# Theory and implementation of DFT-based methods

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# Idea behind density-functional theory (DFT)

Walter Kohn (1923-2016)



Hohenberg-Kohn theorem

The ground state electronic energy is completely determined by the electron density $\rho$

There is a one-to-one correspondence between $\rho$ and the energy $E$

Hohenberg-Kohn theorem shows that you can use the electron density $\rho(\boldsymbol{r})$ instead of the wave function $\Psi(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_n)$

**The functional connecting $\rho$ and $E$ is unknown....**
The goal is to design functionals connecting the electron density with the energy...

Hohenberg & Kohn, Phys Rev 136 (1964) B864

# Kohn-Sham (KS) theory

In the KS formalism, one writes the total energy as

$$E_{KS}[\rho] = T_S[\rho] + E_{ne}[\rho] + J[\rho] + E_{xc}[\rho]$$

where

$$\rho(\boldsymbol{r}) = \sum_i^{occ} |\psi_i(\boldsymbol{r})|^2 \qquad = \quad \text{electronic density}$$

$$T_S[\rho] = \sum_i^{occ} \langle \psi_i | -\frac{\nabla^2}{2} | \psi_i \rangle \qquad = \quad \text{non-interacting kinetic energy}$$

$$E_{ne}[\rho] = -\sum_A^{nuc} \int \frac{Z_A \rho(\boldsymbol{r})}{|\boldsymbol{R}_A - \boldsymbol{r}|} d\boldsymbol{r} \qquad = \quad \text{electron-nucleus attraction}$$

$$J[\rho] = \frac{1}{2} \iint \frac{\rho(\boldsymbol{r}_1)\rho(\boldsymbol{r}_2)}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} d\boldsymbol{r}_1 d\boldsymbol{r}_2 \qquad = \quad \text{classical Coulomb repulsion}$$

$$E_{xc}[\rho] = (T[\rho] - T_S[\rho]) + (E_{ee}[\rho] - J[\rho]) \qquad = \quad \text{exchange-correlation energy}$$

Kohn & Sham Phys Rev 140 (1965) A1133

## Density, Exchange and Correlation

The exchange-correlation energy is defined as

$$E_{xc}[\rho, \zeta] = E_x[\rho, \zeta] + E_c[\rho, \zeta]$$
$$= \int \rho(\mathbf{r}) e_x[\rho(\mathbf{r}), \zeta] d\mathbf{r} + \int \rho(\mathbf{r}) e_c[\rho(\mathbf{r}), \zeta] d\mathbf{r}$$

The total density is

$$\rho = \rho_\alpha + \rho_\beta$$

The spin polarization is

$$\zeta = \frac{\rho_\alpha - \rho_\beta}{\rho} = \frac{n_\alpha - n_\beta}{n}$$

The exchange energy is given by

$$E_x[\rho, \zeta] = E_{x,\alpha}[\rho_\alpha] + E_{x,\beta}[\rho_\beta]$$

The correlation energy is given by

$$E_c[\rho, \zeta] = E_{c,\alpha\alpha}[\rho_\alpha] + E_{c,\beta\beta}[\rho_\beta] + E_{c,\alpha\beta}[\rho_\alpha, \rho_\beta]$$

# Density-functional approximations for exchange

From a practical point of view, the exchange energy is given by

$$E_{x,\sigma} = \int e_x(\rho_\sigma, \nabla\rho_\sigma, \tau_\sigma, \ldots)\,\rho_\sigma\,d\boldsymbol{r}$$
$$\approx \sum_i w_i\, e_x[\rho_\sigma(\boldsymbol{r}_i), \nabla\rho_\sigma(\boldsymbol{r}_i), \tau_\sigma(\boldsymbol{r}_i), \ldots]\,\rho_\sigma(\boldsymbol{r}_i)$$

where

- $\rho(\boldsymbol{r}) = \sum_i^{\mathrm{occ}} |\psi_i(\boldsymbol{r})|^2$ is the one-electron density

- $\nabla\rho(\boldsymbol{r})$ is the gradient of the density

- $\tau(\boldsymbol{r}) = \sum_i^{\mathrm{occ}} |\nabla\psi_i(\boldsymbol{r})|^2$ is the kinetic energy density

