Self Consistent Field Methods for Electronic Structure

Self Consistent Field (SCF) methods were introduced by Hartree, and developed by Slater, Fock and others in the late 1920s to study the electronic structure of atoms with more than one electron. These "Hartree-Fock" methods are widely used to compute properties of atoms, molecules and solids.

The two basic approximations in this method are to treat the atomic nuclei as infinitely heavy and therefore fixed in space at their equilibrium positions, and to approximate the many electron wavefunction as a product of one-electron wave functions that is fully antisymmetrized because electrons are fermions which must obey the Pauli exclusion principle.

The simplification achieved by these approximations is to replace the many-electron Schroedinger equation with an effective one-electron Schroedinger equation for a particle moving in an effective Coulomb potential determined by the wavefunctions of all the other electrons.

The Born Oppenheimer Approximation

The Born-Oppenheimer approximation takes the wavefunction of an atom or molecule to be the product

$$ \Psi = \psi_{\text{electrons}} \psi_{\text{nuclei}} $$

of independent wavefunctions for the electrons and the much heavier nuclei.

The electron wavefunction obeys an approximate many-electron Schroedinger equation with Hamiltonian

$$ H_{\text{B-O}} = \sum_i \frac{p_i^2}{2m} + \frac{1}{4\pi\epsilon_0} \sum_{i=0}^{N-2} \sum_{j=i+1}^{N-1} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} - \frac{1}{4\pi\epsilon_0} \sum_i \sum_k \frac{Z_n e^2}{|\mathbf{r}_i - \mathbf{R}_k|}, $$
where \( \mathbf{r}_i, \mathbf{p}_i \) are the position and momentum operators of the electrons, and \( Z_k, \mathbf{R}_k \) are the nuclear charge and classical position variable of the \( k \)-th nucleus.

For the Helium atom \( Z = 2 \) and the nucleus is assumed fixed at the origin \( \mathbf{R} = 0 \) of the electron coordinate system. For the Hydrogen molecule \( Z = 1 \) and \( R_k \) are taken to be fixed equilibrium positions of the two protons in the ground state of the molecule.

**Slater Determinant for the Many Electron Wavefunction**

Because electrons are fermions and obey the Pauli exclusion principle, the many electron wavefunction must be antisymmetric under exchange of any two electrons.

This property is absolutely essential to reproduce the observed shell structure of atomic electrons and the Fermi surface of electrons in metals.

The position and spin of the \( i \)-th electron can be represented by the combined variables

\[
\mathbf{x}_i = \{ \mathbf{r}_i, s_i \}
\]

where \( s_i \) is the spin quantum number of the electron along a quantization direction (conventionally chosen to be the \( z \) axis).

The *Slater determinant* is a product-form approximation to the many-electron wavefunction in which the \( N \) electrons are in \( N \) different quantum states described by single electron wavefunctions \( \psi_j \)

\[
\psi(\mathbf{x}_0, \mathbf{x}_1, \ldots, \mathbf{x}_{N-1}) = \frac{1}{\sqrt{N!}} \begin{vmatrix}
\psi_0(\mathbf{x}_0) & \psi_1(\mathbf{x}_0) & \cdots & \psi_{N-1}(\mathbf{x}_0) \\
\psi_0(\mathbf{x}_1) & \psi_1(\mathbf{x}_1) & \cdots & \psi_{N-1}(\mathbf{x}_1) \\
\vdots & \vdots & \ddots & \vdots \\
\psi_0(\mathbf{x}_{N-1}) & \psi_1(\mathbf{x}_{N-1}) & \cdots & \psi_{N-1}(\mathbf{x}_{N-1})
\end{vmatrix}.
\]
Self Consistent Field Method for the Ground State of the Helium Atom

If relativistic spin-orbit couplings are neglected, the single electron wavefunctions can be taken to be products of spin and orbital terms. Because there are only two electrons, the approximate ground state wavefunction is antisymmetric in spin with both electrons in the same orbital state

$$\psi(x_0, x_1) = \phi(r_0)\phi(r_1) \left[ \frac{|\uparrow\rangle_0 |\downarrow\rangle_1 - |\downarrow\rangle_0 |\uparrow\rangle_1}{\sqrt{2}} \right].$$

The time-independent two-electron Schroedinger equation in the Born-Oppenheimer approximation becomes

$$\left[ -\frac{1}{2} \nabla_0^2 - \frac{1}{2} \nabla_1^2 - \frac{2}{r_0} - \frac{2}{r_1} + \frac{1}{r_{01}} \right] \phi(r_0)\phi(r_1) = E\phi(r_0)\phi(r_1).$$

This equation is nonlinear in the unknown function $\phi(r)$. It is also non-local because it involves two points in space. The electron-electron interaction term prevents us from separating the equation into two local linear equations.

