

Hartree Fock: An algorithm.

Two questions (broadly) are addressed.

- 1) How should we think of Hartree-Fock equations (interpretation),
- 2) What would it take to write your own Hartree-Fock program?

I will talk first about the details involved (2), then discuss (1).

Input for a Hartree-Fock procedure.

We assume we are given the A_0 integrals over a specified Atomic orbital basis χ_μ , $\mu = 1 \dots N$, to

one-electron integrals:

Two-electron integrals $\sum_{\mu\nu} h_{\mu\nu}$, $\sum_{\mu\nu\lambda\sigma} \langle \mu\nu | \sigma\tau \rangle$ (spatial ints!)

The equations that enter the Hartree-Fock approximation were discussed before. Let me summarize on next page.

Here I use spin-orbitals.

$$\langle \mu\nu || \sigma\tau \rangle = \langle \mu\nu | \sigma\tau \rangle - \langle \mu\nu | \tau\sigma \rangle,$$

$$C^+ S C = I$$

$$ID = C C^+$$

$$E = \sum_{\mu, \nu} h_{\mu\nu} D_{\mu\mu} + \frac{1}{2} \sum_{\mu, \nu} \sum_{\sigma, \tau} \langle \mu\nu || \sigma\tau \rangle D_{\sigma\mu} D_{\tau\nu}$$

$$F_{\mu\nu} = h_{\mu\nu} + \sum_{\sigma, \tau} \langle \mu\nu || \sigma\tau \rangle D_{\sigma\tau}$$

$$IFC = SCS, \text{ with } S \text{ diagonal (canonical HF orbitals)}$$

This is far from an actual algorithm. Let us consider the pieces first, and then stitch them together in an actual program. That is how I often work in practice: From the pieces (Subroutines) to the full program.

① Solving the generalized eigenvalue problem; construct D.

We wish to solve for C, S ,
having IF, S as input

$$\begin{cases} IF C = S C S \\ C^+ S C = I \end{cases}$$

To solve this, define

$$C_p = (S)^{\frac{1}{2}} C$$

$C' = C$ prime

$$C_p^+ C_p = C^+ (S)^{\frac{1}{2}} (S)^{\frac{1}{2}} C = I$$

$$= C^+ S C = I$$

$$(S^{\frac{1}{2}} C) = C_p \quad : \text{ orthonormal vectors.}$$

Then:

$$F (S^{\frac{1}{2}} C) = (S)^{\frac{1}{2}} C = (S)^{\frac{1}{2}} ((S)^{\frac{1}{2}} C) = I$$

$$(S^{-\frac{1}{2}} F S^{-\frac{1}{2}}) (C_p) = (C_p) = I$$

$$F' C' = C' = I$$

A regular eigenvalue problem.
 F' is symmetric / Hermitian.

$$C = (S)^{-\frac{1}{2}} (S^{\frac{1}{2}} C) = (S)^{-\frac{1}{2}} C_p$$

How to calculate $S^{-\frac{1}{2}} \equiv X$?

diagonalize S : $S = U S U^+$

$$(S)^{-\frac{1}{2}} = \frac{1}{\sqrt{S}} \quad (S)^{-\frac{1}{2}} = U (S)^{-\frac{1}{2}} U^+$$

just change the diagonal elements.

By diagonalizing F'
 we get the full set of
 orbital energies, ~~the~~ HAO.

To get lowest energy state, we
 usually fill the lowest energy
 orbitals: occupied MO's.

