CHEM400/740: Quantum Mechanics in Chemistry
Chapter#06: Hartree-Fock Algorithm / DFT Theory

Marcel Nooijen

Contents

1. 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 take first about the details involved 2), then discuss 1).

1.1   Input for a Hartree-Fock Procedure

We assume we are given the AO integrals over a specific Atomic orbital basis $|\mu\rangle, \mu = 1 \cdots N$.

- One-electron integrals: $h_{\mu\nu}, S_{\mu\nu}$.
- Two-electron integrals: $\langle \mu\nu | \sigma\tau \rangle$ (spatial integrals).
- The equations that under the Hartree-Fock approximation were discussed before. Let me summarize. (use spin-orbitals)
  1) Anti-symmetrizer:

$$\langle \mu\nu || \sigma\tau \rangle = \langle \mu\nu | \sigma\tau \rangle - \langle \mu\nu | \tau\sigma \rangle \tag{1}$$

  2) MO's are orthonormal:

$$C^\dagger S C = 1 \tag{2}$$

  3) Density matrix:

$$D = C C^\dagger \tag{3}$$

  4) Energy of Hartree-Fock:

$$E_{HF} = \sum_{\mu,\nu} h_{\mu\nu} D_{\nu\mu} + \frac{1}{2} \sum_{\mu,\nu,\sigma,\tau} \langle \mu\nu || \sigma\tau \rangle D_{\sigma\mu} D_{\tau\nu} \tag{4}$$

  5) Fock matrix:

$$F_{\mu\nu} = h_{\mu\nu} + \sum_{\nu\tau} \langle \mu\nu || \sigma\tau \rangle D_{\nu\tau} \tag{5}$$

  6) Generalized eigenfunction, where ε is diagonal (canonical HF orbitals):

$$FC = SC\varepsilon \tag{6}$$

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

1.2   Solving the Generalized Eigenvalue Problem (Construct D)

We wish to solve for C, ε, having F, S on input.

$$FC = SC\varepsilon \tag{7}$$

$$C^\dagger SC = 1 \tag{8}$$

To solve this, define C' as CP in equation (or computer program):

$$CP = (S)^{\frac{1}{2}}C \tag{9}$$

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

$$= C^\dagger SC = 1 \tag{10}$$

$(S)^{\frac{1}{2}}C = CP$: orthonormal orbitals. Then:

$$FC = SC\varepsilon \tag{11}$$

$$F(S)^{-\frac{1}{2}}(S)^{\frac{1}{2}}C = (S)^{\frac{1}{2}}((S)^{\frac{1}{2}}C)\varepsilon \tag{12}$$

$$((S)^{-\frac{1}{2}}F(S)^{-\frac{1}{2}})(CP) = (CP)\varepsilon \tag{13}$$

$$F'C' = C'\varepsilon \tag{14}$$

Here is a regular eigenvalue problem we can solve. Next, calculate the C matrix:

$$C = (S)^{-\frac{1}{2}}((S)^{\frac{1}{2}}C) = (S)^{-\frac{1}{2}}CP \tag{15}$$

The first step of calculation is to calculate $(S)^{-\frac{1}{2}} = X$. How to calculate X?
Diagonalize the S matrix: $S = uSu^\dagger$.
$$(S)^{-\frac{1}{2}} = u(S)^{-\frac{1}{2}}u^\dagger$$
Just change the diagonal elements.
By diagonalizing F' we get the full set of orbital energies, NAO.
To get lowest energy state, we usually fill the lowest energy orbitals: occupied MO's. From this calculate density matrix for real orbitals.

$$D_{\mu\nu} = \sum_{a,occ} C_{\mu a}C_{\nu a}^\dagger \tag{16}$$

$$D = D^\dagger = D^T \tag{17}$$

1.3   Construct Fock matrix

Constructing the Fock-matrix. Treat spin explicitly.

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

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

$$= h_{\mu\nu} + J_{\mu\nu} - K_{\mu\nu} \tag{18}$$

Note that $J\mu\nu$ represents Coulomb integral; $K_{\mu\nu}$ represents Exchange integral.