To solve this difficult problem Hartree suggested starting from a partially linearized equation obtained by multiplying both sides on the left by $\phi(r_1)$ and integrating over all space in the the variables $r_1$ to obtain

$$\left[ -\frac{1}{2} \nabla_0^2 - \frac{2}{r_0} + \int d^3 r_1 \frac{|\phi(r_1)|^2}{|r_0 - r_1|} \right] \phi(r_0) = E'\phi(r_0),$$

where the third integral term on the left is the Coulomb energy of the first electron in the field due to the charge density of the second, and the shifted eigenvalue

$$E' = E + \frac{1}{2} \int d^3 r \phi(r)\nabla^2\phi(r) + 2 \int d^3 r \frac{\phi(r)^2}{r},$$
differs from ground state energy $E$ by a constant factor independent of $r_0$.

The transformed equation looks like a one-particle Schroedinger equation with an additional integral contribution that depends on the solution we are trying to find.

To solve this equation Hartree suggested using a self-consistent iterative procedure:

- Start with a reasonable guess for $\phi(r)$.
  - Use this guess to evaluate the integral, which now serves as a “potential” energy $V(r_0)$.
  - Solve this linear Schroedinger equation to obtain an improved wavefunction $\phi_{\text{improved}}(r)$.
- Repeat the above steps with $\phi = \phi_{\text{improved}}$ until a self-consistent wavefunction is obtained.

**Approximate Solution Using a Linear Combination of Atomic Orbitals**

To solve the Hartree equation self-consistently, the unknown continuous function $\phi(r)$ must be approximated by a discrete set of unknown real numbers.

Variational LCAO wavefunctions provide a very convenient and widely used discretization. Slater-type orbitals (STO) are most familiar from atomic physics. Gaussian-type orbitals (GTO) are more appropriate for molecular problems and are very widely used in quantum chemistry software packages.

**A Simple GTO Parametrization for the Helium Atom**

Consider a GTO parametrization

$$
\phi(r) = \sum_{p=0}^{L-1} c_p \chi_p(r) = \sum_{p=0}^{P-1} c_p e^{-\alpha_p r^2},
$$
which parametrizes the unknown wavefunction using $PL$ real numbers $c_p, \alpha_p, p = 0, 1, \ldots, P-1$, to be determined by iterative solution of the Hartree equation.

**Using Published GTO Basis Sets**

To perform a full self-consistent calculation to determine all $2P$ parameters is complicated because the $\alpha_p$ occur in the Gaussian exponents. Most practical calculations make use of values in published Basis sets.

The following code uses four angular momentum $\ell = 0$ or s-wave Gaussians

$$\phi(r) = \sum_{p=0}^{3} c_p e^{-\alpha_p r^2},$$

and published values for $P = 4$ exponential coefficients

$$\alpha_0 = 0.297104, \quad \alpha_1 = 1.236745, \quad \alpha_2 = 5.749982, \quad \alpha_3 = 38.216677,$$

and determines the 4 prefactor coefficients $c_0, c_1, c_2, c_3$. This avoids the full nonlinear optimization required to determine all 8 coefficients self-consistently.
**C++ Code for the Helium Atom**

The single-particle Hartree-Fock equation for $\phi(\mathbf{r})$ is

$$\left[ -\frac{1}{2}\nabla^2 - \frac{2}{r} + \sum_{r,s} c_r c_s \int d^3 \mathbf{r}' \frac{\chi'(\mathbf{r}')\chi(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} \right] \sum_q c_q \chi_q(\mathbf{r}) = E' \sum_q c_q \chi_q(\mathbf{r}) .$$

Multiply on the left with $\chi(\mathbf{r})$ and integrate to reduce it to a $4 \times 4$ matrix equation

$$\sum_{p,q} \left[ h_{pq} + \sum_{rs} c_r c_s Q_{pqrs} \right] c_q = E' \sum_{pq} S_{pq} c_q$$

where

$$h_{pq} = \left\langle \chi_p \left| -\frac{1}{2}\nabla^2 - \frac{2}{r} \right| \chi_q \right\rangle = \frac{3\alpha_p\alpha_q\pi^{3/2}}{(\alpha_p + \alpha_q)^{5/2}} - \frac{2\pi e^2}{\alpha_p + \alpha_q} ,$$