From this calculate density
 matrix

$$\begin{aligned}
 P_{\mu\nu} &= \sum_{a, \text{occ}} c_{\mu a} c_{\nu a} \\
 &= \sum_{a, \text{occ}} c_{\nu a} c_{\mu a}
 \end{aligned}
 \left. \vphantom{\sum_{a, \text{occ}}} \right\} \text{real orbitals.}$$

$$D = D^+ = D^T$$

(B) Constructing the Fock-matrix.
Treat spin explicitly.

$$\begin{aligned}
 F_{\mu\nu} &= h_{\mu\nu} + \sum_{\sigma, \tau} \langle \mu\tau | v\sigma \rangle D_{\sigma\tau} \\
 &= h_{\mu\nu} + \sum_{\sigma, \tau} \langle \mu\tau | v\sigma \rangle D_{\sigma\tau} \\
 &\quad - \sum_{\sigma, \tau} \langle \mu\tau | \sigma\nu \rangle D_{\sigma\tau}
 \end{aligned}$$

(in terms of spin-orbitals).

$$\begin{aligned}
 &= h_{\mu\nu} + J_{\mu\nu} - K_{\mu\nu} \\
 &\quad \downarrow \qquad \qquad \downarrow \\
 &\quad \text{Coulomb} \qquad \text{exchange.}
 \end{aligned}$$

The density matrix can be partitioned into 2 pieces

$$D^\alpha = (D^{\alpha\mu\nu}), \quad D^\beta = (D^{\beta\mu\nu})$$

$$D_{\mu\nu}^{(\alpha)} = \sum_{(a,\alpha)} \langle \psi_{(a,\alpha)} | \psi_{(a,\alpha)} \rangle$$

$$D_{\mu\nu}^{(\beta)} = \sum_{(a,\beta)} \langle \psi_{(a,\beta)} | \psi_{(a,\beta)} \rangle$$

Then

$$J_{\mu\nu} = \sum_{\alpha, \sigma} \langle \mu \tau_\alpha | \nu \sigma \rangle D_{\sigma\tau}^{(\alpha)} + \sum_{\beta, \sigma} \langle \mu \tau_\beta | \nu \sigma \rangle D_{\sigma\tau}^{(\beta)}$$

$$= \sum_{\sigma, \tau} \langle \mu \tau | \nu \sigma \rangle (D^{(\alpha)} + D^{(\beta)})_{\sigma\tau}$$

$$= \sum_{\sigma, \tau} \langle \mu \tau | \nu \sigma \rangle D_{\sigma\tau}^{\text{total}}$$

$$J^{(\alpha)} = J^{(\beta)}$$

only depends on total density matrix.

Exchange matrix is spin-dependent:

$$K_{\mu\nu}^{(d)} = \sum_{\sigma, \tau} \langle \mu_{\sigma} \tau_{\sigma} | \sigma_{\sigma} V_{\sigma} \rangle D_{\sigma\tau}^{(d)}$$

σ, τ have same spin, then also μ, ν

$$K_{\mu\nu}^{(\beta)} = \sum_{\sigma, \tau} \langle \mu_{\beta} \tau_{\beta} | \sigma_{\beta} V_{\beta} \rangle D_{\sigma\tau}^{(\beta)}$$

We can therefore assemble a spin-dependent Fock-matrix:

$$F_{\mu\nu}^{(d)} = h_{\mu\nu} + J_{\mu\nu} - K_{\mu\nu}^{(d)}$$

$$F_{\mu\nu}^{(\beta)} = h_{\mu\nu} + J_{\mu\nu} - K_{\mu\nu}^{(\beta)}$$

For closed-shell systems a simplification happens

$$D^{(d)} = D^{(\beta)}; \quad F^{(d)} = F^{(\beta)}$$

$$D^{\text{total}} = D^{(d)} + D^{(\beta)} = 2D^{(d)}$$

$$F_{\mu\nu} = h_{\mu\nu} + \sum_{\sigma, \tau} (2 \langle \mu_{\sigma} | v_{\tau} \rangle - \langle \mu_{\sigma} | \tau_{\nu} \rangle) D_{\sigma\tau}^{(d)}$$

\Rightarrow Unrestricted Hartree-Fock:
Separate treatment of α , β
orbitals.

Restricted HF: only solve
for α -orbitals, β -orbitals are
the same.

