Electronic structure theory: Fundamentals to frontiers.

1. Hartree-Fock theory

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1. **Introduction**

2. **Fundamentals**

3. **Glimpses of advanced topics**
“Every attempt to employ mathematical methods in the study of chemical questions must be considered profoundly irrational and contrary to the spirit of chemistry. If mathematical analysis should ever hold a prominent place in chemistry—an aberration which is happily almost impossible—it would occasion a rapid and widespread degeneration of that science.”

Auguste Comte, 1830.
Quantum mechanics and chemistry

“...in the Schrödinger equation we very nearly have the mathematical foundation for the solution of the whole problem of atomic and molecular structure”

but...

“... the problem of the many bodies contained in the atom and the molecule cannot be completely solved without a great further development in mathematical technique.”

The electronic structure problem

- Within non-relativistic quantum mechanics, and the clamped nucleus approximation, the electronic Schrödinger equation is believed to be exact.

\[
\hat{H} |\Psi\rangle = E |\Psi\rangle \\
\hat{H} = \hat{T} + \hat{V}_{en} + \hat{V}_{ee} \\
= -\frac{1}{2} \sum_i \nabla_i^2 - \sum_i \sum_A \frac{Z_A}{|r_i - R_A|} + \sum_i \sum_{j>i} \frac{1}{|r_i - r_j|} \\
|\Psi\rangle = |\Psi(r_1, r_2, r_3, \ldots, r_n)\rangle \\
E = E(R_1, R_2, R_3\ldots)
\]
Desiderata

• Minima on potential energy surfaces, $V(R_1, R_2 \ldots)$
  • Equilibrium structures (1% precision)
  • Relative energies (to about 1 kcal/mole)
  • Describes structure and thermodynamics

• Saddle points connecting minima
  • Transition structures
  • Barrier heights
  • Link to reaction mechanisms

• Molecular properties, spectroscopy
• Chemical insight
**Schroedinger complexity (scaling)**

- Many-body Schrödinger equation is a partial differential equation in $3n$ unknowns—the positions of the electrons.
  - Exact (brute force) solution will scale approximately exponentially with the number of electrons.

- When done in a given basis of 1-electron expansion functions, this is “full configuration interaction” (FCI).
  - Largest FCI’s involve many-body expansions containing billions of terms, for molecules with 2 or 3 of atoms (!).

- Approximations are imperative. Accuracy vs feasibility.
**Fundamental approximations**

- **(1) The one-body problem ("atomic orbital basis")**
  - One-electron functions are expanded in a finite basis.
  - We use atom-centered functions with some maximum angular momentum (L) on atoms of a given period.
  - Standardized basis sets of increasing L are available.

- **(2) The n-body problem ("electron correlation method")**
  - More about this in a minute… mean field is the simplest possible treatment.

- Well-defined electronic structure models are completely specified by these two approximations.
Desirable properties for electronic structure models

- (1) Accuracy
- (2) Efficiency
- (3) Universally defined
- (4) Potential surface continuity
- (5) Size-consistency
- (6) Variationality
- (7) Exactness for relevant model problems
Outline

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n-electron wave functions are determinants

• The simplest many-electron wave function (a product of orbitals) does not obey Fermi statistics

• A product wave function with antisymmetry is a determinant…
### Slater-Condon rules

- Matrix elements between determinants with 0, 1 ($i$ vs $a$), or 2 ($i,j$ vs $a,b$) spin-orbital differences

<table>
<thead>
<tr>
<th>Operator</th>
<th>0</th>
<th>1</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>$1$</td>
<td>$0$</td>
<td>$0$</td>
</tr>
<tr>
<td>1</td>
<td>$\sum_{i=1}^{n} \langle \phi_i</td>
<td>\hat{h}</td>
<td>\phi_i \rangle$</td>
</tr>
<tr>
<td>2</td>
<td>$\frac{1}{2} \sum_{ij} \langle \phi_i \phi_j</td>
<td>\phi_i \phi_j \rangle$</td>
<td>$\sum_j \langle \phi_j \phi_a</td>
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The Hartree-Fock energy expression

