

Introduction to Kohn-Sham Density Functional Theory: Analysis and Algorithms

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Fundamentals

Macroscopic limit of density functional theory

Derivation of nonlinear elasticity and macroscopic electrostatic equation from Kohn-Sham DFT

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Introduction

Discretization of the Kohn-Sham Hamiltonian

Representation of the Fermi Operator

Density evaluation

Quantum many-body problem

The (non-relativistic) ground state electronic structure of a system is determined by the lowest eigenvalue and eigenfunction of the many-body time independent Schrödinger operator (omitting spin):

$$H\Psi = \left(\sum_i -\frac{1}{2}\Delta_{x_i} + \sum_{i<j} \frac{1}{|x_i - x_j|} - \sum_{i,\alpha} \frac{Z_\alpha}{|x_i - X_\alpha|} \right) \Psi = E\Psi,$$

within the Born-Oppenheimer approximation.

$$E(\{X_\alpha\}) = \inf_{\|\Psi\|=1} \langle \Psi | H | \Psi \rangle.$$

Here the many-body wave function $\Psi(x_1, x_2, \dots, x_N)$ is an antisymmetric function of N variables, according to Pauli's exclusion principle.

Reduction of the quantum many-body problem

Due to curse of dimensionality, the many-body problem is practically impossible to solve, except for tiny systems.

Reductions based on various approximations:

- ▶ Discrete lattice approximation: Tight-binding models.
- ▶ Low-rank approximation: Hartree-Fock; Configurational Interaction; Multi-configurational self-consistent field (MCSCF);
- ▶ Mean-field approximation: Density functional theory (DFT);
- ▶ Coupled clusters;
- ▶ Others ...

Most are not systematic approximations to the many-body problem.

Tight-binding model

Consider one-body effective Hamiltonian, and assume one-body wave functions take the form

$$\psi(x) = \sum_{\alpha,i} c_{i,\alpha} \varphi_i(x - X_\alpha),$$

where φ_i are atomic orbitals. Similar to a generalized finite element discretization.

Hence, the Hamiltonian becomes a matrix acting on $c_{i,\alpha}$.

Nonlinear tight-binding model is also used sometimes. The effective Hamiltonian depends on the density (like a discrete version of density functional theory)

Hartree-Fock theory

Assumes the many-body wave function is a single Slater determinant

$$\Psi = \frac{1}{\sqrt{N!}} \det \begin{vmatrix} \psi_1(x_1) & \psi_2(x_1) & \cdots & \psi_N(x_1) \\ \psi_1(x_2) & \psi_2(x_2) & \cdots & \psi_N(x_2) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_1(x_N) & \psi_2(x_N) & \cdots & \psi_N(x_N) \end{vmatrix}$$

with $\{\psi_i\}$ a set of orthonormal functions.

For example, in this approximation, the kinetic energy reduces to

$$\int_{\mathbb{R}^{3N}} \Psi^* \left(- \sum_i \frac{1}{2} \Delta_{x_i} \right) \Psi = \sum_i \frac{1}{2} \int_{\mathbb{R}^3} |\nabla \psi_i(x)|^2.$$

Hartree-Fock theory (cont'd)

Hartree-Fock equation

$$\left(-\frac{1}{2}\Delta + V_{\text{ext}} + \int_{\mathbb{R}^3} \frac{\rho(y)}{|x-y|} dy - \mathcal{K}\right)\psi_i = \lambda_i\psi_i.$$

\mathcal{K} is the exchange operator:

$$\mathcal{K}\psi_i = \int \frac{\psi_j^*(y)\psi_i(y)}{|x-y|} dy \psi_j(x).$$

As the energy is minimized over a smaller space,

$$E \leq E_{\text{HF}} = E + E_c.$$

The error made E_c is called correlation energy, as a result of ignoring many-body interactions (besides Coulomb and exchange).

Density functional theory

Brief history:

- ▶ Thomas-Fermi: Concepts of using solely the density to describe quantum mechanics (simple empirical models).
- ▶ Hohenberg-Kohn: Proves that for ground state in quantum mechanics is indeed only a function of the electron density.
- ▶ Kohn-Sham: Mean field theory for non-interacting electrons in an effective potential.
- ▶ Levy-Lieb variational principle: Mathematical rigorous foundation.
- ▶ Development of exchange-correlation functional (Becke, Burke, Ernzerhof, Parr, Perdew, Yang, ...)

Density functional theory [Hohenberg-Kohn 1964]: The many-body variational problem can also be reformulated using **electron density** as variable:

$$E = \inf_{\substack{\rho \geq 0, \sqrt{\rho} \in H^1 \\ \int \rho = N}} F[\rho].$$

The basic variable is the electron density:

$$\rho(x) = N \int |\Psi(x, x_2, \dots, x_N)|^2 dx_2 \cdots dx_N.$$

Levy-Lieb formulation:

$$\begin{aligned} E &= \inf_{\substack{\rho \geq 0, \sqrt{\rho} \in H^1 \\ \int \rho = N}} \inf_{\substack{\Psi \in H^1, \Psi \rightarrow \rho \\ \Psi \text{ antisymmetric}}} \langle \Psi | T + V_{ee} | \Psi \rangle + \int V_{\text{ext}} \rho \\ &\equiv \inf_{\substack{\rho \geq 0, \sqrt{\rho} \in H^1 \\ \int \rho = N}} F_{\text{KS}}[\rho]. \end{aligned}$$

Kohn-Sham density functional theory

The energy functional depends on N electron orbitals $\{\psi_i\}$:

$$E_{\text{KS}}(\{\psi_i\}) = \sum_i \frac{1}{2} \int |\nabla \psi_i|^2 + \frac{1}{2} \iint \frac{(\rho - m)(x)(\rho - m)(y)}{|x - y|} + E_{\text{xc}}[\rho].$$

The orbitals are orthonormal, ρ is the electron density given by $\rho(x) = \sum_i |\psi_i(x)|^2$. m is the background charge distribution.

Formally exact. All errors are encoded in the last term, the **exchange-correlation energy**, which contains chemistry, as it models the quantum correlation of electrons. However, the explicit form is unknown and needs approximation.

Input to the model

Background charge: $m(y) = \sum_{y_j \in \Omega} m_j^a (y - y_j)$

- ▶ $\{y_j\}$ = positions of the nuclei (ions).
- ▶ $\{m_j^a\}$ = ionic potential describing the atoms in the system.
 - ▶ All electron model: $m_j^a = \text{delta function}$
 - ▶ Valence electron model (view core electrons as part of the nuclei): m_j^a is (local) pseudopotential.
- ▶ Chemistry: $\{y_j, m_j^a\}$ describes a set of molecules.
- ▶ Materials: $\{y_j, m_j^a\}$ describes a deformed lattice with defects.

Local density approximation

In principle $E_{\text{xc}}[\rho]$ is a nonlocal functional depending on ρ . In the local density approximation, it is assumed that $E_{\text{xc}}[\rho]$ is a local functional:

$$E_{\text{xc}}[\rho] = \int \epsilon_{\text{xc}}(\rho(x)) dx.$$

Taking LDA, the energy functional becomes

$$F_{\text{KS}}(\{\psi_i\}) = \sum_i \frac{1}{2} \int |\nabla \psi_i|^2 + \frac{1}{2} \iint \frac{(\rho - m)(x)(\rho - m)(y)}{|x - y|} + \int \epsilon_{\text{xc}}(\rho(x)).$$

The function ϵ_{xc} is obtained from calculations of Jellium system.

$$\epsilon_{\text{xc}}(\rho) = -\rho^{4/3} + \dots$$

Developments about exchange-correlation functional

- ▶ Theoretically, it is a universal functional of the density field.
- ▶ In practice, it is obtained by physics intuition and argument, plus fitting from quantum Monte Carlo calculations.
- ▶ Examples of functional forms: Becke88, LYP, PBE, so on;
- ▶ Jacob's ladder of exchange-correlation energy: meta-GGA (TPSS), hybrid functionals (B3LYP), etc.

Question: Mathematical derivations? Which asymptotic regime?
(Burke, Friesecke, Solovej, ...)

Alternative formulations

Several alternative formulations for the Kohn-Sham density functional theory:

- ▶ orbitals or wavefunctions
- ▶ density matrix or projection operator, or subspace formulation
- ▶ density (in terms of the Kohn-Sham map)

Subspace problem

The energy functional $F_{\text{KS}}(\{\psi_j\})$ is invariant under rotations of the wave functions. More generally, define the non-orthogonal energy functional as

$$F_{\text{KS}}(\{\psi_i\}) = \sum_{ij} \frac{1}{2} \int \nabla \psi_i^* S_{ij}^{-1} \nabla \psi_j^* + \frac{1}{2} \iint \frac{(\rho - m)(x)(\rho - m)(y)}{|x - y|} + \int \epsilon_{\text{xc}}(\rho(x)).$$

with $S_{ij} = \langle \psi_i, \psi_j \rangle$ and $\rho(x) = \sum_{ij} S_{ij}^{-1} \psi_i^*(x) \psi_j(x)$. The energy functional is invariant under general non-degenerate linear transformation.