(C) Calculating total energy:

$$\begin{aligned}
 E &= \sum_{\mu\nu} h_{\mu\nu} (D_{\mu\mu}^{\alpha} + D_{\mu\mu}^{\beta}) \\
 &+ \frac{1}{2} \sum_{\substack{\mu, \nu \\ \sigma, \tau}} \langle \mu\nu || \sigma\tau \rangle D_{\nu\tau} D_{\mu\sigma} \\
 &= \frac{1}{2} \sum_{\mu, \sigma} h_{\mu\sigma} D_{\sigma\mu} \\
 &+ \frac{1}{2} \sum_{\mu, \sigma} \left(h_{\mu\sigma} + \sum_{\nu, \tau} \langle \mu\nu || \sigma\tau \rangle D_{\nu\tau} \right) D_{\mu\sigma} \\
 &= \frac{1}{2} \sum_{\mu, \sigma} h_{\mu\sigma} D_{\sigma\mu} + \frac{1}{2} \sum_{(\mu, \sigma)} f_{\mu\sigma} D_{\mu\sigma} \\
 &= \frac{1}{2} \sum_{\mu, \sigma} h_{\mu\sigma} D_{\sigma\mu}^{\text{total}} \\
 &+ \frac{1}{2} \sum_{\substack{\mu, \sigma \\ \alpha, \beta}} f_{\mu\sigma}^{(\alpha)} D_{\mu\sigma}^{(\alpha)} + \frac{1}{2} \sum_{\substack{\mu, \sigma \\ \beta}} f_{\mu\sigma}^{(\beta)} D_{\mu\sigma}^{(\beta)}
 \end{aligned}$$

Let us now describe the full Hartree-Fock program.

- 1) Obtain 1- and 2-electron integrals (e.g. from a file)
- 2) Calculate $X = (S)^{-\frac{1}{2}}$

initialize $D^{(in)} = 0$

iterate :

loop.

$D^{(in)}$ D_{in}^{α} , D_{in}^{β}
 Calculate F^{α} , F^{β}
 Solve $(X F^{\alpha} X) C^{\alpha} = C^{\alpha} \epsilon_{\alpha}$
 $(X F^{\beta} X) C^{\beta} = C^{\beta} \epsilon_{\beta}$
 $C^{\alpha} = X C^{\alpha}$ $C^{\beta} = X C^{\beta}$
 → Fill lowest orbitals
 $D_{\alpha}^{(out)} = C^{\alpha} (C^{\alpha})^T$
 $(D^{out})_{\beta} = C^{\beta} (C^{\beta})^T$
 calculate energy.

The error of Hartree-Fock is that we need to iterate.

The Fock matrix depends on input density. Upon diagonalization we get new orbitals, new output density.

Convergence is reached if the input and output density are equal.

=> monitor convergence:

$$\max_{\mu, \nu} \left| D_{\mu\nu}^{(i)} - D_{\mu\nu}^{(o)} \right|$$

$$< \text{threshold} \quad (\text{e.g. } 10^{-7})$$

If convergence, we are done.

If not, then locate better guess for density, for example

$$D_{\text{new}}^{(i)} = \gamma D_{\text{out}}^{(i)} + (1-\gamma) D_{\text{in}}^{(i)}$$

$$\gamma = 1 \quad D_{\text{new}} = D_{\text{out}}$$

$$\gamma = 0.7 \quad : \quad \text{Damped iteration.}$$

In practice most people / programs use DIIS convergence acceleration.

Interpretation of density matrix

Let us assume first we used an orthonormal basis. $|p\rangle$

Molecular orbitals: C_{pa}

$$D_{pq} = \sum_a C_{pa} C_{qa}$$

$$\hat{D} = \sum_{p,q} |p\rangle D_{pq} \langle q|$$

\hat{D} acts like a projection operator

$$D^\dagger = D$$

$$D_{pq} = D_{qp}$$

$$D^2 = D$$

$$\begin{aligned} \sum_g D_{pg} D_{gr} &= \sum_g \sum_a C_{pa} C_{ga} \sum_b C_{gb} C_{rb} \\ &= \sum_{a,b} C_{pa} \delta_{ab} C_{rb} = \\ &\quad \sum_a C_{pa} C_{ra} = D_{pr} \end{aligned}$$

