FAST NUMERICAL METHODS FOR ELECTRONIC STRUCTURE CALCULATIONS

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Outline

- Materials defects and electronic structure
- Fast DFT based electronic structure methods
 - The self consistent field iteration (SCF) and constrained minimization
 - Fast spectral projector approximation via pole expansion and selected inversion (PEXSI)
 - Preconditioner for accelerating SCF
- Examples

Material Defects

- Solids are not perfect crystals
- Defect types:
 - Point defects: vacancy, interstitials, substitutional impurities
 - Line defects: dislocations
 - Surface defects: grain boundaries and interfaces
 - Intrinsic vs extrinsic (impurities)
- Understanding defect:
 - Structure stability
 - Chemical properties
 - Electronic structure
 - Defect mediated diffusion



Studying defects from first principles

Formation energy:

$$\epsilon_f = \lim_{N \to \infty} \left[E_{\nu}(N-1) + \frac{E_0(N)}{N} \right] - E_0(N)$$

- Requires a larger unit cell with many atoms
 - Perfect solid

$$H = \begin{pmatrix} H_{11} & H_{12} & \cdots \\ H_{21} & H_{22} & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix} \xrightarrow{\text{Bloch transformation}} \begin{pmatrix} \widehat{H}_{11} & & \\ & \widehat{H}_{22} & \\ & & \ddots \end{pmatrix}$$

- Solid with defects
 - Supercell with many atoms (hundreds to millions)
 - Need computational tools to compute electronic structure of many-atom systems.

Body Centred

Electronic structure

• Many-electron Schrodinger's equation $H\Psi(r_1, r_2, ..., r_{n_n}) = \Psi(r_1, r_2, ..., r_{n_n})E$

where

$$H = -\sum_{i}^{n_e} \nabla_i^2 + \sum_{i}^{n_e} v_n(r_i) + \frac{1}{2} \sum_{i \neq j} \frac{1}{|r_i - r_j|}$$

• Ground state E_0 vs excited states E_1 , E_2 ...

- $|\Psi_i|^2$ gives the probability density of find electron *i* at r_i
- Electron density $\rho(r_1) = \int dr_2 \cdots dr_{n_e} |\Psi(r_1, r_2, \dots, r_{n_e})|^2$ (contains all information such as chemical bonding, energy etc.)

Solving the electronic structure problem

Solving the Schrodinger equation directly is prohibitively expensive, $O(d^{3n_e})$ degrees of freedom. $d = 10, n_e = 16, d^{3n_e} = 10$ trillion variables

 Wavefunction methods: choose a suitable manybody basis {Φ_i}, and expand the eigenfunction in this basis:

$$\Psi = \sum_{i}^{m} c_{i} \Phi_{i}$$

hopefully *m* is much less than
10 trillion
Solve a linear eigenvalue

problem

$$\widehat{H}c = cE$$

 Density functional theory (DFT): independent particle in a mean field:

$$H\psi_i = \varepsilon_i \psi_i,$$

$$\rho = \sum_{i=1}^{n} |\psi_i|^2$$

$$H = -\nabla^2 + V(r, r')$$

V(r,r') has to capture the electrostatic interaction between an electron and background charge density as well as correlation effects

Kohn-Sham DFT: a nonlinear eigenvalue problem

Total energy minimization

$$\min E_{tot} [\{\psi_i\}_{i=1}^N] = \frac{1}{2} \sum_{i=1}^N \int dx \ |\nabla \psi_i(x)|^2 + \int dx \ V_{ion}(x) \rho(x) + \frac{1}{2} \int dx \int dx' \frac{\rho(x)\rho(x')}{|x - x'|} + E_{xc}[\rho] \rho(x) = \sum_{i=1}^N |\psi_i(x)|^2, \qquad \int dx \ \psi_i^*(x)\psi_j(x) = \delta_{ij}, \qquad x \in \mathbb{R}^3$$

Euler-Lagrange equation

$$H[\rho]\psi_i(x) = \left(-\frac{1}{2}\Delta + V_{ion} + \int dx' \frac{\rho(x')}{|x - x'|} + V_{xc}[\rho]\right)\psi_i(x) = \varepsilon_i\psi_i(x)$$

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

Numerical algorithms

- Discretization: minimize the number of degrees of freedom per atom while maintaining sparsity and accuracy
 - Basis expansion $\psi_j = \sum_{i=1} \alpha_i \phi_i$
 - Basis with local support = sparse matrix operator $\int \phi_i(r) H \phi_j(r) dr = 0$?
 - Domain decomposition

• Nonlinear equation solver: $\rho = f(\rho)$

Newton's method : $\rho_{k+1} = \rho_k - J^{-1}(\rho_k)[f(\rho_k) - \rho_k]$

- Cheap and effective approximation of the Jacobian inverse
- ✓ Fast evaluation of $f(\rho)$