The Kohn-Sham density functional theory is a minimization over occupied subspace. The particular basis $\{\psi_j\}$ is not relevant.

Euler-Lagrange equation

The Euler-Lagrange equation of E_{KS} with respect to ψ_i gives the eigen-equations

$$H[\rho]\psi_i = \left(-\frac{1}{2}\Delta + \int \frac{(\rho - m)(y)}{|x - y|} + V_{\text{xc}}(\rho) \right) \psi_i = \epsilon_i \psi_i$$

$H[\rho]$ is the effective Hamiltonian, depends on ρ and hence on $\{\psi_i\}$. This is a self-consistent equation (nonlinear eigenvalue problem).

The effective potential (depending on ρ) consists of two parts: Coulomb and exchange-correlation.

The Kohn-Sham equation is local, unlike Hartree-Fock equation, which contains the nonlocal exchange operator.

Kohn-Sham map

Given an effective Hamiltonian $H[\rho]$, the density corresponding to the occupied states can be written as

$$\tilde{\rho}(x) = \phi_{\text{FD}}^0(H[\rho] - \mu)(x, x)$$

where $\phi_{\text{FD}}^0(x) = \chi_{x \leq 0}$ is the Heaviside function, Fermi-Dirac distribution at zero temperature. μ is the chemical potential, suitably chosen so that $\int \tilde{\rho} = N$.

The map from ρ to $\tilde{\rho}$ is called **Kohn-Sham map** F .

This is extended to the finite temperature case by taking Fermi-Dirac distribution function instead of the Heaviside function in the above (corresponds to Mermin functional).

Orbital free density functional theory

The orbital-free density functional theory is a further simplification of the Kohn-Sham DFT so that the functional only involves the density.

In particular, the kinetic energy functional is replaced by a functional depends on ρ only, approximates

$$T[\rho] = \inf_{\{\psi_j\} \mapsto \rho} \sum_j \int_{\mathbb{R}^3} |\nabla \psi_j|^2 dx.$$

- ▶ Thomas-Fermi approximation: $\int_{\mathbb{R}^3} \rho^{5/3} dx$.
- ▶ Thomas-Fermi-von Weizsäcker approximation: $\int_{\mathbb{R}^3} \rho^{5/3} dx + \int_{\mathbb{R}^3} |\nabla \sqrt{\rho}|^2 dx$ based on gradient expansion.
- ▶ Wang-Teter and Wang-Govind-Carter functionals based on linear response.

On the mathematical level, the nature of orbital-based and orbital-free DFTs are quite different.

The orbital-free DFT is more of a conventional variational problem in applied mathematics, like Landau-Lifschitz, Ginzburg-Landau, liquid crystals, nonlinear elasticity and so on.

We will focus mainly on orbital-based Kohn-Sham density functional theory from now on.

Issues of Kohn-Sham density functional theory

On the analysis side:

- ▶ Existence is not trivial due to possible loss of compactness;
- ▶ Uniqueness is not always expected as the functionals are non-convex;
- ▶ The property and structure of the solutions are not easy to investigate.

On the numerics side:

- ▶ Conventional cubic scaling algorithms is too expensive. Calls for fast algorithms and efficient parallelization to address large systems.
- ▶ Choices of discretization to achieve the balance between accuracy and efficiency;
- ▶ Issue of numerical analysis: accuracy, convergence, so on.

Existence and uniqueness results

Existence of minimizer of the energy functional:

- ▶ Existence of DFT with LDA approximation [Le Bris 1993]
- ▶ Existence of DFT with GGA approximation (one orbital case) [Anantharaman-Cances 2009]

Existence and uniqueness of finite temperature Kohn-Sham equation: [Prodan-Nordlander 2003]

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Motivation

Physical systems (solids, materials) can be modeled at different scales:

- ▶ Quantum mechanics: Many-body Schrödinger equation, electronic structure models, lattice models, ...
- ▶ Atomistic models: Molecular statics and dynamics with empirical potentials;
- ▶ Continuum theories: Elasticity, dielectricity, micromagnetism, phase field models, ...

Multiscale modeling and analysis: Understanding the connections and coupling between models on different scales.

Continuum theories

We will focus on in this talk two representatives of continuum models:

- ▶ Nonlinear elasticity:

$$\inf_u \int W(\nabla u(x)) - f(x)u(x) dx.$$

- ▶ Macroscopic Maxwell equation:

$$\nabla \cdot D = \rho_f,$$

$$\nabla \cdot B = 0,$$

$$\nabla \times E = -\partial_t B,$$

$$\nabla \times H = J_f + \partial_t D;$$

The continuum theories are obtained by physical principle (minimum action principle, conservation laws, ...) plus *empirical* constitutive relations.

Macroscopic limit

Want to understand the following questions for the connections between micro and macro models:

- ▶ How can we obtain the constitutive relations of the macroscopic models from the microscopic ones?
- ▶ When are the macroscopic models valid characterizations of the system?
- ▶ How does the failure of the macroscopic models happen?
What is the onset of breaking down?

For example, elasticity theory \rightarrow plasticity, fracture.

These questions can be addressed by studying macroscopic limit of microscopic models.

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Related works

For perfect crystal, the thermodynamic limit was studied

- ▶ for KSDFT model without exchange-correlation [Catto-Le Bris-Lions 2001].

For perfect crystal with local defects, the macroscopic limit was studied

- ▶ for KSDFT model without exchange-correlation [Cances-Deleurence-Lewin 2009, Cances-Lewin 2010].

For elastically deformed crystal, the macroscopic limit was studied

- ▶ for KSDFT model [E-Lu preprint].

Derivation of nonlinear elasticity and macroscopic electrostatic equation from DFT

For Kohn-Sham DFT, under sharp stability conditions

- ▶ The equilibrium system is insulating;
- ▶ The equilibrium system is stable with respect to plasmons;
- ▶ The effective dielectric constant for the equilibrium system is positive definite,

the electronic structure for the elastically deformed system is characterized by the Cauchy-Born rule (the electron density and local energy density is determined by the local deformation gradient).

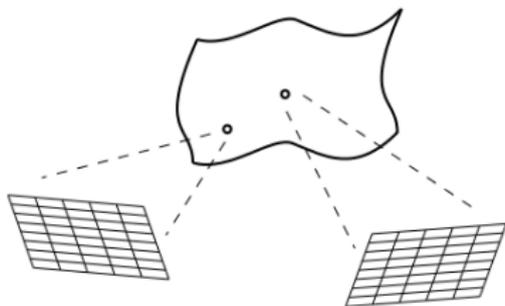
The dielectric response of the system couples with the elastic deformation (sort of piezoelectric effects), and is characterized by an effective Poisson equation.

Cauchy-Born rule for electronic structure

Cauchy-Born rule is a recipe links together micro- and macro-scale models.

Main idea: On the microscopic scale, the smooth macroscopic elastic displacement is effectively linear. Hence, at each point x , the energy density and also other physical quantities should be given by those of a system with homogeneous deformation with deformation gradient $\nabla u(x)$ (Independent of $u(x)$ due to symmetry invariance).

Cauchy-Born rule



Smoothly deformed crystal

Assumption: Atoms follow the prescribed smooth displacement field u .

At equilibrium, the atoms form a crystal εL , with underlying Bravais lattice $\varepsilon \mathbb{L}$ and unit cell $\varepsilon \Gamma$. Take a smooth Γ -periodic displacement field $u(x)$, so that under deformation the atoms are located at $Y_i^\varepsilon = X_i^\varepsilon + u(X_i^\varepsilon)$, where $X_i^\varepsilon \in \varepsilon L$.

Remarks about periodicity of u :

- ▶ The period gives the characteristic length of u : $\mathcal{O}(1)$;
- ▶ With the PBC assumption, only the bulk behavior is present. The interesting surface phenomenon (e.g., surface plasmon) is ruled out.

Continuum limit

The small parameter ε is understood as the ratio between the lattice constant (atomic length scale) and the characteristic length scale of the elastic deformation.

The continuum limit $\varepsilon \rightarrow 0$ will be considered. Physically, the atomic spacing is tiny compared to the macroscopic deformation.

Questions:

- ▶ Derivation of nonlinear elasticity from KSDFT;
- ▶ Characterization of the electronic structure for deformed crystals;
- ▶ Identification of the onset of failure of nonlinear elasticity model (sharp stability conditions).

Electronic structure for perfect crystal

At equilibrium, we assume there exists a Γ -periodic electron density ρ_e , such that

$$\rho_e(x) = F(\rho_e)(x) = \frac{1}{2\pi i} \int_{\mathcal{C}} \frac{1}{\lambda - H_e[\rho_e]} d\lambda(x, x).$$

The effective potential V_e is also Γ -periodic and one can apply the Bloch-Floquet theory

$$H_e = \int_{\Gamma^*} H_\xi d\xi, \quad H_\xi = \sum_n E_n(\xi) |\psi_{n,\xi}\rangle \langle \psi_{n,\xi}|.$$

We assume that the system under consideration is an insulator:

$$\text{dist}(\sigma_Z, \sigma(H_e) \setminus \sigma_Z) = E_g > 0$$

where $\sigma_Z = \bigcup_{n \leq Z} E_n(\Gamma^*)$. Therefore, the Kohn-Sham map is well defined (through Bloch-Floquet theory) for a compact contour \mathcal{C} encloses the occupied spectrum.

