# Parallel Numerical Algorithms

Chapter 7 – Differential Equations
Section 7.4 – Electronic Structure Calculations

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## Outline

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# Electronic Structure Calculations

Models of chemical systems and processes calculate energies of molecular configurations

- Lowest-energy configurations describe electron distribution

    - Electrons occupy *orbitals* around each atom
    - Their occupancy of a given orbital is probabilistic

- The *Born-Oppenheimer approximation* is the separation of treatment of atomic and electronic distribution

    - This approximation is based on the radical difference in size and momentum of nuclei and electrons

- Thus, electronic structure calculations typically focus on computing the free energy of electrons for a fixed configuration of atoms

## Electronic Hamiltonian

- The interactions of a system of $n$ electrons are encoded in a *Hamiltonian operator* $H$

- The *wavefunction* $\Psi(\boldsymbol{x})$ and its energy $E$ is the eigenfunction of the Hamiltonian with the smallest eigenvalue

$$H\Psi(\boldsymbol{x}) = E\Psi(\boldsymbol{x})$$

- $x_1, \ldots, x_n$ are the respective coordinates of the $n$ electrons

- $\Psi(\boldsymbol{x})$ is a probability density function describing the state of the system of electrons

- $\Psi^*(\boldsymbol{x})\Psi(\boldsymbol{x})$ gives the probability of observing the electrons at locations $x_1, \ldots, x_n$

# Time-Independent Schrödinger Equation

The Schrödinger equation describes electronic interactions

- Most often, a time-independent, nonrelativistic form is used
- In this case the $n$-particle Hamiltonian has the form

$$H = -\frac{1}{2m} \sum_{i=1}^{n} \nabla_i^2 + \sum_{i=1}^{n} V(x_i) + \sum_{i=1}^{n} \sum_{j<i} U(x_i, x_j)$$

- The *one-particle component* $V(x_i)$ encodes interactions between electrons and atoms
- The *two-particle component* $U(x_i, x_j)$ encodes electron–electron interactions
- $\Psi$ is generally a function of all electrons, to obtain an approximate solution a simpler *ansatz* is often used

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# Density Function Theory (DFT)

*Density Functional Theory (DFT)*

- Approximate wavefunction ansatz is a *Hartree product* of $n$ single-particle wavefunctions

$$\Psi(x_1, \ldots, x_n) \approx \Psi_1(x_1) \cdots \Psi_n(x_n)$$

- The electron (probability) density given this ansatz is

$$\eta(\boldsymbol{x}) = \sum_{i=1}^{n} \int \cdots \int (\Psi^* \Psi)(\boldsymbol{x}) dx_1 \ldots dx_{i-1} dx_{i+1} \ldots dx_n$$

$$\approx \sum_{i=1}^{n} \Psi_i^*(\boldsymbol{x}) \Psi_i(\boldsymbol{x})$$

- *Hohenberg–Kohn theorem*: one-to-one relationship between the energy density $\eta$ and $\Psi$, $\exists F$ so $E = F(\eta(\boldsymbol{x}))$.

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# Kohn–Sham Equations

The *Kohn–Sham equations* describe the action of the many-body Hamiltonian on the single-electron wavefunctions

$$\left[ -\frac{1}{2m}\nabla^2 + V(\boldsymbol{x}) + V_H(\boldsymbol{x}) + V_{\mathsf{XC}}(\boldsymbol{x}) \right]\Psi_i(\boldsymbol{x}) = \mathcal{E}_i\Psi_i(\boldsymbol{x})$$

- Electron–electron replaced by electron–density potentials

- $V_H(\boldsymbol{x})$ is the Hartree potential holding Coulomb repulsion

- $V_{\mathsf{XC}}(\boldsymbol{x})$ is an approximation to the exchange-correlation potential (including model for Pauli exclusion)

- The exchange-correlation potential $V_{\mathsf{XC}}(\boldsymbol{x})$ has no known simple form