Strategies for solving finite-dimensional KSDFT

Nonlinear minimization problem

$$\min_{X^*X=I} \frac{1}{2} \operatorname{trace}[X^T H_0 X] + \rho^T L^{-1} \rho / 4 + E_{xc} (\rho)$$
$$\rho = \operatorname{diag}(X X^T)$$

First-order necessary condition.

$$H(\rho(X))X = X\Lambda, \ X^{T}X = I$$

where $H(\rho(X)) = H_0 + \text{Diag}(L^{-1}\rho) + V_{xc}(\rho)$



Aufbau principle: take eigenvector associated with the algebraically smallest eigenvalues

 $\mathcal{V}(\rho)$

Self consistent field iteration

 $H[\rho]X = (H_0 + L^{-1}\rho + V_{xc}(\rho))X = X\Lambda$



Fixed point iteration for density or potential

 $\mathcal{V}[\rho] = L^{-1}\rho + V_{xc}[\rho]$

 $\rho = f(\rho)$ Density fixed point

$$\cdots \Rightarrow \rho_k \Rightarrow V_k \equiv \mathcal{V}[\rho_k] \Rightarrow \rho_{k+1} \Rightarrow V_{k+1} \Rightarrow \cdots$$

Potential fixed point

$$V = \mathcal{V}(V)$$

Will focus on potential fixed point for this talk

The fixed-point (Kohn-Sham) map for V

$$V_{out} = \mathcal{V}[F[V_{in}]]$$

- Fixed point solution: $V^* = \mathcal{V}[F[V^*]]$
- From ρ to V:

$$\mathcal{V}[\rho] = L^{-1}\rho + V_{xc}[\rho]$$



• From V to ρ through spectral projector

• $\rho = F[V] = \operatorname{diag}(XX^T) = \operatorname{diag}(\operatorname{step}(H)) \approx \operatorname{diag}(I + e^{\beta(H[V] - \mu)})^{-1}$

- $\beta = 1/k_BT$: inverse temperature
- μ : Chemical potential

Seeking the fixed point

Fixed point iteration (rarely converges)

 $V_{k+1} = \mathcal{V}[F[V_k]]$

Newton's method

$$V_{k+1} = V_k - J^{-1}[V_k] \cdot R_k, \ R_k = \mathcal{V}[F[V_k]] - V_k$$

Quasi-Newton method

$$V_{k+1} = V_k - C_k R_k$$
, where $C_k \approx J_k^{-1}$

Fast algorithm

- Reduce the cost of function evaluation
 - $\mathcal{V}[F(V_k)]: V_k \to H(V_k)X = X\Lambda \to \operatorname{diag}(XX^*) \to V_{k+1} = L^{-1}\rho + V_{xc}(\rho)$
 - Complexity: $O(n_e^3)$

• $XX^* = (X X^{\perp}) \begin{pmatrix} I \\ 0 \end{pmatrix} \begin{pmatrix} X^* \\ X^{\perp^*} \end{pmatrix} = f(H)$ matrix function, but we don't need all of f(H)

- Reduce the number of Quasi-Newton iteration by constructing a good approximation to J^{-1}
 - Analytic expression not feasible
 - Maybe possible to compute *Jw* for some vector *w*

Function Evaluation via Spectra Decomposition

- Density evaluation $\rho = F[V] = \text{diag}(XX^*)$
 - Partially diagonalize H[V]
 - Methods (Block methods preferred):
 - Lanczos
 - Davidson

 $O(n_e^3)$ complexity

- LOBPCG
- Polynomial filtered subspace iteration
- Practical issues:
 - Take advantage of good starting guess
 - Take advantage of good preconditoner
 - Set appropriate convergence criterion
- Potential evaluation $\mathcal{V}[\rho] = V_{ion} + L^{-1}\rho + V_{xc}[\rho]$ $O(n_e) \text{ or } O(n_e \log(n_e)) - LV_H = \rho$



Function Evaluation via Fermi Operator Expansion

Pole expansion

$$XX^* = \oint_C (H - zI)^{-1} dz \approx Im \left[\sum_i^M \omega_i (H - z_i I)^{-1} \right]$$



Choose a special contour to minimize the number of quadrature points (L. Lin et al. 2010)

- Selected Inversion:
 - Compute the diagonal of $(H z_i I)^{-1}$ without computing the full inverse
 - Applicable if *H* is sparse (i.e. not applicable to planewave discretization)
 - Need to perform sparse factorization of $H z_i I$
 - Multiple levels of parallelism

 $O(n_e)$ for 1D, $O\left(n_e^{3/2}\right)$ for 2D, $O(n_e^2)$ for 3D

Takahashi 1973, Erisman & Tinney 1975, Li et al (2008), Lin et al (2009), Amestoy (2010)