Change of coordinates

Electrons live in the Eulerian coordinates, while atoms live in the Lagrangian coordinates. For our problem (elasticity for solids), it is more convenient to put the electronic structure problem in the Lagrangian coordinates.

The deformation is given by $\tau(x) = x + u(x)$, and hence the pullback and pushforward operators between Eulerian and Lagrangian coordinates are

$$(\tau^*f)(x) = f(\tau(x)), \quad (\tau_*g)(y) = g(\tau^{-1}(y)).$$

Effective Hamiltonian operator

Hamiltonian (in the Lagrangian coordinates):

$$H_{\tau}^{\varepsilon} = -\varepsilon^2 J^{1/2} \Delta^{\tau} J^{-1/2} + V_{\tau}^{\varepsilon}(x)$$

with $\Delta^{\tau} = \tau^* \Delta_{\tau^*}$ and $J(x) = \det(\nabla \tau(x))$.

Potential (Coulomb + exchange-correlation):

$$V_{\tau}^{\varepsilon}[\rho](x) = \phi_{\tau}^{\varepsilon}[\rho](x) + \eta(J(x)^{-1} \varepsilon^3 \rho(x));$$

$$- \Delta^{\tau} \phi_{\tau}^{\varepsilon}[\rho] = 4\pi \varepsilon J^{-1}(\rho - m_{\tau}^{\varepsilon});$$

$$\int_{\Gamma} \phi_{\tau}^{\varepsilon}[\rho] dx = 0.$$

The deformation u enters through the background charge distribution:

$$m_{\tau}^{\varepsilon}(x) = J(x) \sum_{X_{\alpha}^{\varepsilon} \in \varepsilon L} \frac{1}{\varepsilon^3} m^a((\tau(x) - \tau(X_{\alpha}^{\varepsilon}))/\varepsilon)$$

Kohn-Sham equation

Look for fixed point of the Kohn-Sham map for the deformed system:

$$\rho(x) = F_{\tau}^{\varepsilon}(\rho)(x) = \frac{1}{2\pi i} \int_{\mathcal{C}} \frac{1}{\lambda - H_{\tau}^{\varepsilon}[\rho]} d\lambda(x, x).$$

Here \mathcal{C} is a fixed contour in the resolvent set of the Hamiltonian enclosing the occupied spectrum.

The right hand side is the diagonal of kernel of a operator (not in trace class), which is not *a priori* well defined. Nevertheless, it can be proved to be well defined for the cases we will consider by elliptic regularity results.

Cauchy-Born rule for electron density

For the system deformed homogeneously with deformation gradient $A = \nabla u(x_0)$, we still have a periodic problem.

By implicit function theorem + stability condition, when $|A|$ is sufficiently small, there exists a solution to the Kohn-Sham equation, denoted as $\rho_{\text{CB}}(x; A)$. Also, $\rho_{\text{CB}}(\cdot; A)$ is Γ -periodic (as defined in Lagrangian coordinates).

According the Cauchy-Born philosophy, one expects

$$\rho^\varepsilon(x) \sim \varepsilon^{-3} \rho_{\text{CB}}(x/\varepsilon; \nabla u(x)).$$

In other words, electron density is given locally by that of the homogeneous deformed system.

Locality of quantum system

Recall that the quantum mechanical model is a rather nonlocal from the first sight.

- ▶ Coulomb interaction is nonlocal;
- ▶ The Pauli exclusion principle (orthogonal constraint) is nonlocal;
- ▶ The Schrödinger eigenvalue problem is nonlocal.

Nevertheless, the Cauchy-Born rule states that the electronic structure at a point only depends on the local surrounding environment. This is related with the property of “near-sightedness” in the physics literature: for insulators, the physics is essentially local [Kohn 1996, Prodan-Kohn 2005].

Stability conditions

The Cauchy-Born rule is valid under sharp stability conditions. In other words, the electron density is well approximated by the Cauchy-Born guess, provided that the equilibrium system is *stable*:

- ▶ Stability of band gap: The equilibrium system is a band insulator.
- ▶ Stability wrt charge density wave: The linearized Kohn-Sham operator is invertible in suitable spaces.
- ▶ Stability of dielectric response: The permittivity tensor is positive definite (The effective Poisson equation is elliptic).

Stability conditions

We will assume that the electronic structure is stable, in the sense of the following two assumptions.

Assumption (Stability of charge density wave)

For every $n \in \mathbb{N}$, $\mathcal{I} - \mathcal{L}_e$ as an operator on $\dot{H}_n^{-1} \cap H_n^2$ is invertible, and the norm of its inverse is bounded independent of n :

$$\|(\mathcal{I} - \mathcal{L}_e)^{-1}\|_{\mathcal{L}(\dot{H}_n^{-1} \cap H_n^2)} \lesssim 1.$$

Assumption (Stability of dielectric response)

The effective permittivity tensor \mathcal{E} is positive definite.

Stability of dielectric response

Recall $\mathcal{E} = \frac{1}{2}(\mathbf{A}_e + \mathbf{A}_e^*) + \frac{1}{4\pi}I$ is the macroscopic permittivity tensor for the undeformed crystal.

The matrix $\mathbf{A}_e = (A_{e,\alpha\beta})$ for $\alpha, \beta = 1, 2, 3$ is given by

$$\begin{aligned} A_{e,\alpha\beta} = & -2\Re \sum_{n \leq Z} \sum_{m > Z} \int_{\Gamma^*} \frac{d\xi}{E_n(\xi) - E_m(\xi)} \\ & \times \overline{\langle \mathbf{u}_{m,\xi}, \partial_{\xi\beta} \mathbf{u}_{n,\xi} \rangle} \langle \mathbf{u}_{m,\xi}, \partial_{\xi\alpha} \mathbf{u}_{n,\xi} \rangle \\ & - \langle \mathbf{g}_{e,\alpha}, \delta_{\rho_e} \mathbf{V}_e (\mathcal{I} - \mathcal{L}_e)^{-1} \mathbf{g}_{e,\beta} \rangle, \end{aligned}$$

and

$$\begin{aligned} g_{e,\alpha}(z) = & 2\Re \sum_{n \leq Z} \sum_{m > Z} \int_{\Gamma^*} \frac{d\xi}{E_n(\xi) - E_m(\xi)} \\ & \times u_{n,\xi}^*(z) u_{m,\xi}(z) \langle \mathbf{u}_{m,\xi}, i\partial_{\xi\alpha} \mathbf{u}_{n,\xi} \rangle; \end{aligned}$$

Linearized Kohn-Sham map

Consider the linearization of the Kohn-Sham map \mathcal{F}_e at the equilibrium density ρ_e . Formally, $\mathcal{L}_e w \rightarrow \mathcal{L}_e(w)$, where

$$\mathcal{L}_e(w) = \frac{1}{2\pi i} \int_{\mathcal{C}} \frac{1}{\lambda - \mathcal{H}_e(\rho_e)} \delta_{\rho_e} V_e(w) \frac{1}{\lambda - \mathcal{H}_e(\rho_e)} d\lambda(x, x).$$

Here $\delta_{\rho_e} V_e$ is the linearized operator of $V_e(\rho)$ at ρ_e , given by (for $n\Gamma$ -periodic function w)

$$\begin{aligned} \delta_{\rho_e} V_e(w)(x) &= \delta\phi_e(w)(x) + \eta'(\rho_e)w(x); \\ -\Delta\delta\phi_e(w)(x) &= 4\pi w, \end{aligned}$$

with periodic boundary condition on $n\Gamma$ and $\int_{n\Gamma} \delta\phi_e = 0$ to fix the arbitrary constant.

Spaces of periodic functions

For a given n , define the periodic Sobolev space

$$W_n^{m,p}(\mathbb{R}^3) = \{f \in \mathcal{S}'(\mathbb{R}^3) \mid \tau_R f = f, \forall R \in n\mathbb{L}; f \in W^{m,p}(n\Gamma)\}$$

with its natural norm $\|f\|_{W_n^{m,p}(\mathbb{R}^3)} = \|f\|_{W^{m,p}(n\Gamma)}$. We will also write H_n^m for $W_n^{m,2}$. Here, $(\tau_R f)(x) = f(x - R)$.