The density matrix can be partitioned by two pieces, D^{α} (spin-up) and D^{β} (spin-down).
For closed shells, D^{α} is equal to D^{β}. However, for open shells we have different α and β orbitals:

$$D_{\mu\nu}^{(\alpha)} = \sum_{a,\alpha} C_{\nu(a\alpha)} C_{\mu(a\alpha)} \tag{19}$$

$$D_{\mu\nu}^{(\beta)} = \sum_{a,\beta} C_{\nu(a\beta)} C_{\mu(a\beta)} \tag{20}$$

Then, the Coulomb matrix $J_{\mu\nu}$ in spatial integrals:

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

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

$$= \sum_{\tau,\sigma} \langle \mu\tau|\nu\sigma \rangle D_{\sigma\tau}^{\text{total}} \tag{21}$$

$$J^{\alpha} = J^{\beta} \tag{22}$$

The Coulomb (dirac) integral only depends on total density matrix.

Exchange matrix is spin-dependent:

$$K_{\mu\nu}^{(\alpha)} = \sum_{\tau,\sigma} \langle \mu_{\alpha}\tau_{\alpha}|\sigma_{\alpha}\nu_{\alpha} \rangle D_{\sigma\tau}^{(\alpha)} \tag{23}$$

$$K_{\mu\nu}^{(\beta)} = \sum_{\tau,\sigma} \langle \mu_{\beta}\tau_{\beta}|\sigma_{\beta}\nu_{\beta} \rangle D_{\sigma\tau}^{(\beta)} \tag{24}$$

For unrestricted open-shell systems (UHF), we can therefore assemble a spin-dependent Fock-matrix:

$$F_{\mu\nu}^{(\alpha)} = h_{\mu\nu} + J_{\mu\nu} - K_{\mu\nu}^{(\alpha)} \tag{25}$$

$$F_{\mu\nu}^{(\beta)} = h_{\mu\nu} + J_{\mu\nu} - K_{\mu\nu}^{(\beta)} \tag{26}$$

For closed-shell systems (RHF), a simplification happens:

$$D_{\mu\nu}^{(\alpha)} = D_{\mu\nu}^{(\beta)} \tag{27}$$

$$F_{\mu\nu}^{(\alpha)} = F_{\mu\nu}^{(\beta)} \tag{28}$$

$$D_{\sigma\tau}^{\text{total}} = D_{\mu\nu}^{(\alpha)} + D_{\mu\nu}^{(\beta)} = 2D^{\alpha} \tag{29}$$

$$F_{\mu\nu} = h_{\mu\nu} + \sum_{\tau,\sigma}(2\langle\mu\sigma|\nu\tau\rangle - \langle\mu\sigma|\tau\nu\rangle) \tag{30}$$

NOTE:

Unrestricted Hartree-Fock (UHF): Separate treatment of α, β orbitals.

Restricted Hartree-Fock (RHF): Only solve for α-orbitals, β-orbitals are the same.

1.4   Calculating Total Energy

There are two ways to calculate the total energy. First way just uses formulas as written. For open-shell system:

$$
\begin{aligned}
E_{\text{HF}} &= \sum_{\mu\nu} h_{\mu\nu}D_{\mu\nu} + \frac{1}{2}\sum_{\mu,\nu,\sigma,\tau}\langle\mu\nu||\sigma\tau\rangle D_{\nu\tau}D_{\mu\sigma} \\
&= \frac{1}{2}\sum_{\mu\sigma} h_{\mu\sigma}D_{\sigma\mu} + \frac{1}{2}\sum_{\mu,\sigma}(h_{\mu\sigma} + \sum_{\nu,\tau}\langle\mu\nu||\sigma\tau\rangle D_{\nu\tau})D_{\mu\sigma} \\
&= \frac{1}{2}\sum_{\mu\sigma} h_{\mu\sigma}D_{\sigma\mu} + \frac{1}{2}\sum_{\mu\sigma} f_{\mu\sigma}D_{\mu\sigma} \\
&= \frac{1}{2}\sum_{\mu\sigma} h_{\mu\sigma}D_{\sigma\mu}^{\text{total}} + \frac{1}{2}\sum_{\mu\sigma} f_{\mu\sigma}^{(\alpha)}D_{\mu\sigma}^{(\alpha)} + \frac{1}{2}\sum_{\mu\sigma} f_{\mu\sigma}^{(\beta)}D_{\mu\sigma}^{(\beta)}
\end{aligned} \tag{31}
$$

For closed-shell system:

$$E_{\text{HF}} = \underbrace{2}_{\alpha\&\beta\text{ spin}} \times \frac{1}{2}(h_{\mu\sigma} + J_{\mu\sigma})D_{\sigma\mu} \tag{32}$$

Different ways to calculate total energy using trace (linear algebra):

$$E_{\text{HF}} = 2 \times \frac{1}{2}\text{Tr}[(h + F)D] \tag{33}$$

Calculate E right after constructing Fock, not after diagonalization $\implies$ new density matrix, D $\implies$ Your energy of each iteration should be above final converged energy.