Selected Inversion

Given an LDL^T factorization

$$H = \begin{pmatrix} 1 \\ \ell & I \end{pmatrix} \begin{pmatrix} \alpha \\ & S \end{pmatrix} \begin{pmatrix} 1 & \ell^T \\ & I \end{pmatrix}$$

Inverse of H

$$H^{-1} = \begin{pmatrix} \alpha^{-1} + \ell^T S^{-1} \ell & -\ell^T S^{-1} \\ -S^{-1} \ell & S^{-1} \end{pmatrix}$$

Observations:

- If ℓ is sparse, we do not need the entire S⁻¹in order to obtain the (1,1) entry of H⁻¹;
- Complexity: $O(n_e)$ for 1D, $O(n_e^{3/2}) 3/2$ for 2D, for 3D $O(n_e^2) 2$;
- For insulators, the off-diagonal entries of S^{-1} may be so small that they can be truncated to yield O(N) complexity

Example





Parallelization

 Multiple levels of parallelism





group *i*

pselinv at pole *i* $(H - z_i I)^{-1}$

$$XX^* \approx Im\left[\sum_{i}^{M} \omega_i (H - z_i I)^{-1}\right]$$

 Parallelism within selected inversion

 P_1

 P_4

 P_7

 P_{10}

 P_2

 P_5

 P_8

 P_{11}





Performance

Box of water

- SIESTA+PEXSI
- 24,000 atoms
- Matrix dimension 184,000
- Sparsity (0.15%/8.4%)



Linear Scaling

- The "near-sightedness" principle (Kohn, Prodan & Kohn)
- Decay properties of the projector operator (J. Lu 2010, M. Benzi et al. 2012)
- Algorithmic design:
 - Localization of the basis (Wannier functions) and truncation of the density matrix
 - Divide-and-conquer (e.g., LS3DF)
- Linear scaling can be achieved for insulators and semiconductors in selected inversion through incomplete factorization and approximate inverse
- Linear scaling cannot be achieved for metals without losing accuracy in general

A true linear scaling algorithm requires the number of SCF iterations to be independent from the system size

The Convergence of SCF

- Fixed point iteration converges from any starting point if the Kohn-Sham map is a global contraction $\|\mathcal{V}[F[V]] \mathcal{V}[F[W]]\| < \|V W\|$
- If the initial guess of V is sufficiently close to V*, fixed point iteration converges if $\sigma(J) < 1$ in the neighborhood of V*
- If the V is sufficiently close to V*, Newton's method converges quadratically, but each step may be expensive.
- Quasi-Newton method with approximate Jacobian and preconditioning leads to linear convergence in general. We want the convergence rate to be independent of system size (unit cell size, number of atoms)

Example



- Sodium (Na) bar with a large amount of vacuum (Metal+Vacuum)
- Solved by KSSOLV package [Yang-Meza-Lee-Wang, 2009]

Convergence



Linearization and local convergence

Fix point iteration: $V_{k+1} = \mathcal{V}[F[V_k]]$

• Linearization around V^* , define error $\delta V_k = V_k - V^*$

$$\delta V_{k+1} = V_{k+1} - V^* = \mathcal{V} \Big[F[V_k] \Big] - \mathcal{V} \Big[F[V^*] \Big] = \frac{\delta^* \mathcal{V}}{\delta \rho} \cdot \frac{\delta F}{\delta V} \cdot \delta V_k$$

- Error goes to 0 if $|\lambda(J)| < 1$
- Properties of J depends on

•
$$\frac{\delta V}{\delta \rho} = L^{-1} + \frac{\delta V_{xc}}{\delta \rho} \equiv L^{-1} + K_{xc}$$

• $\frac{\delta F}{\delta V} \equiv \chi$: independent particle polarizability matrix

Jacobian J

Spectral radius of the Jacobian

- $\sigma(J) = \left\| \frac{\delta v}{\delta \rho} \chi \right\| \le \left\| \frac{\delta v}{\delta \rho} \right\| \cdot \|\chi\|$ global convergence guaranteed if $\sigma(J) < 1$
- Use Fourier analysis
 - $\frac{\delta v}{\delta \rho} = L^{-1} + K_{\chi c}$ is dominated by L^{-1} . So $\lambda \left(\frac{\delta v}{\delta \rho}\right) \sim C \frac{4\pi}{q^2} = \frac{C\ell^2}{\pi}$, where ℓ is the unit cell size.