Using orthonormality

$$\sum_g C_{ga} C_{gb} = \delta_{ab}$$

The eigenvalues of a projector are also 1, or 0

$$D u = u \lambda$$

$$D D u = D u \lambda = u \lambda^2 = u \lambda$$

$$\lambda^2 - \lambda = 0$$

$$\lambda(\lambda - 1) = 0$$

$$\lambda = 0 \text{ or } \lambda = 1$$

\Rightarrow occupied orbitals have eigenvalue 1

$$\begin{aligned} \sum_a C_{pa} C_{qa} & \quad \text{at } C_q c \\ &= \sum_a C_{pa} \delta_{ac} = C_{pc} \end{aligned}$$

Since occupied orbitals are all degenerate, we can rotate them, and they remain eigenstates of D , with eigenvalue 1.

$$D C_q \lambda$$

λ : virtual orbital

$$\sum_a C_{qa} C_{ga} = 0$$

therefore $D C_q \lambda = 0$, for virtual orbitals.

Interpretation: D projects on the occupied space.

The principles are the same in non-orthogonal basis, but details are more complicated. S-matrix needs to be considered.

Review

In the AO basis the idempotency of the density matrix is expressed as

$$D S' D = D$$

for:

$$\begin{aligned} (C C^+) S (C C^+) &= C (C^+ S C) C^+ \\ &= C \sum_{occ} C^+ = C C^+ = D \end{aligned}$$

Some current Hartree Fock programs (e.g. Dalton) minimize

$$E_{HF}[D] \quad \text{under constraints}$$

$$D S D = D, \quad \text{Tr}(D S) = N_{el}$$

$$\begin{aligned} \text{Tr}(D S) &= \text{Tr}(C C^+ S) \\ &= \text{Tr}(C^+ S C) = \text{Tr}(I_{occ}) = N_{el} \end{aligned}$$

Density functional theory is from an operational perspective very similar to Hartree-Fock.
(Kohn-Sham DFT, that is)

The energy expression is replaced by

$$\begin{aligned} E_{KS} &= \sum_{\mu} h_{\mu\mu} D_{\mu\mu} + \frac{1}{2} \sum_{\mu, \nu} \langle \mu \nu | \sigma^2 \rangle D_{\mu\mu} D_{\nu\nu} \\ &+ \frac{1}{2} \sum_{\mu, \nu} \sum_{\sigma, \tau} \langle \mu \nu | \sigma \tau \rangle D_{\sigma\mu} D_{\nu\tau} \\ &+ E_{xc}[D] \end{aligned}$$

$E_{xc}[\rho]$ is the so-called
exchange-correlation functional.
This gives rise to an additional
term to the KS Fock matrix

$$F = h + J + \frac{\partial E_{xc}}{\partial \rho_{\mu\nu}}$$

More later.

Fundamentals of Density Functional Theory.

The Hohenberg-Kohn theorem states that the electronic energy is a functional of the electron density $\rho(\vec{r})$.

Let us first discuss the electron density, for a general wfn $\Psi(1, 2, \dots, N)$. This quantity naturally derives by considering the expectation value of the V^{He} term: the so-called external potential.

$$\langle V^{\text{He}} \rangle = \int \Psi^*(1, 2, \dots, N) [V(1) + V(2) + \dots + V(N)] \Psi(1, 2, \dots, N) d1 \dots dN$$

Since electrons are indistinguishable I can take just $V(1)$, and multiply by $N = N_{\text{el}}$

$$\begin{aligned} \langle V^{\text{He}} \rangle &= N \int \Psi^*(1, 2, \dots, N) V(1) \Psi(1, 2, \dots, N) d1 \dots dN \\ &= \int d1 V(1) \cdot N \int d2 \dots dN \Psi^*(1, 2, N) \Psi(1, 2, N) d2 \dots dN \\ &\equiv \int d1 V(1) \rho(1) d1 \end{aligned}$$

