Optimization for Electronic Structure Calculation

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Electronic Structure Calculation

N particle Schrödinger equation: Physics of material systems — atomic and molecular properties, almost correct (nonrelativistic) physics is quantum mechanics

(a) Thanks: Hege et. al. ZIB Berlin

(b) Thanks: Reinhold Schneider

Numerical simulation of material on atomic and molecular scale
Main goal: Given atomic positions \( \{R_\alpha\}_{\alpha=1}^M \), compute the ground state electron energy \( E_e(\{R_\alpha\}) \).

Ground state electron wavefunction \( \psi_e(r_1, \ldots, r_N; \{R_\alpha\}) \):

\[
\begin{align*}
\left( -\frac{1}{2} \sum_{i=1}^N \Delta_i - \sum_{\alpha=1}^M \sum_{j=1}^N \frac{Z_\alpha}{|r_i - R_\alpha|} + \frac{1}{2} \sum_{i,j=1, i \neq j}^N \frac{1}{|r_i - r_j|} \right) \psi_e \\
= E_e(\{R_\alpha\}) \psi_e
\end{align*}
\]

Curse of dimensionality: Computational work goes as \( 10^{3N} \), where \( N \) is the number of electrons.
Density Functional Theory (DFT)

- The unknown is simple — the electron density $\rho$
- Hohenberg-Kohn Theory (1964)
  - There is a unique mapping between the ground state energy from Schrödinger equation and the electron density
  - Exact form of the functional is unknown
- Independent particle model
  - Electrons move independently in an average effective potential field
  - Add correction for correlation
- Best compromise between efficiency and accuracy. Most widely used electronic structure theory for condensed matter systems.
Kohn-Sham Formulation

- Replace many-particle wavefunctions, $\Psi_i$, with single particle wavefunction, $\psi_i$
- Write Kohn-Sham total energy as

$$E_{KS}(\{\psi_i\}) = \frac{1}{2} \sum_{i=1}^{n_e} \int_\Omega |\nabla \psi_i|^2 + \int_\Omega V_{ion}(\rho)$$

$$+ \frac{1}{2} \int_\Omega \frac{\rho(r)\rho(r')}{|r - r'|} \, drdr' + E_{xc}(\rho)$$

$$\rho(r) = \sum_{i=1}^{n_e} |\psi_i(r)|^2, \int_\Omega \psi_i\psi_j = \delta_{i,j}$$

- Exchange-correlation term, $E_{xc}$, contains quantum mechanical contribution, plus, part of K.E. not converged by first term when using single-particle wavefunctions
Towards Large-scale Simulation

Thanks: Taisuke Ozaki

A DFT calculation of thousands of atoms is still a grand challenge.

$O(N^3) \rightarrow$ Low-order

$10^2$ atom

Lots of successes.
Even material design is attempted with success.

$10^3 - 10^4$ atom

Carbon nanotube

DNA

Functional protein

Time scale

System size
**Discretized Kohn-Sham Formulation**

- **Goal**: find ground state energy/density by minimizing $E_{KS}$.
- **Finite dimensional problem**:

$$\min_{X^*X=I} E_{KS}(X) := E_{\text{kinetic}}(X) + E_{\text{ion}}(X) + E_{\text{Hartree}}(X) + E_{xc}(X),$$

where $X \in \mathbb{C}^{K \times N}$,

$$E_{\text{kinetic}}(X) = \frac{1}{2} \text{tr}(X^* LX)$$

$$E_{\text{ion}}(X) = \text{tr}(X^* V_{ion} X) + \sum_i \sum_l |x_i^* w_l|^2$$

$$E_{\text{Hartree}}(X) = \frac{1}{2} \rho(X)^\top L^\dagger \rho(X)$$

$$E_{xc}(X) = e^\top \epsilon_{xc}(\rho(X)), \quad e = (1, \ldots, 1)^\top$$

$$\rho(X) = \text{diag}(XX^*) = (\sum_{j=1}^N |x_{ij}|^2)_{1 \leq i \leq K}$$
KKT Conditions

- Lagrange function: \( L(X, \Lambda) = E_{KS}(X) - \frac{1}{2} \text{tr}(\Lambda(X^*X - I)) \)

- First-order optimality conditions:
  \[
  \begin{cases}
    \nabla_X L(X, \Lambda) = 0, \\
    X^*X = I,
  \end{cases}
  \implies \begin{cases}
    H(X)X = X\Lambda, \\
    X^*X = I.
  \end{cases}
  \]