# Local density approximation (LDA) exchange

The LDA exchange energy (Dirac formula or D30) is

$$E_x^{LDA} = \int \rho(\mathbf{r}) e_x^{LDA}(\rho) d\mathbf{r} = C_x \int \rho(\mathbf{r})^{4/3} d\mathbf{r}$$

$$\boxed{e_x^{LDA}(\rho) = C_x \rho^{1/3}}$$

where

$$C_x = -\frac{3}{2}\left(\frac{3}{4\pi}\right)^{1/3} = -0.930526\dots$$

has been obtained based on the infinite uniform electron gas (IUEG) or jellium

Dirac, Proc Cam Phil Soc 26 (1930) 376
Loos & Gill, WIREs Comput Mol Sci 6 (2016) 410

# How good is LDA?

Table: Reduced (i.e. per electron) mean error (ME) and mean absolute error (MAE) (in kcal/mol) of the error (compared to UHF) in the exchange energy

|  |  | hydrogen-like ions | | helium-like ions | | neutral atoms | |
|---|---|---|---|---|---|---|---|
|  |  | ME | MAE | ME | MAE | ME | MAE |
| LDA | D30 | 153.5 | 69.7 | 150.6 | 69.5 | 70.3 | 9.1 |

Rule of thumb: LDA underestimates the exchange by 10%

# Generalized gradient approximation (GGA) exchange

Sham has shown that, for an "almost" uniform electron gas,

$$E_x^{\text{GGA}} \approx E_x^{\text{LDA}} - \frac{5}{(36\pi)^{5/3}} \int \rho(\mathbf{r})^{4/3} x^2 \, d\mathbf{r}$$

where

$$x = \frac{|\nabla \rho|}{\rho^{4/3}} \quad \text{is the reduced gradient.}$$

The GGA exchange energy is

$$E_x^{\text{GGA}} = \int F_x^{\text{GGA}}(x) e_x^{\text{LDA}}(\rho) \rho(\mathbf{r}) d\mathbf{r} = C_x \int F_x^{\text{GGA}}(x) \rho(\mathbf{r})^{4/3} d\mathbf{r}$$

$F_x^{\text{GGA}}(x)$ is usually called the GGA enhancement factor and "smart" GGAs have

$$\lim_{x \to 0} F_x^{\text{GGA}}(x) = 1$$

Sham, in Computational Methods in Band Theory, edited by P. M Marcus, J. F. Janak, and A. R. Williams (Plenum, New York, 1971)

# Fashionable GGAs

**B88 [PRA 38 (1988) 3098]**

$$F_x^{B88}(x) = 1 - \frac{0.0042\,x^2}{1 + 0.0252\,x\sinh^{-1}x}$$

**PW91 [PRB 46 (1992) 6671]**

$$F_x^{PW91}(x) = \text{ugly}$$

**G96 [Mol Phys 89 (1996) 433]**

$$F_x^{G96}(x) = 1 - \frac{x^{3/2}}{137}$$

**PBE [PRL 77 (1996) 3865]**

$$F_x^{PBE}(x) = 1.804 - \frac{0.804}{1 + 0.0071x^2}$$

## Are GGAs better than LDA?

Table: Reduced (i.e. per electron) mean error (ME) and mean absolute error (MAE) (in kcal/mol) of the error (compared to UHF) in the exchange energy

|      |      | hydrogen-like ions | | helium-like ions | | neutral atoms | |
|------|------|------|------|------|------|------|------|
|      |      | ME   | MAE  | ME   | MAE  | ME   | MAE  |
| LDA  | D30  | 153.5 | 69.7 | 150.6 | 69.5 | 70.3 | 9.1 |
| **GGA** | B88 | 9.5 | 4.3 | 9.3 | 4.7 | 2.8 | 0.5 |
|      | G96  | 4.4  | 2.0  | 4.4  | 2.2  | 2.1  | 0.5  |
|      | PW91 | 19.4 | 8.8  | 19.1 | 9.3  | 4.5  | 0.8  |
|      | PBE  | 22.6 | 10.3 | 22.3 | 10.7 | 7.4  | 0.6  |

Rule of thumb: GGAs are really good...