Moreover, define the periodic Coulomb space (homogeneous Sobolev space with index -1) $\dot{H}_n^{-1}(\mathbb{R}^3)$ as

$$\dot{H}_n^{-1}(\mathbb{R}^3) = \{f \in \mathcal{S}'(\mathbb{R}^3) \mid \tau_R f = f, \forall R \in n\mathbb{L}; \sum_{k \in \mathbb{L}^*/n} \frac{1}{|k|^2} |\hat{f}(k)|^2 < \infty\}.$$

Here, $\{\hat{f}(k)\}$ denotes the Fourier coefficients of the $n\Gamma$ -periodic function f . Also the higher order spaces \dot{H}_n^{m+1} , defined by the norm

$$\|f\|_{\dot{H}_n^{m+1}(\mathbb{R}^3)} = \|\nabla f\|_{H_n^m(\mathbb{R}^3)}.$$

Analysis of the linearized Kohn-Sham map

Theorem (Uniform boundedness of \mathcal{L}_e)

The operator \mathcal{L}_e is bounded on spaces $\dot{H}_n^{-1} \cap H_n^2$ uniformly in n .

Write $\mathcal{L}_e w = \chi_e \delta_{\rho_e} V_e w$ with the polarizability operator

$$(\chi_e V)(x) = \frac{1}{2\pi i} \int_{\mathcal{C}} \frac{1}{\lambda - \mathcal{H}} V \frac{1}{\lambda - \mathcal{H}} d\lambda(x, x).$$

The proof consists of showing

- ▶ $\delta_{\rho_e} V_e : \dot{H}_n^{-1} \cap H_n^2 \rightarrow H_n^2 + \dot{H}_n^4$ is uniformly bounded;
- ▶ $\chi_e : H_n^2 + \dot{H}_n^4 \rightarrow \dot{H}_n^{-1} \cap H_n^2$ is uniformly bounded.

Polarizability operator

One may represent χ_e in more explicit terms:

$$\chi_e V = 2\Re \sum_{n \leq Z} \sum_{m > Z} \int_{(\Gamma^*)^2} \frac{d\xi d\zeta \langle \psi_{n,\xi}, V \psi_{m,\zeta} \rangle}{E_n(\xi) - E_m(\zeta)} \psi_{n,\xi} \psi_{m,\zeta}^*.$$

For example, for Jellium model ($\mathcal{H} = -\Delta$), we have

$$\widehat{\chi_e V}(k) = m(k) \widehat{V}(k),$$

where

$$m(k) = \frac{1}{8\beta\pi^2 k} \int_0^\infty \frac{d\ell}{\ell} \ln \left(\frac{1 + e^{-\beta}((\ell - k/2)^2 - \mu)}{1 + e^{-\beta}((\ell + k/2)^2 - \mu)} \right).$$

We remark that the behavior the linearized Kohn-Sham map is rather different for metal and insulator. In particular, the boundedness results only hold for insulators (due to a finite band gap).

Ingredients of the estimate for χ_e :

- ▶ $L_n^1 \rightarrow L_n^1$: Show the operator is in trace class, using

$$\|f(x)g(-i\nabla_\xi)\|_{\mathfrak{S}_p(L_n^2)} \lesssim \|f\|_{L_n^p} \|g\|_{IP(\mathbb{L}^*/n)},$$

- ▶ $L_n^\infty \rightarrow L_n^\infty$: Based on Agmon type's argument of regularity of kernel of elliptic operators.
- ▶ $H_n^2 \rightarrow H_n^2$: Estimates of commutators.
- ▶ $\dot{H}_n^1 \rightarrow \dot{H}_n^{-1}$: Based on the generalized trace class technique [Hainzl-Lewin-Séré 2005, Cancès-Deleurence-Lewin 2008].
- ▶ $\dot{H}_n^3 \rightarrow H_n^2$: Uses the “trick of projection”

$$\begin{aligned} Q_V &= \frac{1}{2\pi i} \int_{\mathcal{C}} \frac{1}{\lambda - \mathcal{H}} V \frac{1}{\lambda - \mathcal{H}} d\lambda \\ &= \frac{1}{2\pi i} \int_{\mathcal{C}} \mathcal{P} \frac{1}{\lambda - \mathcal{H}} V \frac{1}{\lambda - \mathcal{H}} \mathcal{P}^\perp d\lambda \\ &\quad + \frac{1}{2\pi i} \int_{\mathcal{C}} \mathcal{P}^\perp \frac{1}{\lambda - \mathcal{H}} V \frac{1}{\lambda - \mathcal{H}} \mathcal{P} d\lambda, \end{aligned}$$

where \mathcal{P} is the projection operator on the occupied space.

What happens when the stability condition is violated?

Instability of charge density wave (plasmon instabilities):

- ▶ Wigner crystal: Crystal formation of Fermi gas at low density
- ▶ Change of lattice structure: The electrons and nuclei may have different (and possibly incommensurate) crystal structures
- ▶ Defects formation: Possibility to have electronic defects (in analogy to crystal defects).

More on stability

There are three scales of instability in the system (electronic, atomic and continuum). Due to our assumption that the atoms follow the smooth displacement, we are only looking at the stability of electronic structure.

Without the assumption, the situation becomes more complicated. Then the system could present instability in electronic structure and also instability in atom positions (phonon analysis).

It is of interest to identify the boundary of these instabilities. Questions like whether the atomistic stability still holds while the electronic structure become unstable.

Main results

Theorem (E-Lu, preprint)

Under stability assumptions, there exist constants a , ε_0 and M , such that if $\varepsilon \leq \varepsilon_0$ and if $M_A = \sup_j \|\nabla^j u\|_{L^\infty} \leq a$, then there exists $\rho^\varepsilon \in L^\infty_\varepsilon$ with the property:

- ▶ ρ^ε is a solution to the Kohn-Sham equation:

$$\rho^\varepsilon(x) = \mathcal{F}_\tau^\varepsilon(\rho^\varepsilon)(x).$$

- ▶ $\|\rho^\varepsilon - \varepsilon^{-3} \rho_{\text{CB}}(x/\varepsilon; \nabla u(x))\|_{L^\infty_\varepsilon} \leq M\varepsilon^{1/2}$, i.e.,
 $\|\tilde{\rho}^\varepsilon - \rho_{\text{CB}}(x; \nabla u(\varepsilon x))\|_{L^\infty} \leq M\varepsilon^{1/2}$, where $\tilde{\rho}^\varepsilon(x) = \varepsilon^3 \rho(\varepsilon x)$,
and ρ^ε satisfies the normalization constraint:

$$\int_\Gamma \rho^\varepsilon(x) dx = Z\varepsilon^{-3}.$$

Theorem (E-Lu, preprint)

- ▶ *Moreover, The macroscopic potential satisfies a second-order elliptic equation of the form:*

$$\begin{aligned} A_{\alpha\beta} \partial_{x_\alpha} \partial_{x_\beta} U_0(x) + \frac{1}{4\pi} L_2 U_0(x) + B_\alpha \partial_{x_\alpha} U_0(x) \\ + D - \langle m_2(x, \cdot) \rangle = 0 \end{aligned}$$

This is a piezo-electric effect: Mechanical deformation introduces an electric potential.

Sketch of the proof

General strategy:

- ▶ Build a higher order approximated solution to the Kohn-Sham equation ρ^0 using asymptotic expansion:

$$\rho^0 = \varepsilon^{-3} \rho_{\text{CB}}(x/\varepsilon; \nabla u(x)) + \varepsilon^{-2} \rho_1(x, x/\varepsilon) + \dots$$

- ▶ Start from the approximated solution ρ^0 , use Newton iteration to find the unique fixed point nearby. The stability condition guarantees the convergence and uniformity with ε .

The overall strategy is standard, but technically both steps are non-conventional and require careful analysis.

Some remarks

- ▶ The Cauchy-Born rule for the energy and also the expression for the stored energy density follow.
- ▶ To simplify the presentation, the result is not written in its optimal form. In particular, the norm can be sharpened into $\dot{H}_\varepsilon^{-1} \cap H_\varepsilon^2$ and higher order approximation can be constructed.
- ▶ The effective permittivity at macroscopic level has been studied for undeformed crystal in reduced Hartree-Fock model in [Cances-Lewin 2010], in the cases that the amplitude of the external potential is small (linear perturbation regime).

Characterization of the occupied space

We know that for the perfect crystal, the electronic structure can be understood by Bloch-Floquet theory, which gives a clear picture. In particular, the occupied space can be represented by the Bloch wave functions $\psi_{n,\xi}(x)$.

$$H_{\xi}\psi_{n,\xi} = E_{n,\xi}\psi_{n,\xi}.$$

Another useful set of basis functions for the occupied space is Wannier functions

$$W_{n,R}(x + R') = \int_{\Gamma^*} e^{i\xi \cdot (R' - R)} \psi_{n,\xi}(x) d\xi,$$

The Wannier functions decays exponentially for band insulators [Kohn 1959, Nenciu 1983, Panati 2007].

Wannier functions for deformed crystals

How about deformed crystals that translational symmetry is broken? The Bloch-Floquet theory no longer applies. What is the generalization of Wannier functions?

Project Wannier functions for the equilibrium state onto the occupied space of the deformed system.

Let $\{W_{e,k}^\varepsilon\}$ be the set of (rescaled) Wannier functions for the equilibrium configuration. The projected Wannier functions

$$W_{\tau,k}^\varepsilon = P_\tau^\varepsilon W_{e,k}^\varepsilon$$

form a basis for the occupied space for H_τ^ε provided that the displacement is small. The functions $W_{\tau,k}^\varepsilon$ are still exponentially localized.