- Various approximations for $V_{\mathsf{XC}}$ mix theory and heuristics

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## Solving the Kohn–Sham equations

The Kohn–Sham equations give $\Psi_i(\boldsymbol{x})$ as

single particle wavefunctions $= f(\text{electron density})$

while the electron density $\eta(\boldsymbol{x})$ is defined by

electron density $= g(\text{single particle wavefunctions})$

DFT solves for these iteratively

1. Define an initial guess for the density $\eta^{(0)}(\boldsymbol{x})$

2. Solve the Kohn–Sham equations with $\eta^{(j)}(\boldsymbol{x})$ to get $\Psi_i^{(j)}(\boldsymbol{x})$

3. Calculate a new Kohn–Sham electron density

$$\eta^{(j+1)}(\boldsymbol{x}) = \sum_{i=1}^{n} \Psi_i^{(j)}(\boldsymbol{x})^* \Psi_i^{(j)}(\boldsymbol{x})$$

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## Electron Density Representation

A basis is defined for the spatial domain to get a numerical representation of $\eta(x)$

- *Plane waves* provide harmonic representation (sparse/compact/local in Fourier basis)

- *Gaussian* (sparse/compact/local) functions local to orbitals

  - Typically lowest-energy configuration associates each electron with a single base orbital

  - Compact support of basis functions enable sparse representations of single-electron wavefunctions

  - If system is sufficiently large, potentials are well approximated by sparse representations

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## Discretized Kohn-Sham Equations

- Introduce a spatial basis $\{\phi_1, \ldots, \phi_m\}$ for single-electron wavefunctions

$$\Psi_i(\boldsymbol{x}) = \sum_{\mu=1}^{m} c_{\mu i} \phi_\mu(\boldsymbol{x})$$

- The basis need not be orthonormal, and we generally have *overlap matrix* $\boldsymbol{S}$, where

$$s_{\mu\nu} = \int \phi_\mu(\boldsymbol{x})\phi_\nu(\boldsymbol{x})d\boldsymbol{x}$$

- Density matrix $\boldsymbol{D}$ then given by

$$\eta^{(j+1)}(\boldsymbol{x}) = \sum_{\mu=1}^{m} \sum_{\nu=1}^{m} \underbrace{\sum_{i=1}^{n} c_{\mu i}^* c_{\nu i}}_{d_{\mu\nu}} \phi_\mu(\boldsymbol{x})^* \phi_\nu(\boldsymbol{x})$$

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# Discretized Kohn-Sham Equations

- Projecting onto $\phi_\mu(\boldsymbol{x})$ and integrating Kohn–Sham equations with $\Psi_i(\boldsymbol{x}) = \sum_{\nu=1}^m c_{\nu i}\phi_\nu(\boldsymbol{x})$, we get

$$
\int \phi_\mu(\boldsymbol{x})^*\Big[-\frac{1}{2m}\nabla^2 + V(\boldsymbol{x}) + V_H(\boldsymbol{x}) + V_{\mathsf{XC}}(\boldsymbol{x})\Big]\Psi_i(\boldsymbol{x})d\boldsymbol{x}
$$

$$
= \mathcal{E}_i \int \phi_\mu(\boldsymbol{x})^*\Psi_i(\boldsymbol{x})d\boldsymbol{x}
$$

$$
\sum_{\nu=1}^m f_{\mu\nu}c_{\nu i} = \mathcal{E}_i \sum_{\nu=1}^m s_{\mu\nu}c_{\nu i} \quad \text{so} \quad \boldsymbol{FC} = \boldsymbol{SC}\begin{bmatrix}\mathcal{E}_1 & & \\ & \ddots & \\ & & \mathcal{E}_n\end{bmatrix}
$$

- The columns of $\boldsymbol{C}$ are obtained by solution of a generalized eigenvalue problem involving *Fock matrix $\boldsymbol{F}$*

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## DFT with a Plane Wave Basis Set

- Every basis function in a plane wave basis set is based on a 3D periodic lattice in Fourier space