I can also integrate over spin to get

$$\int d^3\vec{r} V(\vec{r}) \rho(\vec{r}) d$$

For a single Slater determinant:

$$\begin{aligned} \rho(\vec{r}) &= \sum_a \psi_a^*(\vec{r}) \psi_a(\vec{r}) \quad \langle \sigma | \sigma \rangle \\ &= \sum_{a, \alpha} |\psi_a^\alpha(\vec{r})|^2 + \sum_{a, \beta} |\psi_a^\beta(\vec{r})|^2 \\ &= \rho^\alpha(\vec{r}) + \rho^\beta(\vec{r}). \end{aligned}$$

In terms of the density matrix

$$\rho^\sigma(\vec{r}) = \sum_{\mu, \nu} \chi_\mu^*(\vec{r}) \chi_\nu(\vec{r}) P_{\mu\nu}^{[\sigma]}$$

The density is closely related to the finite basis density matrix.

To discuss the Hohenberg-Kohn Theorem, consider a family of Hamiltonians that differ in the external potential

$$\begin{aligned} H_a &= \hat{T} + \mathcal{V}_a + \hat{V}^{ee} \\ &= \hat{T} + \mathcal{V}_a + \hat{W} \quad (\text{I use } \hat{W} \text{ for } \hat{V}^{ee}) \end{aligned}$$

Then consider two such Hamiltonians H_a, H_b , in which potentials differ (by more than a constant). It is easily shown that such H_a, H_b have different ground ~~states~~ ^{states} ψ_a, ψ_b .

Let us assume ψ_a, ψ_b are each non-degenerate. Then the

Hohenberg-Kohn theorem says
that also ρ_a and ρ_b have
to be different.

Hence

$$H_a = \hat{T} + V_a + \hat{W}, \quad H_a \psi_a = E_a \psi_a; \quad \rho_a$$

$$H_b = \hat{T} + V_b + \hat{W}, \quad H_b \psi_b = E_b \psi_b; \quad \rho_b.$$

~~$$V_a \neq V_b + C$$~~

$$V_a \neq V_b + C$$

$$\Rightarrow \rho_a(\vec{r}) \neq \rho_b(\vec{r}) \quad \text{at least somewhere.}$$

Proof:

$$\langle \psi_b | H_a | \psi_b \rangle > E_a$$

$$\langle \psi_a | H_b | \psi_a \rangle > E_b$$

Used: Variational principle, non-degenerate
ground states; $\psi_a \neq c \psi_b$.

$$\text{Hence: } (\langle \psi_b | H_a | \psi_b \rangle - \langle \psi_a | H_a | \psi_a \rangle) \\ + (\langle \psi_a | H_b | \psi_a \rangle - \langle \psi_b | H_b | \psi_b \rangle) > 0$$

$$\text{or: } \int V_a(\mathbf{r}) \rho_b(\mathbf{r}) d\mathbf{r} - \int V_a(\mathbf{r}) \rho_a(\mathbf{r}) d\mathbf{r} \\ + \int V_b(\mathbf{r}) \rho_a(\mathbf{r}) d\mathbf{r} - \int V_b(\mathbf{r}) \rho_b(\mathbf{r}) d\mathbf{r} > 0$$

The terms $\hat{T} + \hat{W}$ cancel (verify in
exercise).

$$\Rightarrow \int (V_a(\mathbf{r}) - V_b(\mathbf{r})) (\rho_b(\mathbf{r}) - \rho_a(\mathbf{r})) d\mathbf{r} > 0$$

Since this is a strict inequality
it follows $\rho_a(r) \neq \rho_b(r)$, at least
somewhere.

Hence $\rho_a(r) \xrightarrow{\leftarrow} \rho_b(r)$

There is a 1-1 relation between
 $\rho_a(r)$ and the corresponding
ground state density $\rho_a(r)$.

$$\text{or: } \rho_a(r) \rightarrow \psi_a(r) \rightarrow \hat{H}_a = T + \mathcal{V}_a + \hat{W}$$

$$\rightarrow H_a \psi_\lambda = E_\lambda \psi_\lambda$$

The density has a 1-1 correspondence
to H_a and then determines
all energies of the system.

In quantum chemistry:

$S(r)$ determines positions +
charges of nuclei $\rightarrow \hat{H} \rightarrow$
all properties !!