•
$$\chi = 2 \sum_{n=1}^{N} \sum_{m=N+1}^{\infty} \frac{(\psi_n \odot \psi_m)(\psi_n \odot \psi_m)T}{\varepsilon_n - \varepsilon_m}$$

- $\lambda(\chi) \sim -\gamma < 0$ for metal;
- $\lambda(\chi) \sim -\beta q^2$ for insulator;

 $\sigma(J)$ is bounded for insulator, but the bound may not be less than 1, and grows with system size for metals

Quasi-Newton Methods

•
$$V_{k+1} = V_k - C_k r_k$$
, where $C_k \approx J_{r(k)}^{-1}$, $J_r = I - J(V_k)$
• $r_k = V_k - \mathcal{V}[F[V_k]]$
• Let $s_k = V_k - V_{k-1}$, $y_k = r_k - r_{k-1}$
 $C_k = \operatorname{argmin} \frac{1}{2} ||C - C_{k-1}||_F^2$
s.t. $S_k = CY_k$
 $S_k = (s_k s_{k-1} \cdots s_{k-l})$, $Y_k = (y_k y_{k-1} \cdots y_{k-l})$
 $V_{k+1} = V_k - C_{k-1} r_k - (S_k - C_{k-1} Y_k) Y_k^+ r_k$
What to use for C_0 ?

Choosing $C_0 = \alpha I$ yields the Anderson method (works well for insulators, but not for metals)

How to improve?

- Construct a better C_0 (better approximation to J_r^*);
- Subtracting the exact solution V_* from both sides of $V_{k+1} = V_k - C_0(\mathcal{V}[F(V_k)] - V_k)$ yields $\delta V_{k+1} = (I - C_0 J_r) \delta V_k$ So C_0 can be viewed as a preconditioner for a preconditioned fixed point iteration
- Should choose C_0 such that $\sigma(I C_0 J_r) < 1$

Elliptic preconditioner

- Want C_0 to be approximately $J_r^{-1} = (I + L^{-1}\chi)^{-1}$
- Apply C_0 to w_k amounts to approximately solving $(I + L^{-1}\chi)z_k = w_k$ or $(L + \chi)z_k = Lw_k$

$$(-\nabla \cdot (a(x)\nabla) + 4\pi b(x))z_k = -\Delta w_k$$

Choose a(x) and b(x) based on the property of χ :

- $a(x) = 1 + 4\pi\beta$, b(x) = 0, simple insulator with optimal mixing coefficient
- a(x) = 1, $b(x) = \gamma$, simple metal
- a(x), b(x) can be spatially dependent for metal + insulator.
- $a(x) \ge 1, b(x) \ge 0 \Rightarrow A$ is an elliptic operator and semi-positive definite.
- Standard method to achieve O(N) scaling for elliptic preconditioner: Multigrid, FMM, H-matrix, HSS etc.

Convergence



Application: Electronic Structure and Aromaticity of Graphene Nanoflakes





- Edge type:
 - zigzag (ZZGNF)
 - Armchair (ACGNF)
- Electron count: 4N or 4N+2
- Size: up to 20 nm
- Interested in:
 - Stability
 - Energy gap (electric conductivity)
 - Bonding patterns (aromaticity)
 - Edge effects

Results

GNF	# atoms	ncpus	PEXSI (sec)	EIGEN (sec)
$C_{180}H_{36}$	216	160	3.6	2.4
$C_{684}H_{72}$	756	640	7.6	21.6
$C_{2222}H_{132}$	2,376	640	25.3	125.6
$C_{111400}H_{300}$	11,700	2,560	183	4,321



$$E_{ef} = E_{GNF} - N_c E_C$$
(graphene) $- N_H E_H(H_2)$



SEI Layer in Li-ion Battery MD Simulation



Scientific questions:

- What are the chemical mechanisms of solidelectrolyte interphase (SEI) formation?
- How does the composition of the electrolyte affect interface/interphase reactivity and mass transport to the interface?
- ✓ How does the molecular structure of the electrolyte change near the anode interface and affect SEI formation and evolution?
- What fundamental chemical insights can be used for future design of electrolyte/anode systems, from knowledge of the mechanism of SEI formation and the relation to electrolyte structure, dynamics, and interface reactivity?

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Computation challenge

Ab initio (quantum) molecular dynamics



- Current performance: for 10,000-atom 3D systems
 - tens of minutes per MD step
 - months for a picosecond trajectory
- Goal: 1 minute per MD step, days per trajectory

Conclusion

- Solving Kohn-Sham DFT Nonlinear Eigenvalue Problem is equivalent to finding a fixed point of the Kohn-Sham map
- Acceleration techniques for:
 - Reducing function evaluation cost
 - Reducing the number of SCF iterations by providing a better precondtioner (via solving a variable coefficient elliptic PDE)
- Enable the analysis of large-scale nanosystems and complex materials
- More needs to be done to reduce QMD time
 - How to reuse PEXSI from one SCF iteration to another