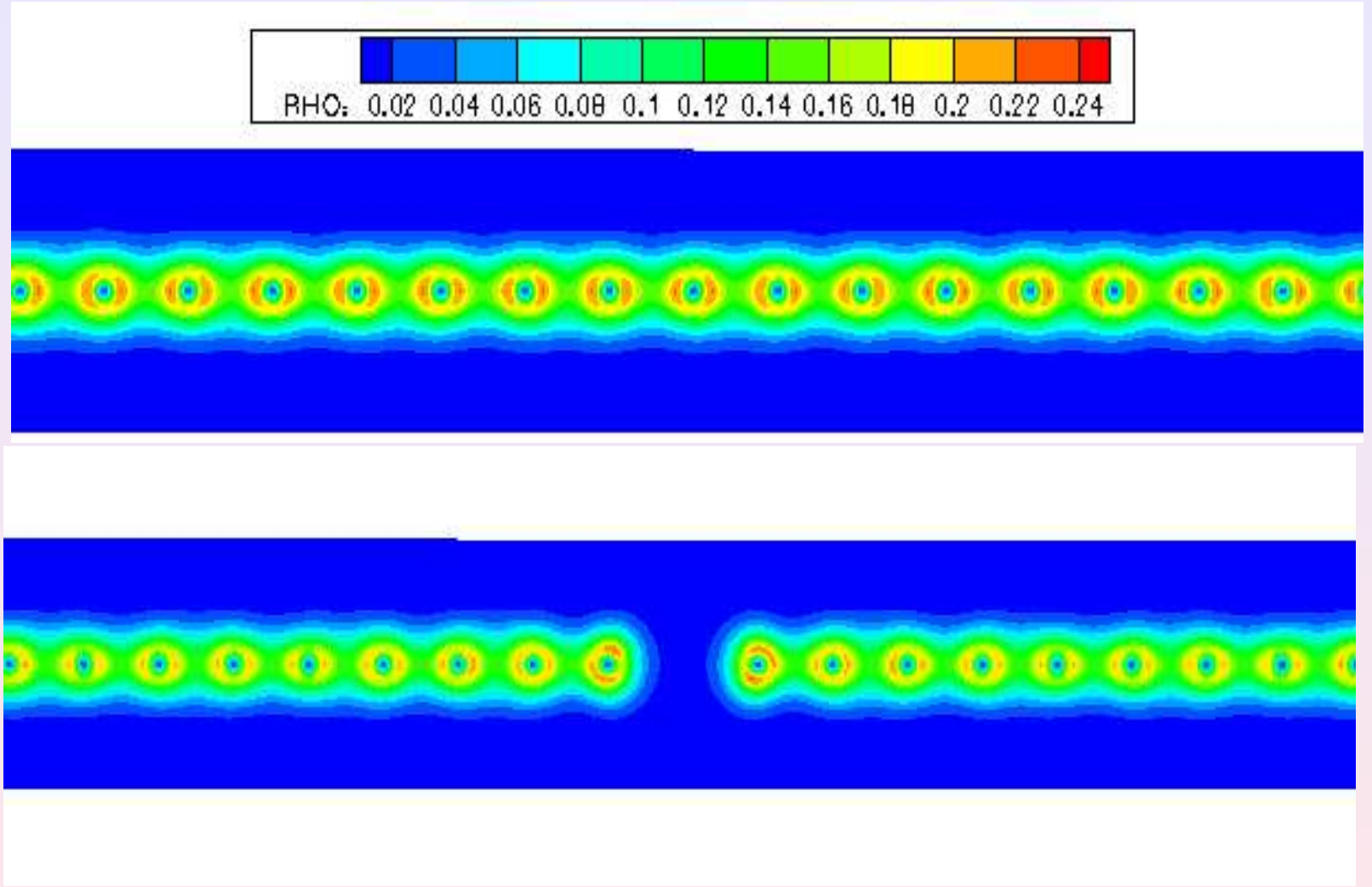


Figure: Electronic density of a Carbon chain, computed with the linear scaling algorithm presented.

Summary and Conclusions

1. Effective linear scaling methods for the study of solids in the context of Density Functional Theory.
2. Modeling justified by asymptotic analysis.
3. Numerical algorithms guided by the analysis.
4. Arbitrary accuracy achieved by using higher order asymptotics.