Cauchy-Born rule for the projected Wannier functions

Denote the center of the Wannier function for the equilibrium configuration $W_{e,k}^\varepsilon$ as centered at $c_k^\varepsilon = \varepsilon c_k$.

Take the Wannier function associated with the homogeneously deformed system: $W_{A(c_k^\varepsilon),k}^\varepsilon$ with $A(c_k^\varepsilon) = \nabla u(c_k^\varepsilon)$.

Theorem (E-Lu, 2010)

Under the same assumption as the previous theorem, we have

$$\|(I + \varepsilon^2 \Delta)(W_{\tau,k}^\varepsilon - W_{A(c_k^\varepsilon),k}^\varepsilon)\|_{L^2} \leq C\varepsilon.$$

In other words, the Cauchy-Born construction gives a good approximation to the Wannier functions of the deformed system. The Wannier functions are stable under deformation.

Example of Cauchy-Born rule for Wannier functions

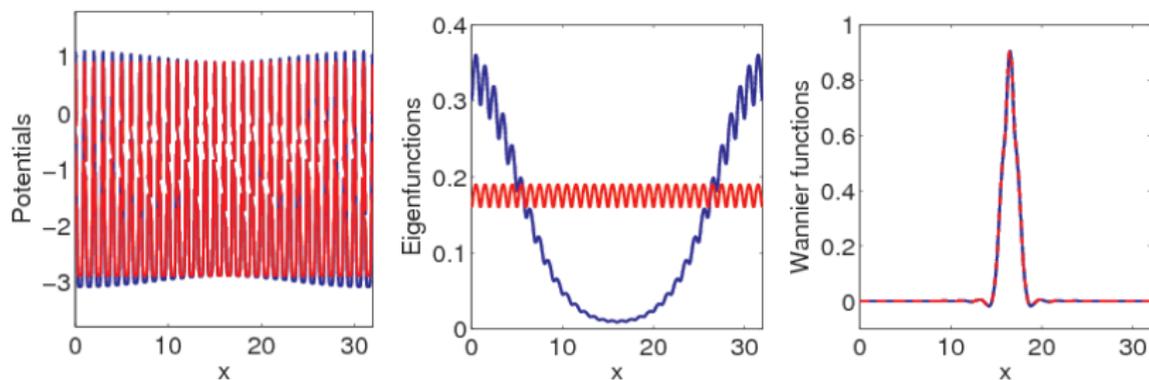


Figure: Example of Cauchy-Born rule construction of Wannier functions:
Parameter $\varepsilon = 1/32$

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Time dependent density functional theory

Time dependent (current) density functional theory:

$$i\hbar \frac{\partial \psi_j}{\partial t} = \frac{1}{2m_e} \left(-i\hbar \nabla - \frac{e}{c} (A + A_{\text{ext}}) \right)^2 \psi_j + e(V + V_{\text{ext}}) \psi_j,$$

$$-\Delta \phi = \frac{e}{\epsilon_0} (\rho - m),$$

$$\frac{1}{c} \frac{\partial}{\partial t} \left(\frac{1}{c} \frac{\partial}{\partial t} A + \nabla \phi \right) - \Delta A = \frac{e}{c\epsilon_0} J,$$

$$\nabla \cdot A = 0,$$

$$V(t, x) = \phi(t, x) + \eta(\rho(t, x)),$$

Model assumptions:

- ▶ ALDA approximation for exchange-correlation scalar potential;
- ▶ No exchange-correlation vector potential;
- ▶ Spin degeneracy is ignored.

Time dependent density functional theory (cont'd)

The electron density and current are given by

$$\rho(t, \mathbf{x}) = \sum_{j=1}^N |\psi_j(t, \mathbf{x})|^2,$$

$$\mathbf{J}(t, \mathbf{x}) = \frac{\hbar}{m_e} \sum_{j=1}^N \Im(\psi_j^*(t, \mathbf{x}) \nabla \psi_j(t, \mathbf{x})) - \frac{e}{m_e c} \rho(t, \mathbf{x}) \mathbf{A}(t, \mathbf{x}).$$

The system describes the quantum dynamics of electrons under the effect of external potentials A_{ext} and V_{ext} .

The system consists of nonlinear Schrödinger equations (many electrons) coupled with microscopic (vacuum) Maxwell equations.

Nondimensionalization and macroscopic scaling

We consider the physical situation that the external fields V_{ext} and A_{ext} are slowly varying in space. Denotes ε as the small parameter characterizing the ratio between the lattice parameter and the external fields.

$$i \frac{\partial \psi_j}{\partial t} = \frac{1}{2} (-i\varepsilon \nabla - \varepsilon(A + A_{\text{ext}}))^2 \psi_j + (V + V_{\text{ext}}) \psi_j,$$

$$-\Delta \phi = \varepsilon(\rho - m),$$

$$\frac{\partial^2}{\partial t^2} A - \Delta A + \frac{\partial}{\partial t} \nabla \phi = \varepsilon^2 J,$$

$$\nabla \cdot A = 0,$$

$$V(t, \mathbf{x}) = \phi(t, \mathbf{x}) + \eta(\varepsilon^3 \rho(t, \mathbf{x})).$$

$$\rho(t, \mathbf{x}) = \sum |\psi_j(t, \mathbf{x})|^2,$$

$$J(t, \mathbf{x}) = \varepsilon \sum \Im(\psi_j^*(t, \mathbf{x}) \nabla \psi_j(t, \mathbf{x})) - \varepsilon \rho(t, \mathbf{x}) A(t, \mathbf{x}).$$

Macroscopic limit

Assume that without external fields, the ground state of the system forms a perfect lattice and is an insulator (finite gap in the spectrum).

Questions:

- ▶ Derivation of macroscopic Maxwell equation, in particular, the constitutive relations;
- ▶ Identification of sharp stability conditions (future work);
- ▶ Dynamic coupling of elastic deformation and electromagnetic fields (future work).

[E, Lu and Yang, in press]

Macroscopic Maxwell equation

By asymptotic analysis, the following macroscopic Maxwell equation is obtained in the macroscopic limit:

$$\nabla \cdot (\mathcal{E}(\omega) \widehat{E}(\omega, \mathbf{x})) = \widehat{\rho}_{\text{ext}}(\omega, \mathbf{x}),$$

$$\nabla \cdot \widehat{B}(\omega, \mathbf{x}) = 0,$$

$$\nabla \times \widehat{E}(\omega, \mathbf{x}) = i\omega \widehat{B}(\omega, \mathbf{x}),$$

$$\nabla \times \widehat{B}(\omega, \mathbf{x}) = -i\omega \mathcal{E}(\omega) \widehat{E}(\omega, \mathbf{x}) + \widehat{J}_{\text{ext}}(\omega, \mathbf{x}),$$

with $\rho_{\text{ext}}, J_{\text{ext}}$ given by V_{ext} and A_{ext} .

Here the effective dynamic permittivity \mathcal{E} is given by the electronic structure (at equilibrium). Note that the permeability tensor is the same as in the vacuum (comments ...)

Note that the above system is written in Fourier space and is dispersive.

Dynamic permittivity tensor

We have $\mathcal{E}_{\alpha\beta}(\omega) = \delta_{\alpha\beta} + A_{e,\alpha\beta}(\omega)$.

$$\begin{aligned}
 A_{e,\alpha\beta}(\omega) &= \sum_{n \leq Z} \sum_{m > Z} \int_{\Gamma^*} \frac{d\xi}{\omega + \omega_{mn}(\xi)} \overline{\langle u_{n,\xi}, \partial_{\xi_\alpha} u_{m,\xi} \rangle} \langle u_{n,\xi}, \partial_{\xi_\beta} u_{m,\xi} \rangle \\
 &\quad - \sum_{n \leq Z} \sum_{m > Z} \int_{\Gamma^*} \frac{d\xi}{\omega - \omega_{mn}(\xi)} \langle u_{n,\xi}, \partial_{\xi_\alpha} u_{m,\xi} \rangle \overline{\langle u_{n,\xi}, \partial_{\xi_\beta} u_{m,\xi} \rangle} \\
 &\quad - \frac{2i}{\omega} \Im \sum_{n \leq Z} \sum_{m > Z} \int_{\Gamma^*} \overline{\langle u_{n,\xi}, \partial_{\xi_\alpha} u_{m,\xi} \rangle} \langle u_{n,\xi}, \partial_{\xi_\beta} u_{m,\xi} \rangle d\xi \\
 &\quad - \left\langle \mathbf{g}_{e,\omega,\alpha}, \delta_{\rho_e} V_e (\mathcal{I} - \chi_{e,\omega} \delta_{\rho_e} V_e)^{-1} \mathbf{g}_{e,\omega,\beta} \right\rangle,
 \end{aligned}$$

where we have used the shorthand $\omega_{mn}(\xi) = E_m(\xi) - E_n(\xi)$. Recall that $\delta_{\rho_e} V_e$ is the linearized effective potential operator at equilibrium.