- \( \Lambda = X^*H(X)X \), not necessarily a diagonal matrix

- Kohn-Sham Hamiltonian:
  \[
  H(X) := \frac{1}{2} L + V_{\text{ion}} + \sum_i w_i w_i^* + \text{diag} \left( \Re(L^\dagger)\rho(X) + \partial_\rho \epsilon_{xc}(\rho(X))^\top e \right).
  \]
Orbital Free DFT (OFDFT)

- Expresses the system by only using the charge density
- Avoids computing $N$ eigenpairs
- Pros: main group elements and nearly-free-electron-like metals
- Cons: not for covalently bonded and ionic systems

Orbital Free total energy:

$$E_{OF}(\rho) = T_{OF}(\rho) + E_{ext}(\rho) + E_H(\rho) + E_{xc}(\rho) + E_{ll}$$

$T_{OF}(\rho)$: kinetic energy density functional (KEDF)

$$T_{TFW}(\rho) = C_{TF}T_{TF}(\rho) + \mu T_{vW}(\rho),$$

$$T_{LR}(\rho) = T_{TF}(\rho) + \mu T_{vW}(\rho) + C_{TF} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} K(r - r')\rho^\alpha(r)\rho^\beta(r')drdr'$$

Other terms are the same as KSDFT
Orbital Free DFT (OFDFT)

- Variational problem

\[
\inf \ E_{OF}(\rho) \text{ s.t. } \rho \in L^1(\mathbb{R}^3), \ \rho^{\frac{1}{2}} \in H^1(\mathbb{R}^3), \ \rho \geq 0, \ \int_{\mathbb{R}^3} \rho(r)dr = N.
\]

- KKT Conditions:

\[
\begin{align*}
\mathcal{H}_{OF} \varphi &\triangleq \left( -\frac{\mu}{2} \Delta + \frac{\delta \left( T_{OF}(\rho) - \mu T_{vW}(\rho) \right)}{\delta \rho} + V_{eff}(\rho) \right) \varphi = \lambda \varphi, \\
\int_{\mathbb{R}^3} \varphi^2 &= N,
\end{align*}
\]

- Discretized Form:

\[
\min_{c \in \mathbb{R}^n} E_{OF}(\rho(c)), \quad \text{s.t.} \quad c^\top Bc = 1.
\]
Self Consistent Field Iteration (SCF)

SCF Algorithm:

1. Find the $p$-smallest eigenpairs $(X, \Lambda)$:

$$H(\rho_k)X = X\Lambda$$
$$X^*X = I$$

2. Calculate $\rho_{out}(X) = \text{diag}(XX^*)$.

3. $\rho_{k+1} = (1 - \alpha)\rho_k + \alpha\rho_{out}$.

4. Increment $k$ and go to step 1 until $\rho_{k+1} - \rho_k$ is small enough.

Our motivation:

- Computation for the linear eigenvalue problem can be expensive
- Convergence of SCF is not clear
- Optimization Algorithms for solving DFT directly?
Consider

$$\min E(X), \quad \text{subject to} \quad X^\top X = I.$$ 

At iteration $i$

$$X^{(i+1)} \leftarrow \text{Orthogonalize} \leftarrow X^{(i)} - \sigma W^{(i)} X^{(i)}$$

$$X^{(i+1)} \leftarrow \text{solution } Y(\tau) \text{ of } Y = X^{(i)} + \frac{\sigma}{2} W^{(i)} (X^{(i)} + Y)$$

- $W^{(i)}$ is a skew-symmetric matrix defined by

$$W^{(i)} = \nabla E(X^{(i)}) \left(X^{(i)}\right)^* - X^{(i)} \left(\nabla E(X^{(i)})\right)^*$$

- $[Y^{(i)}]'(0) = -W^{(i)}X^{(i)} = \text{tangential part of } -\nabla E(X^{(i)})$
Understanding SCF: the Hessian of $E_{KS}$

Convenient scaling: $E_s(X) := \frac{1}{2} E_{KS}(X)$.

Gradient: $\nabla E_s(X) := H(X) X$.

**Exact Hessian**

Suppose that $\epsilon_{xc}(\rho)$ is twice differentiable with respect to $\rho$. Given a direction $S \in \mathbb{C}^{K \times N}$, the Hessian-direction product for $E_s(X)$ is

$$\nabla^2 (E_s(X))[S] = H(X) S + \text{diag}(J ((\bar{X} \odot S + X \odot \bar{S}) e)) X,$$

where $J = \Re L^\dagger + \partial^2_\rho (\epsilon_{xc}^T e)$.