- The domain is treated as periodic, which makes physical sense for solids (less so for molecular system with heterogeneous structure)

- The Coulomb potential $V_H(x)$ and Laplace operator $\nabla^2$ are well-approximated in Fourier space

- Local potentials decay in real-space, motivating use of mixed representations

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## DFT with Gaussian and Plane Waves

The simultaneous use of both Gaussian and plane wave bases gives the *GPW method*

- GPW split the potentials in the the Kohn-Sham equations into two parts

  - A short-range part that can be resolved using localized Gaussian basis functions

  - A long-range part that is solved using fast methods in the plane-wave bases

- Convergent sum $\Rightarrow$ two rapidly convergent sums

- Methods like GPW provide algorithms for DFT that formally achieve linear scaling with system size

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## Density Matrix as a Sign Function

- Many other methods exist for solving the Kohn-Sham equations (for some representation of potential)

- Recent methods developed by leverage relationship between density matrix $D$, overlap matrix $S$, and Hamiltonian matrix $H$ (component of the Fock matrix)

$$D = (1/2)(I - \text{sign}(S^{-1}H - \mu I))S^{-1}$$

- The sign function pushes the negative/positive eigenvalues to $-1/+1$ so

$$\text{sign}(A) = A(A^2)^{-1/2} = U\Sigma|\Sigma|^{-1}U^T$$

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# Computing the Matrix Sign Function

- The sign function $\text{sign}(\boldsymbol{A})$ of symmetric matrix $\boldsymbol{A}$ is given by taking the eigenvalue decomposition $\boldsymbol{A} = \boldsymbol{U}\boldsymbol{\Sigma}\boldsymbol{U}^T$ and replacing $\boldsymbol{\Sigma}$ with a diagonal matrix of signs

- Sign function can be found by repeated squaring

$$\boldsymbol{A}_{i+1} = (1/2)\boldsymbol{A}_i(3\boldsymbol{I} - \boldsymbol{A}_i)^2$$

which converges quadratically to

$$\text{sign}(\boldsymbol{A}) = \boldsymbol{A}(\boldsymbol{A}^2)^{-1/2}$$

provided $\boldsymbol{A}_0 = c\boldsymbol{A}$ and $c < ||\boldsymbol{A}||^{-1}$

- This method is done for DFT with *screening* of intermediate terms (discarding negligible matrix elements) to preserve sparsity in each $\boldsymbol{A}_i$

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## Hartree–Fock Method

The *Hartree–Fock (HF) method* provides a more accurate representation of electron exchange

- HF is still a mean-field treatment that does not treat electron–electron interactions explicitly

- HF uses a *Slater determinant* as a wavefunction ansatz

$$\Psi(\boldsymbol{x}) \approx \det \left( \begin{bmatrix} \Psi_1(x_1) & \cdots & \Psi_1(x_2) \\ \vdots & & \vdots \\ \Psi_n(x_1) & \cdots & \Psi_n(x_n) \end{bmatrix} \right)$$

- This wavefunction ansatz is an antisymmetrized Hartree product (DFT wavefunction ansatz)

- The *antisymmetry* (any permutation yields to a sign flip) allows the wavefunction to satisfy *Pauli exclusion*

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## Self Consistent Field Iteration

HF is solved by the *Self Consistent Field (SCF)* iteration, which is very similar to DFT

- For density matrix $D$, the *Fock matrix* is given by

$$f_{\mu\nu} = h_{\mu\nu}^{\text{core}} + \sum_{\lambda\sigma} d_{\lambda\sigma}(2(\mu\nu|\lambda\sigma) - (\mu\lambda|\nu\sigma))$$

  where $h_{ij}^{\text{core}}$ is the core-Hamiltonian and $(\mu\nu|\lambda\sigma)$ are the electron–repulsion integrals

- Due to explicit calculation of exchange terms $(\mu\lambda|\nu\sigma)$, Fock matrix construction is more expensive in HF than DFT

- SCF iteratively computes $F$ from $D$ then $D$ from solutions to the generalized eigenproblem with $F$