Dynamic permittivity tensor (cont'd)

The dynamic polarizability operator $\chi_{e,\omega}$ and the vector valued functions $g_{e,\omega}$ are given by

$$\begin{aligned}\chi_{e,\omega} V &= - \sum_{n \leq Z} \sum_{m > Z} \int_{\Gamma^*} \frac{d\xi}{\omega + \omega_{mn}(\xi)} u_{n,\xi} u_{m,\xi}^* \langle u_{n,\xi}, V u_{m,\xi} \rangle \\ &\quad + \sum_{n \leq Z} \sum_{m > Z} \int_{\Gamma^*} \frac{d\xi}{\omega - \omega_{mn}(\xi)} u_{n,\xi}^* u_{m,\xi} \langle u_{m,\xi}, V u_{n,\xi} \rangle, \\ g_{e,\omega} &= - \sum_{n \leq Z} \sum_{m > Z} \int_{\Gamma^*} \frac{d\xi}{\omega + \omega_{mn}(\xi)} u_{n,\xi} u_{m,\xi}^* \langle u_{n,\xi}, i \nabla_{\xi} u_{m,\xi} \rangle \\ &\quad + \sum_{n \leq Z} \sum_{m > Z} \int_{\Gamma^*} \frac{d\xi}{\omega - \omega_{mn}(\xi)} u_{n,\xi}^* u_{m,\xi} \langle i \nabla_{\xi} u_{m,\xi}, u_{n,\xi} \rangle.\end{aligned}$$

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Self consistent iteration and direct minimization

Self consistent iteration

Look for a fixed point of the Kohn-Sham map

$$\rho = F_{\text{KS}}(\rho).$$

Direct minimization

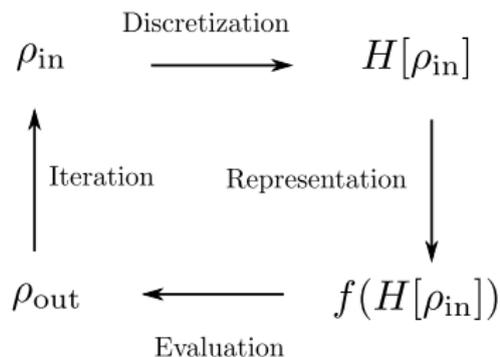
Minimize the Kohn-Sham energy functional directly

$$E_{\text{KS}}(\{\psi_i\}) = \frac{1}{2} \sum_{i=1}^N \int |\nabla \psi_i(\mathbf{x})|^2 d\mathbf{x} + \int V_{\text{ext}}(\mathbf{x}) \rho(\mathbf{x}) d\mathbf{x} + E_{\text{xc}}[\rho] \\ + \sum_{\ell} \gamma_{\ell} \sum_{i=1}^N |\langle b_{\ell}, \psi_i \rangle|^2 + \frac{1}{2} \iint \frac{\rho(\mathbf{x}) \rho(\mathbf{y})}{|\mathbf{x} - \mathbf{y}|} d\mathbf{x} d\mathbf{y}.$$

Flowchart in a general scope

Kohn-Sham map at finite temperature

$$\rho = F_{KS}(\rho) = \text{diag } f(H[\rho] - \mu) = \text{diag } \frac{2}{1 + e^{\beta(H[\rho] - \mu)}}.$$



Mixing scheme for self consistent iteration

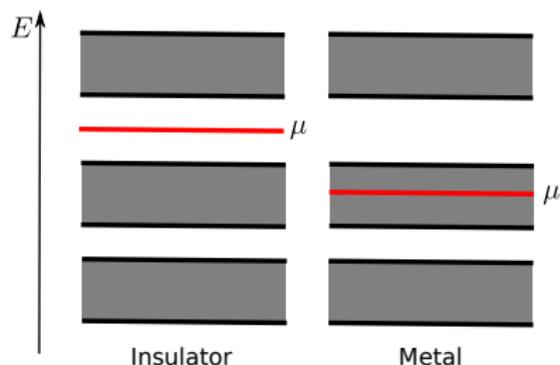
Mixing schemes can be understood in the context of solving the nonlinear equation $\rho = F_{\text{KS}}(\rho)$:

- ▶ Simple mixing (linear mixing);
- ▶ Pulay mixing [Pulay 1980];
- ▶ Quasi-Newton method: Anderson mixing [Anderson 1965], Broyden mixing [Johnson 1988] and multiseccant versions;
- ▶ Newton method [Gao, Yang and Meza preprint];

- ▶ Preconditioners: ...

Our focus in the rest of the talk will be the [evaluation of Kohn-Sham map](#): To obtain $F_{\text{KS}}(\rho)$.

General behavior of metallic and insulating system



	Insulator	Metal
Band gap	finite	0
Density matrix decay	exponential	algebraic

- ▶ General scheme for both metallic and insulating systems;
- ▶ Special $\mathcal{O}(N)$ techniques for insulating systems.

Difference between metal and insulator

Differences can be understood from several perspective:

- ▶ Localization (Linear scaling algorithms);
- ▶ Behavior of linear response (Self-consistent iteration);
- ▶ Charge screening (Multiscale methods).

Representative examples:

- ▶ Metal: Jellium model, $H = -\Delta$;
- ▶ Insulator: Array of deep narrow potentials.
Analytical solvable example?

Discretization

Conventional basis sets:

- ▶ Fourier space (Plane-wave);
- ▶ Real space (Finite difference, finite element);
- ▶ Wavelet basis (multiscale).

Atomic orbital as basis functions:

- ▶ Tight binding (parametrized atomic orbital);
- ▶ Gaussian type orbitals (GTO);
- ▶ Numerical atomic orbital (NAO) [Blum et al 2009].

Mixed basis functions with atomic orbital:

- ▶ Augmented plane-wave (APW) [Slater 1937];
- ▶ Linear augmented-plane-wave (LAPW) [Andersen 1975];
- ▶ Projector augmented-wave (PAW) [Blöchl 1994];
- ▶ Enriched finite element [Sukumar and Pask 2009].

Discontinuous basis functions

Representation

- ▶ Spectral decomposition:

$$(\text{diag } f(H[\rho]))(x) = \sum_n f(E_n) |\Psi_n(x)|^2.$$

- ▶ Fermi Operator expansion:

$$\text{diag } f(H[\rho]) \approx \sum_{i=1}^P \text{diag } f_i(H[\rho]),$$

where $f_i(H[\rho])$ are simple (polynomials, rational functions) that the matrix function can be evaluated directly.

Evaluation

Diagonalization:

- ▶ Jacobi-Davidson Diagonalization.
- ▶ Chebyshev filtering [Zhou, Saad, Tiago et al 2006]

Fermi operator expansion:

- ▶ Polynomial expansion [Goedecker and Colombo 1994]
- ▶ Rational expansion [Baroni and Giannozzi 1992] [Lin, Lu, Ying et al 2009]

Special techniques for insulators

- ▶ Divide and Conquer [Yang 1991]
- ▶ Orbital minimization [Mauri, Galli and Car 1993]
- ▶ Density matrix minimization [Li, Nunes and Vanderbilt 1993]
- ▶ Localized subspace iteration [García-Cervera, Lu and E 2007]
- ▶ Orbital minimization with localization [E and Gao 2010]

Summary of our work

- ▶ Discretization: **Discontinuous basis functions** with small number of basis functions per atom for chemical accuracy.
- ▶ Representation: **Pole expansion** for Fermi-Dirac function with optimal representation cost.
- ▶ Evaluation: **Selected inversion** technique achieving $\mathcal{O}(N)$ for quasi-1D system, $\mathcal{O}(N^{1.5})$ for quasi-2D system, and $\mathcal{O}(N^2)$ for 3D bulk system.
- ▶ Linear scaling algorithms for insulators:
 - ▶ **Localized subspace iteration**;
 - ▶ **Orbital minimization with localization**.
- ▶ Multiscale **sublinear scaling algorithms** for insulating materials with local defects.

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Existing discretization methods

Uniform grid (Fourier, real space)

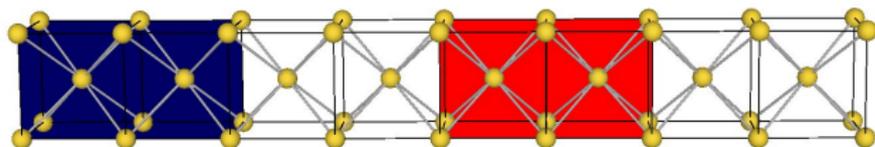
- ▶ Large number of basis functions per atom (500 ~ 5000).

Atomic orbitals and mixed basis functions:

- ▶ Fine tuning of parameters.
- ▶ Different parameters for different exchange-correlation functional.
- ▶ Overcomplete and incomplete basis sets.
- ▶ Interstitial region.
- ▶ Basis function with large support: metallic system.

Discontinuous Galerkin framework with locally adaptive basis

Goal: Construct **local** basis functions **on the fly** by **solving a small part of the system**.