$$S_{pq} = \langle \chi_p | \chi_q \rangle = \left( \frac{\pi}{\alpha_p + \alpha_q} \right)^{3/2} ,$$

and

$$Q_{pqrs} = \int d^3 \mathbf{r}_1 \int d^3 \mathbf{r}_2 \chi_p(\mathbf{r}_1)\chi_r(\mathbf{r}_1) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \chi_q(\mathbf{r}_1)\chi_s(\mathbf{r}_1)$$

$$= \frac{2\pi^{5/2}}{(\alpha_p + \alpha_q)(\alpha_r + \alpha_s)\sqrt{\alpha_p + \alpha_q + \alpha_r + \alpha_s}} .$$
Iterative Algorithm to Solve the Hartree-Fock Equation

The matrix equation for the unknown prefactor coefficient vector \( \mathbf{C} = \{c_0, c_1, c_2, c_3\} \) is not linear, so it is solved iteratively.

- Choose an initial \( \mathbf{C} \), for example \( \mathbf{C} = \frac{1}{\sqrt{4}} \{1, 1, 1, 1\} \)
  - Compute the \( 4 \times 4 \) matrix coefficients \( h_{pq} \) and \( S_{pq} \) and the \( 4 \times 4 \times 4 \times 4 \) matrix coefficients \( Q_{pqrs} \).
  - Construct a \( 4 \times 4 \) matrix \( \mathbf{A} \) with coefficients
    \[
    A_{pq} = h_{pq} + \frac{\sum_{rs} Q_{pqrs} c_r c_s}{\sum_{rs} c_r S_{rs} c_s}.
    \]
  - Solve the generalized eigenvalue problem
    \[
    \mathbf{A} \mathbf{C} = \mathbf{E}' \mathbf{S} \mathbf{C}
    \]
    for the eigenvector corresponding to the lowest eigenvalue. This equation can be solved using the LAPACK DSYGVD routine.

- Repeat the steps above using the eigenvector corresponding to the lowest eigenvalue until a self-consistent solution is obtained within the desired accuracy.

- The ground state energy is given by
  \[
  E = 2 \sum_{pq} c_p c_q h_{pq} + \sum_{pqrs} Q_{pqrs} c_p c_q c_r c_s.
  \]
/*
   Uses http://www.netlib.org/lapack/
   c++  -o helium-hf helium-hf.cpp  -llapack
*/

#include <cmath>
#include <cstdlib>
#include <fstream>
#include <iostream>
#include <string>
#include <vector>
using namespace std;

#include "lapack.hpp"

const double pi = 4 * atan(1.0);

typedef vector< vector<double> > matrix;
typedef vector< vector< vector<double> > > matrix4;

vector<double> C, alpha;
matrix A, H, S;
matrix4 Q;

void initialize(size_t N)
{
    C.resize(N);
    alpha.resize(N);
    A.resize(N);
    H.resize(N);
    S.resize(N);
    Q.resize(N);
    for (int i = 0; i < N; i++) {
        A[i].resize(N);
        H[i].resize(N);
        S[i].resize(N);
        Q[i].resize(N);
        for (int j = 0; j < N; j++) {
            Q[i][j].resize(N);
            for (int k = 0; k < N; k++)
                Q[i][j][k].resize(N);
        }
    }
}

void compute_coefficients()
{ 
   int N = alpha.size();
   for (int p = 0; p < N; ++p) {
      for (int q = 0; q < N; ++q) {
         H[p][q] = 3 * alpha[p] * alpha[q] * pow(pi, 3.0/2.0)
         * pow(alpha[p] + alpha[q], 5.0/2.0)
         - 2 * pi / (alpha[p] + alpha[q]);
         S[p][q] = pow(pi / (alpha[p] + alpha[q]), 3.0/2.0);
         for (int r = 0; r < N; ++r)
            for (int s = 0; s < N; ++s)
               Q[p][q][r][s] = 2 * pow(pi, 5.0/2.0)
               / (alpha[p] + alpha[q])
               / (alpha[r] + alpha[s])
               / sqrt(alpha[p] + alpha[q] + alpha[r] + alpha[s]);
      }
   }
}

int main()
{
   cout << " Hartree-Fock method for the Helium Atom using 4 s-wave GTO\n"
      << " Uses LAPACK DSYGVD to solve the Generalized Eigenvalue Problem"
      << endl;
}
size_t N = 4;
initialize(N);
alpha[0] = 0.297104;
alpha[1] = 1.236745;
alpha[2] = 5.749982;
alpha[0] = 38.21667;


return 0;