• The Hartree-Fock energy follows directly from the Slater-Condon rules:

\[ E_{HF} = \sum_i \langle i | T + V_e | i \rangle + \frac{1}{2} \sum_{ij} (ij||ij) \]

• The HF energy can also usefully be expressed in the atomic orbital basis in terms of the 1-particle density matrix, which itself depends on the MO coefficients…

\[ E_{HF} = \sum_{\mu\nu} H_{\mu\nu} P_{\mu\nu} + \frac{1}{2} \sum_{\mu\nu\lambda\sigma} P_{\mu\nu} (\mu\lambda||\nu\sigma) P_{\lambda\sigma} \]

\[ P_{\mu\nu} = \sum_i C_{\mu i} C_{\nu i} \]
Minimizing the HF energy

• The Hartree-Fock energy expression cannot be directly minimized with respect to either MO coefficients or the density matrix, because they are dependent variables.

• The resulting MO’s must be orthonormal:
  • Treating these as constraints leads to the eigenvalue problem $\mathbf{FC} = \mathbf{SCE}$

• Equivalently, the density matrix must be idempotent:
  • $\mathbf{PP} = \mathbf{P}$ (or $\mathbf{PSP} = \mathbf{P}$ in the atomic orbital basis).
Computational steps in HF calculations

(1) Given a guess at the density matrix, $\mathbf{P}$, (describing the arrangement of the electrons), make the Hamiltonian matrix describing their effective interactions, $\mathbf{F} = \mathbf{F}(\mathbf{P})$.
   - Electron-electron, electron-nuclear and kinetic energy terms
   - Electron-electron terms are computationally dominant: $A^2$
   - Includes Coulomb, and exact exchange terms.

(2) Diagonalize the effective Hamiltonian to obtain the eigenvalues and eigenvectors, and use them to make $\mathbf{P}$.
   - Computational effort proportional to $A^3$

(3) If the new $\mathbf{P}$ is different to the old $\mathbf{P}$, go back to (1).
One-particle basis sets in quantum chemistry

• Gaussian atomic orbitals are most commonly used:
  • Analytical matrix element evaluation is efficient

• Un-normalized primitive Gaussian basis function:

\[ |a_x, a_y, a_z; \alpha \rangle = N (x - A_x)^{a_x} (y - A_y)^{a_y} (z - A_z)^{a_z} e^{-a(r-A)^2} \]

• Contracted Gaussians:
  – Degree of contraction \( K \) (e.g. 1-6)

\[ |a_x, a_y, a_z \rangle = \sum_{i=1}^{K} c_i |a_x, a_y, a_z; \alpha \rangle \]

• Basis sets are standardized. The 3 lowest levels:
  • Minimal basis set (STO-3G) (5 functions per C)
  • Split valence basis (3-21G) (9 functions per C)
  • Polarized split valence basis (15 per C)
**Shells and shell-pairs**

- For efficiency, basis sets are composed of **shells**
  - A shell is a set of basis functions having common angular momentum (L), exponents and contraction coefficients
  - s shell (L=0)
  - p shell (L=1): \{x,y,z\}
  - d shell (L=2): \{xx,yy,zz,xy,xz,yz\}

- **Shell pairs**: are products of separate shells
  - The shell-pair list is a fundamental construction
  - One electron matrix elements involve the shell pair list
  - Two-electron matrix elements involve the product of the shell pair list with itself (Coulomb interactions).
The significant shell pair list