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## Electron-Repulsion Integral Computation

A key computational bottleneck in Hartree-Fock is calculation of the electron–repulsion integrals (ERI tensor)

- These are generally screened so a subset is computed

- An integral $(\mu\nu|\lambda\sigma)$ is derived from $\boldsymbol{D}_{ab}$ where $\{a, b\} \in \{\mu, \nu, \lambda, \sigma\}$ and contributes to each $\boldsymbol{F}_{ab}$

- Both $\boldsymbol{F}$ and $\boldsymbol{D}$ are symmetric so we consider $\binom{4}{2} = 6$ permutations

- If we compute a 4D block of $(\mu\nu|\lambda\sigma)$ of size $s$, require $\Theta(\sqrt{s})$ entries of $\boldsymbol{F}$ and $\boldsymbol{D}$

- Thus computing the $O(n^4)$ elements of the ERI tensor with $p$ processors can be done with $O(n^2/\sqrt{p})$ communication

- For sufficiently large systems, suffices to keep $O(n^2)$ terms

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# Configuration Interaction

Hartree-Fock represents an $n$-electron wavefunction using a determinant of $n$ basis functions

- Given a basis set of $m > n$ functions (orbitals), we can define $\binom{m}{n}$ Slater determinants of $n$-electrons, which 'occupy' different subsets of functions (orbitals)

- *Configuration-interaction (CI)* works on a basis that includes all $\binom{m}{n}$ combinations

- Eigendecomposition of the resulting matrix (dimension exponential in $m$) gives exact solution to electronic Schrödinger equation for given basis

- *Quantum Monte Carlo* methods select a subset of determinants by using weighted sampling

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## Møller-Plesset Perturbation Theory

*Møller-Plesset perturbation* methods, modify the Hamiltonian slightly to take into account some 'excited-state' configurations

- *Brillouin theorem* – single-electron excitations have no integral affect (first-order perturbation is analytically zero)

- MP2 and MP3 are second and third order perturbations

- MP2 can be computed directly from the ERI tensor as a correction, requiring $O(n^4)$ cost

- MP3 requires a tensor contraction between two order four tensors, requiring $O(n^6)$ cost

- The dominant part of the cost in MP3 is the tensor contraction, which can be done by matrix-matrix multiplication

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# Coupled-Cluster Theory

A more computationally robust alternative to CI is presented by *coupled-cluster (CC) methods*

- CC methods try to take into account electron correlation, by taking into account all possible excitations of $k$ electrons

  - *CCSD*: (singles and doubles) $k = 2$, $O(n^6)$ cost

  - *CCSDT*: (singles, doubles, and triples) $k = 3$, $O(n^8)$ cost

  - *CCSDTQ*: (... and quadruples) $k = 4$, $O(n^{10})$ cost

- CC methods use a wavefunction ansatz of the form $\Psi \approx e^{T_1 + \cdots + T_k} \Psi_0$ where $\Psi_0$ is the HF Slater determinant

- The exponential is expanded in polynomial form and truncated, resulting in a set of tensor contractions that define possible electron state transitions

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## Coupled-Cluster Calculation

- Coupled-cluster and related methods are dominated by matrix-multiplication (tensor contractions)

- The tensor representations have antisymmetry

- Methods attempt to lower complexity by leveraging sparsity or low rank structure
  - Density Fitting
  - Resolution of Identity
  - Tensor Hypercontraction, etc.

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# Sources of Parallelism in Quantum Chemistry

- DFT and SCF methods often use dense linear algebra

    - Symmetric (generalized) eigenvalue problem

    - Matrix multiplication, QR, Fourier transform

- Localized bases can introduce sparsity (e.g. GPW)

    - Sparse matrix products and eigenvalue problems

- Integral calculation can be done effectively in parallel (some load balance challenges with screening)

- Tensor contractions in post-HF methods are parallelizable

    - Tensor transposition or in-place contraction pose data-layout transformation challenges

## General References

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