Let us describe the full Hartree-Fock program.

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

   Initialize: $D^{(\text{in})} = 0, F^{(\text{in})} = h$

   Iterate (Loop): $D^{(\text{in})} \qquad D_{(\text{in})}^{\alpha}, D_{(\text{in})}^{\beta}$

   Calculate: F^{α}, F^{β}

   Solve the generalized eigenvalue problem:

$$(XF^{\alpha}X)CP^{\alpha} = CP^{\alpha}\varepsilon_{\alpha}$$

$$(XF^\beta X)CP^\beta = CP^\beta \varepsilon_\beta$$

$$C^\alpha = XCP^\alpha$$

$$C^\beta = XCP^\beta$$

$$D_\alpha^{(\text{out})} = C^\alpha (C^\alpha)^T$$

$$D_\beta^{(\text{out})} = C^\beta (C^\beta)^T$$

Finally, calculate the energy.

NOTE:

- The crux of Hartree-Fock is that we need to iterate.
- The Fock matrix depends on input density. Upon diagonalization, we can get new orbitals and new output density.
- Convergence is matched if the input and output density are equal.

  $\implies$ How to check?

  $\implies$ Monitor convergence: $\boxed{\text{Max}_{\mu\nu} |D_{(\text{in})}^{(\sigma)} - D_{(\text{out})}^{(\sigma)}| < \text{threshold (e.g. } 10^{-7})}$.

  This means the absolute value of the maximum deviation between input density and output density is below the threshold.

- If convergence, we are done.

  If not, then create better guess by using linear combination of density, for example:

$$D_{\text{new}}^\sigma = \gamma D_{\text{out}}^\sigma + (1 - \gamma) D_{\text{in}}^\sigma \tag{34}$$

For $\gamma = 1$: $D_{\text{new}} = D_{\text{out}}$.

For $\gamma = 0.7$: Damped iteration.

In practice, most people/programs use DIIS convergence acceleration. DIIS: Dirac inverse of iterative subspace.(Peter Pulay, 1985).

Summary 1.1

Hartree-Fock Theory:

- minimize the energy of a single determinant.
- in a finite AO basis. $\Rightarrow$ Roothaan HF calculation.
- iterative procedures to minimize energy: $\boxed{\text{self-consistant field method}}$.

  self-consistant: $F(D^{\text{in}}) \to D^{\text{out}}$, if $D^{\text{in}} = D^{\text{out}}$ for self-consistant solution.

  field: Fock matrix describes V^{ee} in average way (mean field calculations).

  e.g. $J - K$: effective one-electron potential.

  $\quad V^{Ne} + J - K$: full potential.

1.5 Interpretation of Density Matrix

let us assume first er used an orthonormal basis, $|p\rangle$. For orthonormality:

$$\langle \alpha | \beta \rangle = S_{\alpha\beta} \tag{35}$$

$$\langle p | q \rangle = S_{pq} = 1 \tag{36}$$

Here, molecular orbital D_{pq}, instead of $D_{\mu\nu}$.

$$D_{pq} = \sum_a C_{pa} C_{qa} \tag{37}$$

$$\hat{D} = \sum_{pq} |p\rangle D_{pq} \langle q| \tag{38}$$

Note that $\hat{D}$ acts like a projection operator:

$$\hat{D}^\dagger = \hat{D} \tag{39}$$

$$\hat{D}_{pq} = \hat{D}_{qp} \tag{40}$$

$$\hat{D}^2 = \hat{D} \qquad \text{(idempotent)} \tag{41}$$

$$\sum_q D_{pq} D_{qr} = \sum_q \sum_a C_{pa} C_{qa} \sum_b C_{qb} C_{rb}$$

$$= \sum_{a,b} C_{pa} \delta_{ab} C_{rb}$$

$$= \sum_a C_{pa} C_{ra} = D_{pr} \tag{42}$$

Note that use orthonormality in equation(42): $\sum_q C_{qa} C_{qb} = \delta_{ab}$.