- If there are $O(N)$ functions in the shell list, then, naively,
  - The shell pair list is $O(N^2)$ in size
  - The two-electron integral list is $O(N^4)$ in size (!!)
- The product of Gaussian functions is a Gaussian at $P$
  \[
  e^{\frac{-\alpha (r-A)^2 - \beta (r-B)^2}{\alpha + \beta}} = e^{\frac{-\alpha \beta (A-B)^2}{(\alpha + \beta)}} e^{-(\alpha + \beta)(r-P)^2}
  \]
  \[
  P = \frac{\alpha A + \beta B}{\alpha + \beta}
  \]
- Pre-factor dies off with separation of the product functions, so:
- In a large molecule, there are only $O(N)$ shell pairs
  - There are a linear number of one-electron matrix elements
  - There are $O(N^2)$ two-electron integrals (the Coulomb problem)
1 and 2-electron integrals in HF calculations

• The effective Hamiltonian (Fock operator) is:
  \[ F_{\mu\nu} = H_{\mu\nu} + J_{\mu\nu} + K_{\mu\nu} \]
  • One-electron integrals (H) are very cheap*

• Two-electron integrals arise in the Coulomb (J) matrix:
  \[ J_{\mu\nu} = \sum_{\lambda\sigma} \langle \mu\nu | \lambda\sigma \rangle P_{\lambda\sigma} \]
  \[ \langle \mu\nu | \lambda\sigma \rangle = \int \int d\mathbf{r}_1 d\mathbf{r}_2 \omega_{\mu} (\mathbf{r}_1) \omega_{\nu} (\mathbf{r}_1) | \mathbf{r}_1 - \mathbf{r}_2 |^{-1} \omega_{\lambda} (\mathbf{r}_2) \omega_{\sigma} (\mathbf{r}_2) \]

• And in the exact exchange (K) matrix:
  \[ K_{\mu\nu} = \sum_{\lambda\sigma} \langle \mu\lambda | \nu\sigma \rangle P_{\lambda\sigma} \]
2-electron repulsion integrals (ERI’s)

- Consider the simplest integral (no angular momentum)

\[ [ss|ss] = N \int dr_1 \int dr_2 e^{-\alpha(r_1-A)^2} e^{-\beta(r_1-B)^2} \frac{1}{|r_1 - r_2|} e^{-\gamma(r_2-C)^2} e^{-\delta(r_2-D)^2} \]

- We recall (and see) this is an interaction between 2 shell pairs
- It may be evaluated as m=0 (note generalization to auxiliary index, m, that will be used to add angular momentum) from:

\[ [ss|ss]^{(m)} = [0]^{(m)} = K_{AB} K_{CD} (\alpha + \beta + \delta + \gamma)^{1/2} F_m(T) \]

\[ K_{AB} = 2^{1/2} \pi^{5/4} \left( \frac{1}{\alpha + \beta} \right) e^{-\frac{\alpha \beta}{\alpha + \beta} (A-B)^2} \]

\[ F_m(T) = \frac{1}{0} dt t^{2m} e^{-T t^2} \]

\[ T = \left[ \frac{(\alpha + \beta)(\delta + \gamma)}{(\alpha + \beta + \delta + \gamma)} \right] R^2 \]

\[ R = P - Q \]
Adding angular momentum: simplest way

Angular momentum can be added analytically by differentiating the fundamental integral repeatedly. Each differentiation adds one quantum of $L$.

If you really want to see an explicit example, consider:

$$[p_s s | s s] = \left( \frac{-1}{2\alpha} \right) K_{CD} \left( \frac{dK_{AB}}{dA_i} \right) (\alpha + \beta + \delta + \gamma)^{\frac{1}{2}} F_o (T) + K_{AB} K_{CD} (\alpha + \beta + \delta + \gamma)^{\frac{1}{2}} \frac{dF_0 (T)}{dA_i}$$

$$= K_{AB} K_{CD} \left( \frac{-\beta}{\alpha + \beta} \right) (A - B)_i (\alpha + \beta + \delta + \gamma)^{\frac{1}{2}} F_0 (T) + K_{AB} K_{CD} \left( \frac{-1}{\alpha + \beta} \right) R_i \left( \frac{(\alpha + \beta)(\delta + \gamma)}{(\alpha + \beta + \delta + \gamma)} \right) (\alpha + \beta + \delta + \gamma)^{\frac{1}{2}} F_1 (T)$$