- ▶ **Local solve in a buffer** to obtain basis functions **adapted to the environment**;
- ▶ **Discontinuous Galerkin** framework to discretize the system using these (discontinuous) basis functions.

See Lin Lin's talk (Thursday) for more details

DG Formulation

Minimize the DG discrete effective energy functional to get the density (for given effective potential):

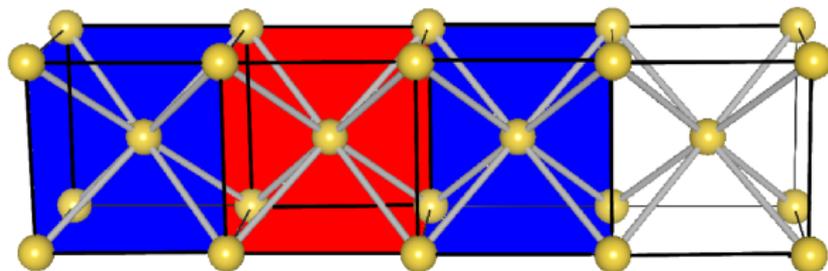
$$E_{\text{DG}}(\{\psi_i\}) = \frac{1}{2} \sum_{i=1}^N \langle \nabla \psi_i, \nabla \psi_i \rangle_{\mathcal{T}} + \langle V_{\text{eff}}, \rho \rangle_{\mathcal{T}} + \sum_{\ell} \gamma_{\ell} \sum_{i=1}^N |\langle \mathbf{b}_{\ell}, \psi_i \rangle_{\mathcal{T}}|^2 \\ - \sum_{i=1}^N \langle \{\{\nabla \psi_i\}\}, [[\psi_i]] \rangle_{\mathcal{S}} + \frac{\alpha}{h} \sum_{i=1}^N \langle [[\psi_i]], [[\psi_i]] \rangle_{\mathcal{S}}.$$

$$[[u]] = u_1 n_1 + u_2 n_2 \quad \text{on } S.$$

$$\{\{q\}\} = \frac{1}{2}(q_1 + q_2) \quad \text{on } S.$$

Constructing adaptive local basis function

- ▶ Buffer region associated with E_k : $Q_k \supset E_k$.
- ▶ Restrict the effective Hamiltonian on Q_k by assuming the periodic boundary condition on ∂Q_k and obtain H_{eff,Q_k} .
- ▶ Take the first several eigenfunctions of H_{eff,Q_k} called $\{\varphi_{k,j}\}$, $j = 1, \dots, J_k$ and restrict them on E_k .

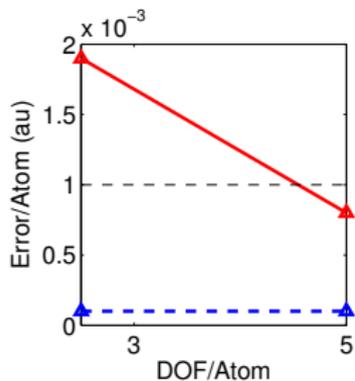


Red: E_k ;

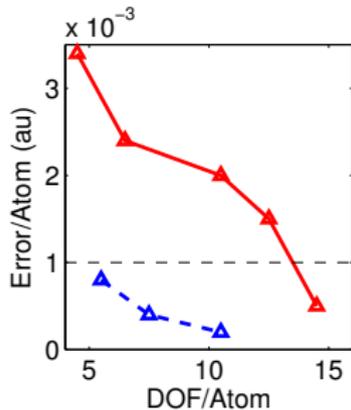
Red+Blue: Q_k

Numerical results: Accuracy

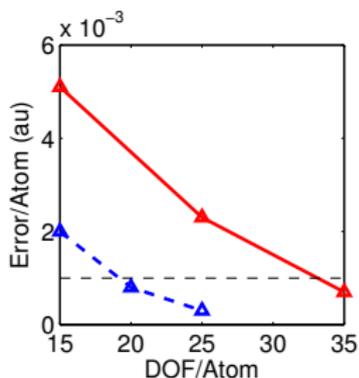
(a) Quasi-1D Na
($1 \times 1 \times 4$ Cells)



(b) Quasi-2D Na
($1 \times 4 \times 4$ Cells)

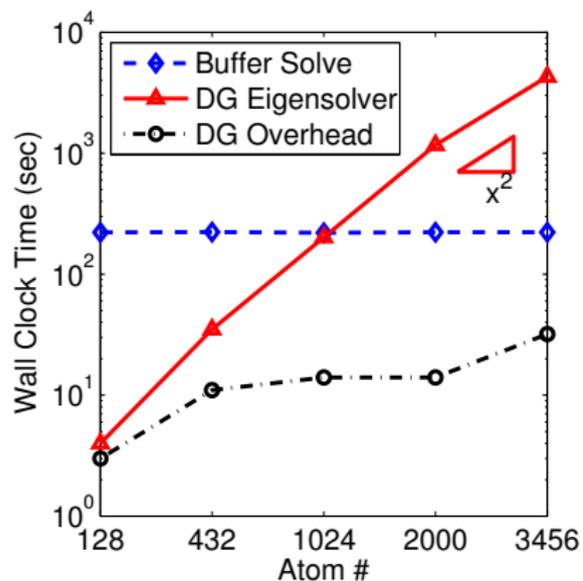


(c) Bulk 3D Na
($4 \times 4 \times 4$ Cells)



Buffer length per dimension: 2 unit cells (Red); 3 unit cells (Blue)

Numerical results: Efficiency



Computational time per processor comparison:

Atom#	Proc#	Global time	DG time
128	64	35 s	4 s
432	216	248 s	35 s

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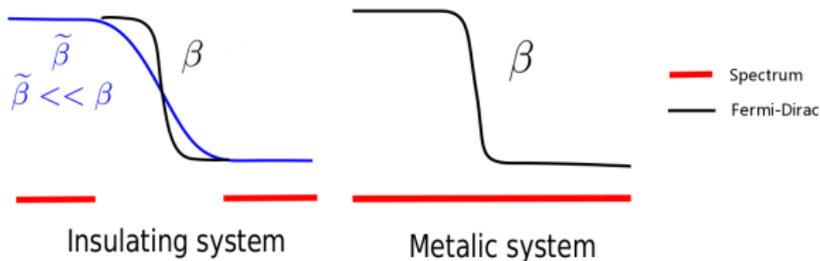
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Fermi Operator Expansion

$$\frac{2}{1 + e^{\beta(H - \mu I)}} \approx \left\{ \sum_{i=1}^P c_i \left(\frac{H - \mu I}{\Delta E} \right)^i + \sum_{i=1}^Q \frac{\omega_i}{(z_i I - (H - \mu I)/\Delta E)^{q_i}} \right\}$$

- ▶ β inverse temperature; ΔE width of the spectrum of the discretized Hamiltonian;
- ▶ Want P, Q, q_i be as small as possible given β and ΔE .



Past work

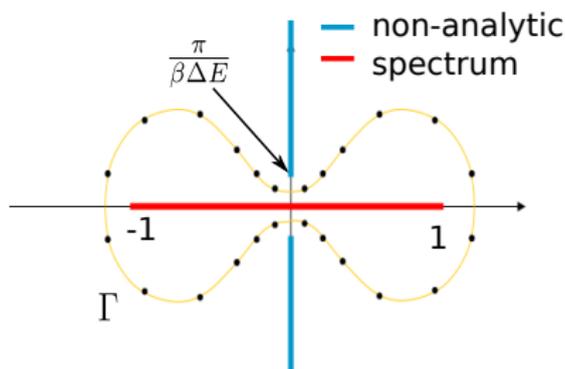
P : Number of polynomials. Q : Number of rational functions. q_i : the order of each rational function.

- ▶ $P \sim \mathcal{O}(\beta\Delta E), Q = 0$ [Goedecker and Colombo 1994];
- ▶ $P = 0, Q \sim \mathcal{O}(\beta\Delta E), q_i \equiv 1$ [Baroni and Giannozzi 1992];
- ▶ $P = 0, Q \sim \mathcal{O}(\beta\Delta E)^{1/2}, q_i \equiv 1$ [Ozaki 2007];
- ▶ $P \sim C, Q \sim \mathcal{O}(\beta\Delta E)^{1/2}, q_i \equiv 1$
[Ceriotti, Kühne and Parrinello 2008];
- ▶ **Multipole expansion**: $P \sim C, Q \sim \mathcal{O}(\log(\beta\Delta E)), q_i \sim C$
[Lin, Lu, Car and E 2009];
- ▶ **Pole expansion**: $P = 0, Q \sim \mathcal{O}(\log(\beta\Delta E)), q_i \equiv 1$
[Lin, Lu, Ying and E 2009].