**Note:** The second part corresponds to $(H'(X)[S])X$.

**Good news:** the Hessian-direction product is not too expensive.
SCF from the Viewpoint of Optimization

see also: Yang Meza, Wang ’07

The linear eigenvalue problem in each SCF iteration is equivalent to:

$$\min \quad q(X) := \frac{1}{2} \langle H(X_k)X, X \rangle \quad \text{s.t.} \quad X^*X = I.$$ 

On the other hand, a direct calculation reveals:

$$\frac{1}{2} \langle H(X_k)X, X \rangle = \Re \langle H(X_k)X_k, X - X_k \rangle$$

$$+ \frac{1}{2} \Re \langle H(X_k)(X - X_k), X - X_k \rangle + \text{const.}$$

- The second part $H'(X_k)[X - X_k]X$ is omitted in SCF.
- similar to Gauss-Newton methods

Our Goals: Provable global convergence + fast local convergence.
Levenberg-Marquardt Type Regularization

- SCF iteration is similar to Gauss-Newton (GN) method.

- Regularization of SCF by Levenberg-Marquardt type approach:

\[
\min m_k^L(X) := \frac{1}{2} \langle H(X_k)X, X \rangle + \frac{\tau_k}{2} \|X - X_k\|_F^2
\]

s.t. \(X^*X = I\),

with regularization parameter \(\tau_k > 0\).

- First-order optimality conditions:

The solution \(X = X_{k+1}\) satisfies

\[
(H(X_k) + \tau_k I)X_{k+1} = X_{k+1}\Lambda_{k+1} + \tau_k X_k \quad \text{and} \quad X_{k+1}^*X_{k+1} = I,
\]

where \(\Lambda_{k+1} = \Lambda_{k+1}^* \in \mathbb{C}^{N \times N}\) is a Lagrange multiplier.
using the exact Hessian:

\[ m_k^N(X_k + S) := \Re \langle H(X_k)X_k, S \rangle + \frac{1}{2} \Re \langle H(X_k)S, S \rangle \]
\[ + \frac{1}{2} \Re \langle S, \text{diag}(J((\bar{X}_k \odot S + X_k \odot \bar{S})e)X_k) \rangle \]
\[ + \frac{\tau_k}{\nu} \|S\|_F^\nu, \]

\[ \frac{\tau_k}{\nu} \|S\|_F^\nu: \text{trust region like strategy for ensuring global convergence.} \]

Compute the regularized Newton step:

\[ \min m_k^N(X) \]
\[ \text{s.t. } X^*X = I. \]

Cartis, Gould, Toint ’10, ’11, ’12 on cubic regularization
Convergence Results

Assumption:
The gradient $\nabla E_s(X) = H(X)X$ is Lipschitz on the convex hull of the Stiefel manifold $\{X; X^*X = I\}$.

Let $G_k = \nabla E_s(X_k) = H(X_k)X_k$ and define

$$W_k = G_k X_k^* - X_k G_k^*$$

Global Convergence Result:

$$W_l = 0 \text{ for some } l \geq 0 \text{ or } \lim_{k \to \infty} \|W_k\|_F = 0.$$ 

Note: $W_k X_k$ = tangential part of $G_k$ in the canonical inner product.
Nonlinear equations with respect to $\rho$ as

$$\rho = \text{diag}(X(\rho)X(\rho)^T).$$

$X$ is determined by the eigenvalue problem:

$$\begin{cases} \hat{H}(\rho)X = X\Lambda, \\ X^TX = I, \end{cases}$$

the Hamiltonian matrix

$$\hat{H}(\rho) := \frac{1}{2}L + V_{\text{ion}} + \text{Diag}(L^\dagger \rho) + \text{Diag}(\mu_{\text{xc}}(\rho)^T e).$$
Formulating the KS Equation as a Fixed Point Map

- The Hamiltonian matrix

\[ H(V) := \frac{1}{2} L + V_{ion} + \text{Diag}(V) \]

- The potential

\[ V := V(\rho) = L^\dagger \rho + \mu_{xc}(\rho)^T \epsilon \]

- Nonlinear equations with respect to

\[
\begin{cases}
V = V(F_\phi(V)), \\
F_\phi(V) = \text{diag}(X(V)X(V)^T).
\end{cases}
\]
The Jacobian of the Fixed Point Maps