This process is tedious, error-prone and may be inefficient (one may redo similar derivatives for different integrals).
Adding angular momentum by recursion

• To permit re-use of intermediates, recurrence-based formulations are natural. Our previous example can be re-cast in this way as:

\[ [a + 1_i s | ss]^{(m)} = \left( \frac{\beta}{\alpha + \beta} \right)_{i} (A - B)_{i} [as | ss]^{(m)} + \left( \frac{1}{\alpha + \beta} \right)_{i} R_{i} [as | ss]^{(m+1)} \]

\[-a_{i} \left\{ \left( \frac{1}{\alpha + \beta} \right) [as | ss]^{(m)} - \left( \frac{1}{\alpha + \beta} \right)^{2} [as | ss]^{(m+1)} \right\} \]

• Obviously the recurrences become more complicated when higher angular momentum is involved… a variety of efficient schemes exist (McMurchie-Davidson, Obara-Saika and offshoots, Prism).
Multiple choice questions...

• Is the restricted Hartree-Fock method size-consistent?
  – (a) yes – always
  – (b) no – never
  – (c) sometimes

• Predict the effect of the Hartree-Fock approximation on the calculated binding energy of the H₂ molecule relative to twice that of the H atom.
  – (a) too high
  – (b) too low
  – (c) about right
Flavors of Hartree-Fock theory

• Correspond to treatment of constraints

• No constraints at all – general HF (GHF)

• MO’s are a single spin – unrestricted HF (UHF)

• MO’s of both spins are the same – restricted HF (RHF)
Restricted HF and bond-breaking

- Take the H2 problem as an example.

- The RHF solution has a fixed ratio of ionic:covalent character.

- Towards dissociation this becomes worse and worse…
  - Hence at a critical distance, UHF becomes lower in energy
  - UHF is exact for H2 at long distance

- This is the symmetry dilemma.
Stability analysis

- Corresponds to checking the character of a given constrained Hartree-Fock solution.
  - Is it a local minimum (stable) or not (unstable).

- Unstable solutions are saddle points of some order, and their energy can be lowered by release of constraints.
  - UHF is needed for bond-breaking – but when does a bond actually break?
  - When is GHF needed?
  - And we have not mentioned complex HF….
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The objective is to minimize the energy. The tight-binding problem represents one SCF iteration:

$$E = Tr(\hat{\rho} \hat{f})$$

The density cannot be minimized without constraints. There are two types:

- **Idempotency (purity):** ensures that the density matrix derives from a single Kohn-Sham determinant

  $$\hat{\rho} \hat{\rho} = \hat{\rho}$$

- **Electron number.**

  $$Tr(\hat{\rho}) = n$$
Density matrix locality in real space (Roi Baer)

- R. Baer, MHG, JCP 107, 10003 (1997)

- For ordered systems, density matrix elements decay exponentially with distance.
- The range (for $10^{-D}$ precision) is bounded by:

$$W(P) = D \sqrt{\frac{3\hbar^2}{4m_e (\Delta E)_{gap}}}$$

- Decay length proportional to inverse square root of gap.
  - Electronic structure of good insulators is most local occupied orbitals can be well localized.
  - Metals and small gap semiconductors are more nonlocal occupied orbitals cannot be well localized.
Number of significant neighbors versus precision

- log precision

linear neighbors

3 sample gaps

1 eV
3 eV
6 eV
(1) Only a linear number of density elements are significant on length scales longer than the decay length.

(2) When the linear scaling regime is reached depends on the effective dimensionality, \( d \), going roughly as \( n^d \)

10 significant neighbors leads to 10, 100, 1000 atoms in 1,2,3-d

(3) An ansatz will be required to develop effective fast methods on systems below the linear scaling regime.

(4) We must work directly in a localized basis to reflect real space locality in sparse matrices.