The eigenvalue of a projector are also "1" or "0".
"1" means vector doesn't change. "0" means perpendicular. Proof:

$$Du = u\lambda \tag{43}$$

$$D \cdot Du = (Du)\lambda = u\lambda^2 = u\lambda \tag{44}$$

$$\lambda^2 - \lambda = 0 \tag{45}$$

$$\lambda = 1 \text{ or } \lambda = 0 \tag{46}$$

[a]. Occupied orbitals have eigenvalue 1. a for occupied orbitals.

$$\sum_q \sum_a C_{pa} (C_{qa} C_{qc}) = \sum_a C_{pa} \delta_{ac} = C_{pc} \tag{47}$$

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

[b]. Virtual orbitals have eigenvalue 0. r for virtual orbitals.

$$\sum_q C_{qa} C_{qr} = 0 \tag{48}$$

Therefore, $DC_{q\lambda} = 0$, for virtual orbitals.

1.5.1   Interpretation

D projector on the occupied space.

The principle are the same in non-orthonormal basis, but details are more complicated. The symmetric matrix needs to be considered. In the AO basis the idempotency of the density matrix is expressed as, $DSD = D$. for:

$$D = CnC^\dagger \tag{49}$$

$$\begin{aligned}
DSD &= (CnC^\dagger)S(CnC^\dagger) \\
&= Cn(C^\dagger S C)nC^\dagger \\
&= Cn1nC^\dagger \qquad (n \cdot n = n \text{ diagonal}) \\
&= CnC^\dagger \\
&= D \tag{50}
\end{aligned}$$

NOTE: The expression, $DSD = D$, analogue of idempotent [projector] in an non-orthonormal basis.

Some current Hartree-Fock programs (e.g. Dalton) minimize $E_{\text{HF}}[D]$ under constraints, $DSD = D, Tr(DS) = N_{el}$.

$$Tr(DS) = Tr(CC^\dagger S) = Tr(C^\dagger SC) = Tr(1) = N_{el} \tag{51}$$

2. Fundamentals of Density Functional Theory

Density functional theory is from a generational perspective very similar to Hartree-Fock (Kohn-Sham DFT). The energy expression is replaced by E_{KS}.

$$E_{KS} = h_{\mu\nu}D_{\mu\nu} + \frac{1}{2}\sum_{\mu\nu\sigma\tau}\langle\mu\nu|\sigma\tau\rangle D_{\sigma\mu}D_{\nu\tau} + E_{xc}[D] \tag{52}$$

NOTE:

- $\frac{1}{2}\sum_{\mu\nu\sigma\tau}\langle\mu\nu|\sigma\tau\rangle D_{\sigma\mu}D_{\nu\tau}$ is 2-electron Dirac Coulomb term.
- $E_{xc}[D]$ is so-called exchange-correlation functional. This gives rise to an additional term to the

KS Fock matrix.

$$F = h + J + \frac{\partial E_{xc}}{\partial D_{\mu\nu}} \tag{53}$$

- Results from DFT depend on 'empirical' choice of E_{ec}. (e.g. B3Lyp, Bp98, PBE, $\cdots$)
  Results for geometries and vibrational frequencies are very good. (B3Lyp for molecules)
  Thermo-chemistry: Not bad (within 3-5 kcal/mol often).

2.1 Hohenberg–Kohn Theorem

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 wavefunction $\psi(1, 2, \cdots, N)$. This quantity naturally derives by considering the expectation value of the V^{Ne} term, so-called external potential.

$$\langle V^{Ne} \rangle = \int \psi^*(1, 2, \cdots, N)[\hat{V}^{Ne}(1) + \hat{V}^{Ne}(2) + \cdots + \hat{V}^{Ne}(N)]\psi(1, 2, \cdots, N)d1 \cdots dN \tag{54}$$

$$\hat{V}^{Ne} = \sum_i \hat{V}^{Ne}(i) \tag{55}$$

Since electrons are indistinguishable. I can take just $\hat{V}^{Ne}(1)$, and multiply by $N(N_{el})$.