Let \( \{\lambda_i(V), q_i(V)\} \) be the eigenpairs of \( H(V) \):

\[
\lambda_1(V) \leq \ldots \leq \lambda_p(V) \leq \lambda_{p+1}(V) \leq \ldots \leq \lambda_n(V).
\]

The eigenvalue decomposition of \( H(V) \):

\[
H(V) = Q(V)\Pi(V)Q(V)^T,
\]

The function \( F_\phi(V) \) in (19) is equivalent to

\[
F_\phi(V) = \text{diag}(Q(V)\phi(\Pi(V))Q(V)^T),
\]

where \( \phi(\Pi) = \text{Diag}(\phi(\lambda_1(V)), \phi(\lambda_2(V)), \ldots, \phi(\lambda_n(V))) \) and

\[
\phi(t) := \begin{cases} 
1 & \text{for } t \leq \frac{\lambda_p(V)+\lambda_{p+1}(V)}{2}, \\
0 & \text{for } t > \frac{\lambda_p(V)+\lambda_{p+1}(V)}{2}.
\end{cases}
\]
Suppose that $\lambda_{p+1}(V) > \lambda_p(V)$. Then the directional derivative of $F_\phi(V)$ at $V$ is

$$\partial_V F_\phi(V)[z] = \text{diag} \left( Q(V) \left( g_\phi(\Pi(V)) \circ (Q(V)^T \text{Diag}(z) Q(V)) \right) Q(V)^T \right),$$

where $g_\phi(\Pi(V)) \in \mathbb{R}^{n \times n}$ is defined as

$$(g_\phi(\Pi(V)))_{ij} = \begin{cases} \frac{1}{\lambda_i(V) - \lambda_j(V)} & \text{if } i \in \alpha_k, j \in \alpha_l, k \leq r_p(V), l > r_p(V), \\ -\frac{1}{\lambda_i(V) - \lambda_j(V)} & \text{if } i \in \alpha_k, j \in \alpha_l, k > r_p(V), l \leq r_p(V), \\ 0 & \text{otherwise.} \end{cases}$$

The Jacobian of $\nabla(F_\phi(V))$ at $V$ is

$$\partial_V \nabla(F_\phi(V))[z] = J(F_\phi(V)) \partial_V F_\phi(V)[z], \quad \text{for all } z \in \mathbb{R}^n.$$
Convergence of the SCF iteration

- SCF recursively computes:

\[
H(V^i)X(V^{i+1}) = X(V^{i+1}) \Lambda(V^{i+1}),
\]

\[
X(V^{i+1})^T X(V^{i+1}) = I,
\]

and then the potential is updated as

\[
V^{i+1} = \mathcal{V}(F_\phi(V^i)).
\]

- The simple mixing scheme replaces (22) by updating

\[
V^{i+1} = V^i - \alpha(V^i - \mathcal{V}(F_\phi(V^i))).
\]
Convergence of the SCF iteration

- **Assumption:** the second-order derivatives of $\epsilon_{xc}(\rho)$:

  \[ \| \partial \mu_{xc}(\rho) e \|_2 \leq \theta, \quad \text{for all } \rho \in \mathbb{R}^n. \]

- It holds

  \[ \| \partial V F_\phi(V) \|_2 \leq \frac{1}{\delta} \quad \text{and} \quad \| \partial V \nabla(F_\phi(V)) \|_2 \leq \frac{\| L^\dagger \|_2 + \theta}{\delta}. \]
Local Convergence of the SCF iteration

Let $V^*$ be a solution of the KS equation. Suppose that the eigenvalue gap satisfies

$$\delta > -\lambda_{\text{min}}^* := -\min\{0, \lambda_{\text{min}}(J(F_{\phi}(V^*)))\}.$$ 

There exists an open neighborhood $\Omega$ of $V^*$, such that the sequence $\{V^i\}$ generated by the simple mixing scheme using $V^0 \in \Omega$ and a step size

$$\alpha \in \left(0, \frac{2\delta}{\|L^\dagger\|_2 + \theta + \delta}\right)$$

converges to $V^*$ with R-linear convergence rate no more than

$$\max \left\{ \left(1 - \alpha \frac{\delta + \lambda_{\text{min}}^*}{\delta}\right), \left(\alpha \frac{\|L^\dagger\|_2 + \theta + \delta}{2\delta} - 1\right) \right\}.$$
The condition $\delta > -\lambda_{\min}^*$ holds if

$$\max(\theta - \lambda_{\min}(L^\dagger), 0) < \delta.$$  

when $J(F_\phi(V^*))$ is positive semidefinite, we have $\lambda_{\min}^* = 0$ and the condition $\delta > -\lambda_{\min}^*$ holds.