We can make a mapping

$$H_a = T + \mathcal{V}_a + \hat{W} \rightarrow \psi_a \rightarrow \rho_a$$

$$E_a = \langle \psi_a | T + \hat{W} | \psi_a \rangle + \int \mathcal{V}_a(r) \rho_a(r) dr$$

$$E_{TW}[\rho_a] = \langle \psi_a | T + \hat{W} | \psi_a \rangle$$

$$= E_a - \int \mathcal{V}_a(r) \rho_a(r) dr$$

then $E[\rho] = E_{\text{TW}}(\rho) + \int V^{\text{He}}(r) \rho(r) d\vec{r}$

This is a functional of the density (a functional associates a number with each function in its domain, here $\rho(\vec{r})$)

The functional by construction reaches its minimum for $\rho = \rho_g$, and $E = E_0$.

The Hohenberg-Kohn principle / proof can be thought of as a construction using auxiliary potentials V_a . The functional is only defined for densities that are ground state densities of some Hamiltonian H_a , with external potential V_a . They are called V -representable densities.

Levy and Lieb made another construction: the constraint search:

Define $E[\rho] = \text{Sub}_{\psi \rightarrow \rho} \langle \psi | H | \psi \rangle$

i.e. Search over all ψ that integrate to ρ , and take the min as the minimum over all such ψ . This avoids issues with degeneracies, and so-called V -representability.

The weakness of both the Levy-Lieb and Hohenberg-Kohn principles is that they are only existence proofs. We have no explicit way of doing the search.

See also the paper I wrote, and posted on the web site, for more critique and discussion.

In current practice one postulates functionals, often satisfying some desirable criteria. But there is no systematic way to improve things.

In Kohn-Sham density functional theory, one minimizes the energy of a single determinant

$$\langle \Psi_h | \hat{T} + \hat{V}^{H_2} + V^{\text{Hartree}} | \Psi_h \rangle + E_{xc}[\rho]$$

In a finite basis this reduces to

$$\sum_{\mu, \nu} h_{\mu\nu} D_{\mu\nu} + \frac{1}{2} \sum_{\mu, \nu, \sigma, \tau} (V_{\mu\nu}/\epsilon_0) D_{\sigma\nu} D_{\sigma\tau} + \int E_{xc}(\rho)(\mathbf{r}) d\mathbf{r}$$

For example $E_{xc}(\rho) = \frac{4}{3} \int \rho(\mathbf{r}) d\mathbf{r}$

This is Dirac's formula for exchange.

More complicated $\bar{E}_{xc}(\rho)$ are used. These days often \bar{E}_{xc} is found as a functional of $D_{\mu\nu}$, or the molecular orbitals.

A key ingredient is the use of the conventional kinetic energy expression for a single determinant.

In practice the same self-consistent field procedure can be used as for the Hartree-Fock approximation. It leads to a Fock matrix of the form

$$F_{\mu\nu}^{KS} = h_{\mu\nu} + J_{\mu\nu} + \int \frac{\partial \bar{E}_{xc}(\rho)}{\partial \rho}(\mathbf{r}) \chi_{\mu}^*(\mathbf{r}) \chi_{\nu}(\mathbf{r}) d\mathbf{r}$$

The last term replace $-K_{\mu\nu}$ from H.F., and is typically evaluated using numerical integration.

The total energy upon stationarity is given before.

Highly efficient ways of implementing both HF and KS are available.

In practice one can evaluate

$$J_{\mu\nu} = \int \chi_{\mu}^*(\mathbf{r}) \chi_{\nu}(\mathbf{r}) d\mathbf{r} \int \frac{1}{r_{12}} \rho(\mathbf{r}_2) d\mathbf{r}_2$$

In different ways.

DFT, which does not include exact exchange, i.e. a fraction of the K_{xy} matrix, can be implemented very efficiently.

In chemistry most DFT approaches work partly with exact exchange.

They are referred to as hybrid DFT methods.

I mainly wanted to describe the formal considerations of DFT here.