$$\begin{aligned}
\langle V^{Ne} \rangle &= N \int \psi^*(1, 2, \cdots, N)\hat{V}(1)\psi(1, 2, \cdots, N)d1 \cdots dN \\
&= \int d1\hat{V}(1) \cdot N \int d2 \cdots dN\psi^*(1, 2, N)\psi(1, 2, N)d2 \cdots dN \\
&= N \int d1\hat{V}(1)\rho(1)d1
\end{aligned} \tag{56}$$

$\rho(\vec{r})$ is the probability to find an electron at position $\vec{r}$. This is also the distribution of electrons.

$$\rho(\vec{r}) = N \int dr_2 dr_3 \cdots dr_N \psi^*(r_2, r_3, \cdots, r_N)\psi(r_2, r_3, \cdots, r_N) \tag{57}$$

- For a single Slater determinant:

$$\begin{aligned}
\rho(\vec{r}) &= \sum_a \psi_a^*(\vec{r})\psi_a(\vec{r})\langle\sigma|\sigma\rangle \\
&= \sum_{a,\alpha} |\psi_a^\alpha(r)|^2 + \sum_{a,\beta} |\psi_a^\beta(r)|^2 \\
&= \rho^\alpha(\vec{r}) + \rho^\beta(\vec{r})
\end{aligned} \tag{58}$$

- In terms of density matrix:

$$\rho(\vec{r}) = \sum_{\mu,\nu} \chi_\mu^*(r)\chi_\nu(r)D_{\mu\nu}^{[\sigma]} \tag{59}$$

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

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

$$\hat{H}_a = \hat{T} + V_a + \hat{V}^{ee}$$
$$= \hat{T} + V_a + \hat{w} \tag{60}$$

NOTE:

- Kinetic energy, $\hat{T}$ and $\frac{1}{r_{ij}}$ interactions between electrons, $\hat{V}^{ee}$ are always same.
- Often use $\hat{w}$ for $\hat{V}^{ee}$ in DFT literatures.

Then consider two such Hamiltonians $\hat{H}_a$, $\hat{H}_b$, in which potentials differ (by more than a constant). It is easily shown that such $\hat{H}_a$, $\hat{H}_b$ have different ground states ψ_a, ψ_b. Here is a plausible issue, not a proof:

if $\psi_a = \psi_b$ everywhere, then:

$$(\hat{H}_a - \hat{H}_b)\psi_a(\vec{r}) = (E_a - E_b)\psi_a(\vec{r})$$
$$= (V_a(\vec{r}) - V_b(\vec{r}))\psi_a(\vec{r})$$
$$= C\psi_a(\vec{r}) \tag{61}$$

$$(V_a(\vec{r}) - V_b(\vec{r}) - C)\psi_a(\vec{r}) = 0 \tag{62}$$

Note that $\psi_a(\vec{r}) = 0$ at all points when $V_a(\vec{r}) \neq V_b(\vec{r}) + C$.

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:

$$\hat{H}_a = \hat{T} + V_a + \hat{w}; \qquad \hat{H}_a\psi_a = E_a\psi_a; \qquad \rho_a \tag{63}$$
$$\hat{H}_b = \hat{T} + V_b + \hat{w}; \qquad \hat{H}_b\psi_b = E_b\psi_b; \qquad \rho_b \tag{64}$$

Conclusion: $\rho_a(\vec{r}) \neq \rho_b(\vec{r})$ at least somewhere.

Proof:

$$\langle \psi_b | \hat{H}_a | \psi_b \rangle > E_a \tag{65}$$
$$\langle \psi_a | \hat{H}_b | \psi_a \rangle > E_b \tag{66}$$

Used: variational principle, non-dependent ground states. Hence:

$$(\langle \psi_b | \hat{H}_a | \psi_b \rangle - \overbrace{\langle \psi_a | \hat{H}_a | \psi_a \rangle}^{E_a}) + (\langle \psi_a | \hat{H}_b | \psi_a \rangle - \overbrace{\langle \psi_b | \hat{H}_b | \psi_b \rangle}^{E_b}) > 0 \tag{67}$$

$$\int V_a(1)\rho_b(1)d1 - \int V_a(1)\rho_a(1)d1 + \int V_b(1)\rho_a(1)d1 - \int V_b(1)\rho_b(1)d1 > 0 \tag{68}$$

$$\int (V_a(1) - V_b(1))(\rho_b(1) - \rho_a(1))d1 > 0 \qquad (69)$$

Note that the terms of $\hat{T} + \hat{w}$ cancel (varity in exercise).