Convergence of using Fermi-Dirac distribution:

$$\frac{4}{\beta} > -\lambda_{\min}^*,$$

where $\lambda_{\min}^* := \min\{0, \lambda_{\min}(J(F_\phi(V^*)))\}.$
The Jacobian of $\nu(F_\phi(V))$ at $V$ is

$$\partial_\nu \nu(F_\phi(V))[z] = J(F_\phi(V)) \partial_\nu F_\phi(V)[z], \quad \text{for all } z \in \mathbb{R}^n,$$

where

$$\partial_\nu F_\phi(V)[z] = \text{diag} \left( Q(V) \left( g_\phi(\Pi(V)) \circ (Q(V)^T \text{Diag}(z) Q(V)) \right) Q(V)^T \right).$$

Newton method

$$V^{i+1} = V^i - \alpha \left( I - J(F_\phi(V^i)) \partial_\nu F_\phi(V^i) \right)^{-1} \left( V^i - \nu(F_\phi(V^i)) \right),$$

Approximate Newton method

$$V^{i+1} = V^i - \alpha \left( I - D^i \right)^{-1} \left( V^i - \nu(F_\phi(V^i)) \right),$$
Approximate Newton Methods

- Setting $D^i := \tau^i J(\rho)$:

\[
V^{i+1} = V^i - \alpha \left( I - \tau^i J(F_\phi(V^i)) \right)^{-1} \left( V^i - \nabla \left( F_\phi(V^i) \right) \right).
\]

- Setting $D^i = \tau^i L^\dagger$:

\[
V^{i+1} = V^i - \alpha \left( I - \tau^i L^\dagger \right)^{-1} \left( V^i - \nabla \left( F_\phi(V^i) \right) \right).
\]

The Kerker preconditioner (pointed out by Lin Lin)

- Setting $D^i = L^\dagger W^i$ for a diagonal $W^i$:

\[
V^{i+1} = V^i - \alpha \left( I - L^\dagger W^i \right)^{-1} \left( V^i - \nabla \left( F_\phi(V^i) \right) \right).
\]

The method of elliptic preconditioner of Lin and Chao.
Speedup factors

- **Definition**

\[
\text{speedup-factor}(k_0, k) = \frac{\text{wall clock time for a } k_0\text{-core run}}{\text{wall clock time for a } k\text{-core run}}.
\]

- **T_0**: the calculation of the total energy \( E(X) \) and its partial derivative \( E_X \).

- **T_1**: all other wall clock time in each algorithm.
Speedup factor with respect to $T_0$

- **$C_{60}$**
  - SCF
  - OptM–WY
  - OptM–QR

- **alanine**
  - SCF
  - OptM–WY
  - OptM–QR

- **2JMO**
  - SCF
  - OptM–WY
  - OptM–QR

- **Fasciculin2**
  - SCF
  - OptM–WY
  - OptM–QR

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Speedup factor with respect to $T_1$

- **$C_{60}$**
  - SCF
  - OptM–WY
  - OptM–QR

- **alanine**
  - SCF
  - OptM–WY
  - OptM–QR

- **2JMO**
  - SCF
  - OptM–WY
  - OptM–QR

- **Fasciculin2**
  - SCF
  - OptM–WY
  - OptM–QR
Ratio: $T_0/(T_0 + T_1)$

![Graphs showing ratio of $T_0$ for different molecules and number of cores](image)

- **$C_{60}$**
  - SCF, OptM−WY, OptM−QR
  - Number of cores: 1, 2, 4, 8, 16

- **alanine**
  - SCF, OptM−WY, OptM−QR
  - Number of cores: 1, 2, 4, 8, 16, 32

- **2JMO**
  - SCF, OptM−WY, OptM−QR
  - Number of cores: 16, 32, 64, 128, 256
Numerical Results on OFDFT

Figure: (a) and (c) are the contours of the ground state charge density at plane $z = 0$ for $Al_{1688}$ and $Al_{4631}$, respectively. (b) and (d) are the corresponding adaptive mesh distribution of (a) and (c), respectively.
Numerical Results: Residual

(a) al

(b) graphene30

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Optimization for DFT
BICMR, 2014
Quadratic Convergence is Observable

(a) alanine

(b) c12h26