Parallel Numerical Algorithms
Chapter 7 – Differential Equations
Section 7.4 – Electronic Structure Calculations

Edgar Solomonik

Department of Computer Science
University of Illinois at Urbana-Champaign

CS 554 / CSE 512
Outline

1. Electronic Structure Calculations
2. Density Functional Theory
   - Kohn–Sham Equations
   - Solving the Kohn–Sham Equations
3. Hartree-Fock Method
   - Self Consistent Field (SCF) Iteration
   - Cost of Integral Computation
4. Post-Hartree-Fock Methods
   - Configuration Interaction
   - Møller-Plesset Perturbation Methods
   - Coupled-Cluster Methods
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* $\Psi(x)$ and its energy $E$ is the eigenfunction of the Hamiltonian with the smallest eigenvalue

$$H \Psi(x) = E \Psi(x)$$

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

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

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

\[
\eta(x) = \sum_{i=1}^{n} \int \cdots \int (\Psi^* \Psi)(x) \, dx_1 \cdots dx_{i-1} \, dx_{i+1} \cdots dx_n \\
\approx \sum_{i=1}^{n} \Psi_i^*(x) \Psi_i(x)
\]

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

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

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

- Electron–electron replaced by electron–density potentials
- \( V_H(x) \) is the Hartree potential holding Coulomb repulsion
- \( V_{XC}(x) \) is an approximation to the exchange-correlation potential (including model for Pauli exclusion)
- The exchange-correlation potential \( V_{XC}(x) \) has no known simple form
- Various approximations for \( V_{XC} \) mix theory and heuristics
The Kohn–Sham equations give $\Psi_i(x)$ as single particle wavefunctions $= f(\text{electron density})$

while the electron density $\eta(x)$ is defined by
electron density $= g(\text{single particle wavefunctions})$

DFT solves for these iteratively

1. Define an initial guess for the density $\eta^{(0)}(x)$
2. Solve the Kohn–Sham equations with $\eta^{(j)}(x)$ to get $\Psi^{(j)}_i(x)$
3. Calculate a new Kohn–Sham electron density

$$\eta^{(j+1)}(x) = \sum_{i=1}^{n} \Psi^{(j)}_i(x)^* \Psi^{(j)}_i(x)$$
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
**Discretized Kohn-Sham Equations**

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

\[
\Psi_i(\mathbf{x}) = \sum_{\mu=1}^{m} c_{\mu i} \phi_\mu(\mathbf{x})
\]

- The basis need not be orthonormal, and we generally have *overlap matrix* \( S \), where

\[
s_{\mu \nu} = \int \phi_\mu(\mathbf{x}) \phi_\nu(\mathbf{x}) d\mathbf{x}
\]

- Density matrix \( D \) then given by

\[
\eta^{(j+1)}(\mathbf{x}) = \sum_{\mu=1}^{m} \sum_{\nu=1}^{m} \sum_{i=1}^{n} c_{\mu i}^* c_{\nu i} \phi_\mu(\mathbf{x})^* \phi_\nu(\mathbf{x}) \underbrace{d_{\mu \nu}}_{\text{Overlap matrix}}
\]
Discretized Kohn-Sham Equations

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

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

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

- The columns of $C$ are obtained by solution of a generalized eigenvalue problem involving Fock matrix $F$
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 sends for solids (less so for molecular systems 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.
DFT with Gaussian and Plane Waves

The simultaneous use of both Gaussian and plane wave bases gives the \textit{GPW method}.

- GPW split the potentials in 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
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)

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

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

$$\text{sign}(A) = A(A^2)^{-1/2} = U\Sigma|\Sigma|^{-1}U^T$$
Computing the Matrix Sign Function

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

- Sign function can be found by repeated squaring

\[
A_{i+1} = \left( \frac{1}{2} \right) A_i (3I - A_i)^2
\]

which converges quadratically to

\[
\text{sign}(A) = A (A^2)^{-1/2}
\]

provided \( A_0 = c A \) and \( c < \| A \|^{-1} \).

- This method is done for DFT with screening of intermediate terms (discarding negligible matrix elements) to preserve sparsity in each \( A_i \).
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

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

- 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*
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 $F$
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 \(D_{ab}\) where \(\{a, b\} \in \{\mu, \nu, \lambda, \sigma\}\) and contributes to each \(F_{ab}\)
- Both \(F\) and \(D\) 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 \(F\) and \(D\)
- 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
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
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
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.
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.
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

- David Sherril’s online notes: http://vergil.chemistry.gatech.edu/notes/


References


References