Pole expansion

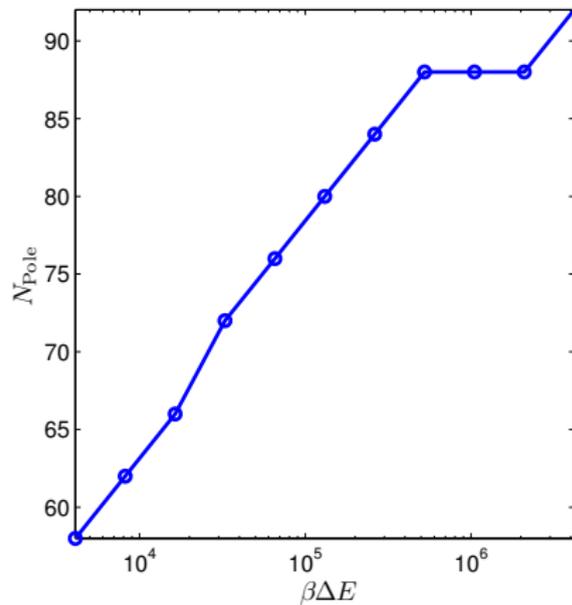
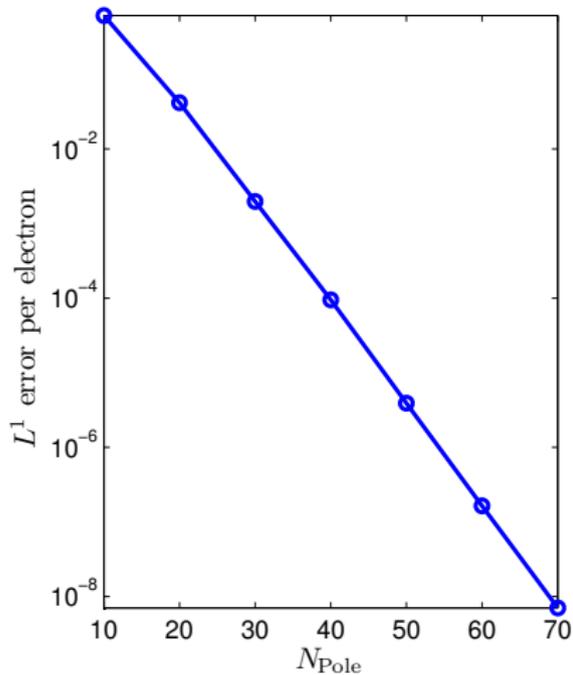
$$f(x) = \frac{2}{1 + e^{\beta\Delta E x}} = \frac{1}{2\pi i} \oint_{\Gamma} \frac{f(z)}{z - x} dz \approx \frac{1}{2\pi i} \sum_{i=1}^P \frac{f(z_i) w_i}{z_i - x}.$$

Optimal choice of the contour Γ , integration points $z_i \in \mathbb{C}$ and integration weights $w_i \in \mathbb{C} \rightarrow$ Number of discretization points $\sim \mathcal{O}(\log(\beta\Delta E))$.



Geometric convergence with small pre-constant

2D discretized Laplacian with small perturbation: energy gap around 10^{-6} au.



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Evaluate density based on the Fermi operator expansion:

$$\rho \approx \text{diag} \sum_{i=1}^P \frac{\omega_i}{z_i I - H}.$$

- ▶ Naive approach: Invert $z_i I - H$ first and then take the diagonal: cubic scaling.
- ▶ Fast diagonal extraction? Use sparse matrix algebra.
[Selected inversion](#) [Lin, Lu, Ying et al 2009]

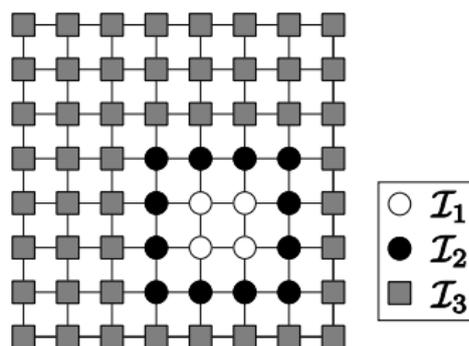
Selected inversion: Basic idea

Gauss elimination:

$$A = \begin{pmatrix} \alpha & a^T \\ a & \hat{A} \end{pmatrix} = \begin{pmatrix} 1 & \\ \ell & I \end{pmatrix} \begin{pmatrix} \alpha & \\ & \hat{A} - a\ell^T \end{pmatrix} \begin{pmatrix} 1 & \ell^T \\ & I \end{pmatrix},$$

$$A^{-1} = \begin{pmatrix} \alpha^{-1} + \ell^T S^{-1} \ell & -\ell^T S^{-1} \\ -S^{-1} \ell & S^{-1} \end{pmatrix}, \quad \ell = a\alpha^{-1}, S = \hat{A} - a\ell^T.$$

If ℓ is **sparse**, computing the $(1, 1)$ element of A^{-1} does not require all elements of S^{-1} .



Se1Inv: Selected Inversion for Sparse Symmetric Matrix

Se1Inv is a selected inversion algorithm for general sparse symmetric matrix written in Fortran
[Lin, Yang, Meza, et al, in press]

- ▶ Symbolic Analysis: matrix reordering
- ▶ LDL^T factorization
- ▶ Selected inversion

Numerical results: SelInv

Problems from Harwell-Boeing Test Collection and the University of Florida Matrix Collection.

problem	n	selected inversion time	direct inversion time	speedup
bcsstk14	1,806	0.01 sec	0.13 sec	13
bcsstk24	3,562	0.02 sec	0.58 sec	29
bcsstk28	4,410	0.02 sec	0.88 sec	44
bcsstk18	11,948	0.24 sec	5.73 sec	24
bodyy6	19,366	0.09 sec	5.37 sec	60
crystm03	24,696	0.78 sec	26.89 sec	34
wathen120	36,441	0.34 sec	48.34 sec	142
thermal1	82,654	0.44 sec	95.06 sec	216
shipsec1	140,874	17.66 sec	3346 sec	192
pwtk	217,918	14.55 sec	5135 sec	353
parabolic_fem	525,825	20.06 sec	7054 sec	352
tmt_sym	726,713	13.98 sec	> 3 hours	> 772
ecology2	999,999	16.04 sec	> 3 hours	> 673
G3_circuit	1,585,478	218.7 sec	> 3 hours	> 49

Parallel implementation

5-pt discretization of 2D Laplacian operator:

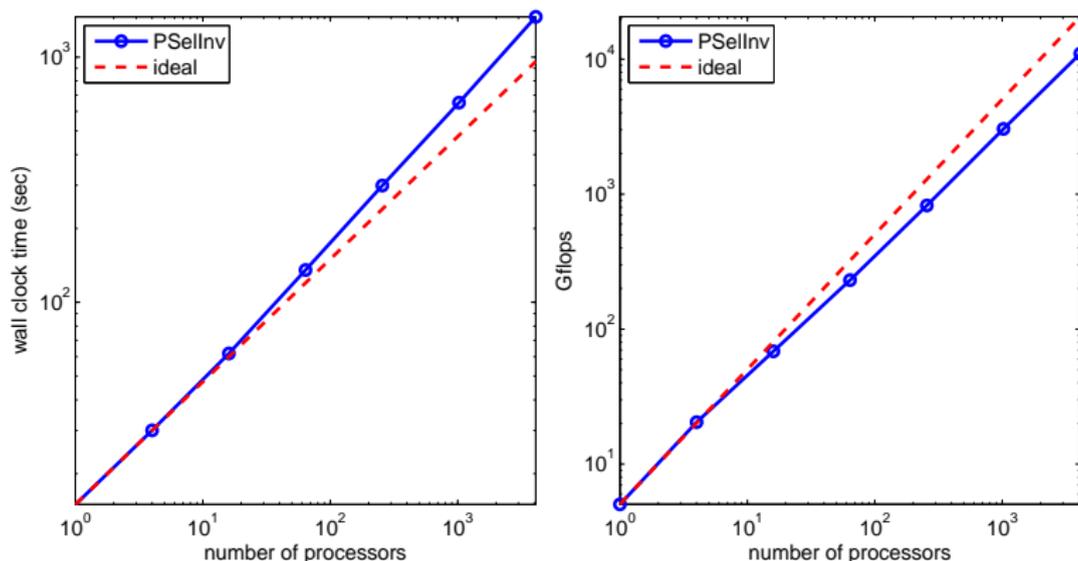


Figure: Log-log plot of total wall clock time and total Gflops with respect to number of processors, compared with ideal scaling. The largest matrix solved has $(4.3 \text{ billion})^2$ degrees of freedom.

[Lin, Yang, Lu, et al, preprint]

Conclusion and Outlook

Summary

- ▶ Understanding the macroscopic limit of the Kohn-Sham density functional theory, based on sharp stability conditions:
 - ▶ Nonlinear elasticity;
 - ▶ Macroscopic Maxwell equations;
- ▶ Algorithmic development for metallic systems
 - ▶ Discontinuous Galerkin framework with locally adapted basis;
 - ▶ Fermi operator expansion with optimal scaling;
 - ▶ Selected inversion for sparse discrete Hamiltonian matrix;
- ▶ (not mentioned) Linear and sublinear scaling algorithms for density functional theory.

Density functional theory is a challenge and opportunity for applied mathematicians. Many open questions remain on both analytical and numerical sides.