2.2   The Significance of Hohenberg–Kohn Theorem

Since this is a strict inequity it follows $\rho_a(1) \neq \rho_b(1)$, at least somewhere. Hence, $V_a(1) \leftrightarrows \rho_a(1)$. There is a one-to-one relation between $V_a(1)$ and the corresponding ground state density, $\rho_a(1)$.

$$\rho_a(1) \rightarrow V_a(1) \rightarrow \hat{H}_a = \hat{T} + V_a + \hat{w} \rightarrow \hat{H}_a \psi_\lambda = E_\lambda \psi_\lambda.$$

The density has a one-to-one correspondence to $\hat{H}$, and then determine all energies of the system. In quantum chemistry:

$\rho(r)$ determine position + charge of nuclei $\rightarrow \hat{H} \rightarrow$ all properties.

We can make a mapping:

$$H_a = \hat{T} + V_a + \hat{w} \rightarrow \psi_a \rightarrow \rho_a$$
$$E_a = \langle \psi_a | \hat{T} + \hat{w} | \psi_a \rangle + \int V_a(r) \rho_a(r) dr$$
$$E_{TW}[\rho_a] = \langle \psi_a | \hat{T} + \hat{w} | \psi_a \rangle = E_a - \int V_a(r) \rho_a(r) dr$$

Then,

$$E[\rho] = E_{TW}[\rho] + \int V^{Ne}(r) \rho(r) dr \qquad (70)$$

This is a functional of the density (a functional associates a number with each function in its domain, here $\rho(r)$). 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 external potentials V_a. The functional is defined for densities that are ground state densities of Hamiltonian $\hat{H}_a$, with external potential V_a. They are called N-representable electron density.

Levy and Lieb made another construction: the constrained-search principle. Define:

$$E[\rho] = Sub_{\psi \rightarrow \rho} \langle \psi | \hat{H} | \psi \rangle \qquad (71)$$

Search over all ψ that integrate to ρ and take the energy as the minimum over all such ψ. This avoids issues with degeneracies and so-called N-representability.

The weakness of both the Levy-Lieb and Hohenberg–Kohn principle 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 website for more discussion.

2.3   DFT in Practice

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

$$E^{KS} = \langle \phi_{KS} | \hat{T} + \hat{V}^{Ne} + \hat{V}^{Hartree} | \phi_{KS} \rangle + E_{ec}[\rho] \qquad (72)$$

NOTE:

- $V^{Hartree}$: Dirac Coulomb term from HF. e.g. J matrix for electron 1, $V(1) = \int \frac{1}{r_{12}}\rho(2)d2$.
- $E_{xc}(\rho)$: Exchange correlation energy.

In a finite basis this reduces to:

$$E^{KS} = h_{\mu\nu}D_{\mu\nu} + \frac{1}{2}\sum_{\mu\nu\sigma\tau}\langle\mu\nu|\sigma\tau\rangle D_{\sigma\mu}D_{\tau\nu} + \int \varepsilon_{ec}(\rho)(1)d1 \tag{73}$$

For example, 'local density' approximation: $\varepsilon_{ec}(\rho) = -\frac{2}{3}\rho^{4/3}(1)$. (Dirac's formula for exchange)

More complicated $E_{ec}(\rho)$ are used. Usually, E_{ec} 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 a Fock matrix of the form:

$$F_{\mu\nu}^{KS} = h_{\mu\nu} + J_{\mu\nu} + \int \frac{\partial E_{xc}}{\partial\rho}\chi_{\mu}^{*}(1)\chi_{\nu}(1)d1 \tag{74}$$

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.

$$J_{\mu\nu} = \int \chi_{\mu}^{*}(1)\chi_{\nu}(1)d1 \int \frac{1}{r_{12}}\rho(r_2)dr_2 \tag{75}$$

DFT, which does not include exact exchange, a fraction of the $K_{\mu\nu}$ matrix, can be implemented very efficiently. In chemistry, most DFT approaches work with exact exchange. They are referred to as hybrid DFT methods.

The above part mainly describes the formal considerations of DFT.