

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

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

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

- x_1, \dots, x_n are the respective coordinates of the n electrons
- $\Psi(\mathbf{x})$ is a probability density function describing the state of the system of electrons
- $\Psi^*(\mathbf{x})\Psi(\mathbf{x})$ gives the probability of observing the electrons at locations x_1, \dots, 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
- Ψ is generally a function of all electrons, to obtain an approximate solution a simpler *ansatz* is often used

Density Functional Theory (DFT)

Density Functional Theory (DFT)

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

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

- The electron (probability) density given this ansatz is

$$\begin{aligned} \eta(\mathbf{x}) &= \sum_{i=1}^n \int \cdots \int (\Psi^* \Psi)(\mathbf{x}) dx_1 \dots dx_{i-1} dx_{i+1} \dots dx_n \\ &\approx \sum_{i=1}^n \Psi_i^*(\mathbf{x}) \Psi_i(\mathbf{x}) \end{aligned}$$

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

Kohn–Sham Equations

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

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

- Electron–electron replaced by electron–density potentials
- $V_H(\mathbf{x})$ is the Hartree potential holding Coulomb repulsion
- $V_{XC}(\mathbf{x})$ is an approximation to the exchange-correlation potential (including model for Pauli exclusion)
- The exchange-correlation potential $V_{XC}(\mathbf{x})$ has no known simple form
- Various approximations for V_{XC} mix theory and heuristics

Solving the Kohn–Sham equations

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

single particle wavefunctions = f (electron density)

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

electron density = g (single particle wavefunctions)

DFT solves for these iteratively

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

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

Electron Density Representation

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

- *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 $\{\phi_1, \dots, \phi_m\}$ 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

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

Discretized Kohn-Sham Equations

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

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

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

- The columns of \mathbf{C} are obtained by solution of a **generalized eigenvalue problem** involving *Fock matrix* \mathbf{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 sense for solids (less so for molecular system with heterogeneous structure)
- The Coulomb potential $V_H(\mathbf{x})$ and Laplace operator ∇^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 *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

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

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

Computing the Matrix Sign Function

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

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

which converges quadratically to

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

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

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

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

- 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*

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}^{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

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

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 $\Psi \approx e^{T_1 + \dots + T_k} \Psi_0$ where Ψ_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

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