# Meta-generalized gradient approximation (MGGA) exchange

Because it wasn't enough, people have introduced $\tau$ in functionals

$$e_x^{MGGA}(\rho, x, \tau) = e_x^{LDA}(\rho) F_x^{MGGA}(x, \tau)$$

**or**

$$e_x^{MGGA}(\rho, x, \alpha) = e_x^{LDA}(\rho) F_x^{MGGA}(x, \alpha)$$

where $0 \leq \alpha < \infty$ is the curvature of the Fermi hole*:

$$\boxed{\alpha = \frac{\tau - \tau_W}{\tau_{IUEG}} = \frac{\tau}{\tau_{IUEG}} - \frac{x^2}{4 C_F}} \qquad C_F = \frac{3}{5}(6\pi^2)^{2/3}$$

$$\tau_W = \frac{|\nabla \rho|^2}{4\,\rho} \quad \text{is the von Weizsäcker kinetic energy density}$$

$$\tau_{IUEG} = C_F \rho^{5/3} \quad \text{is the kinetic energy density of the IUEG}$$

Well thought-out MGGAs ensure that

$$\lim_{x \to 0} \lim_{\alpha \to 1} F_x^{MGGA}(x, \alpha) = 1$$

*Remember ELF!? ELF $= (1 + \alpha^2)^{-1}$

## Fashionable MGGAs

**M06-L [JCP 125 (2006) 194101]**

$F_{\mathrm{x}}^{\mathrm{M06\text{-}L}}(x) = $ awful (17 parameters)

**TPSS [PRL 91 (2003) 146401]**

$F_{\mathrm{x}}^{\mathrm{TPSS}}(x) = $ not pretty

**mBEEF [JCP 140 (2014) 144107]**

$F_{\mathrm{x}}^{\mathrm{mBEEF}}(x) = $ very ugly (64 parameters)*

**SCAN [PRL 115 (2015) 036402]**

$F_{\mathrm{x}}^{\mathrm{SCAN}}(x) = $ long (constraint with "model" systems)

*spits you out a Bayesian error estimate for the same price

## Are MGGAs better than GGAs?

Table: Reduced (i.e. per electron) mean error (ME) and mean absolute error (MAE) (in kcal/mol) of the error (compared to UHF) in the exchange energy

|        |         | hydrogen-like ions | | helium-like ions | | neutral atoms | |
|--------|---------|-------|------|-------|------|------|------|
|        |         | ME    | MAE  | ME    | MAE  | ME   | MAE  |
| LDA    | D30     | 153.5 | 69.7 | 150.6 | 69.5 | 70.3 | 9.1  |
| GGA    | B88     | 9.5   | 4.3  | 9.3   | 4.7  | 2.8  | 0.5  |
|        | G96     | 4.4   | 2.0  | 4.4   | 2.2  | 2.1  | 0.5  |
|        | PW91    | 19.4  | 8.8  | 19.1  | 9.3  | 4.5  | 0.8  |
|        | PBE     | 22.6  | 10.3 | 22.3  | 10.7 | 7.4  | 0.6  |
| **MGGA** | M06-L | 44.4  | 88.8 | 12.0  | 24.0 | 4.2  | 2.9  |
|        | TPSS    | 0.0   | 0.0  | 0.7   | 0.4  | 0.7  | 1.1  |
|        | revTPSS | 0.0   | 0.0  | 0.5   | 0.3  | 3.5  | 2.5  |
|        | MS0     | 0.0   | 0.0  | 0.4   | 0.2  | 1.3  | 2.4  |
|        | MVS     | 0.0   | 0.0  | 0.3   | 0.2  | 2.7  | 0.9  |
|        | SCAN    | 0.0   | 0.0  | 0.3   | 0.2  | 1.2  | 1.6  |

Rule of thumb: MGGAs are slightly better than GGAs...
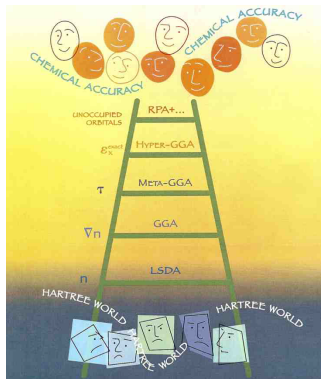
# A zoo of functionals

Pick your poison...



Peter Elliott    1

Burke, JCP 136 (2012) 150901

# Jacob's ladder of DFT

| Level | Name | Variables | Examples |
|-------|------|-----------|----------|
| 1 | LDA | $\rho$ | VWN,PZ81,X$\alpha$ |
| 2 | GGA | $\rho,\nabla\rho$ | BLYP,OLYP,PW86,PW91,PBE,PBEsol |
| 3 | meta-GGA | $\rho,\nabla\rho,\nabla^2\rho,\tau$ | BR,B95,TPSS,SCAN |
| 4 | hyper-GGA | + HF exchange | BH&H, B3LYP,B3PW91,O3LYP,PBE0 |
| 5 | generalized-RPA | + HF virtual orbitals | OEP2 |

# The good, the bad and the ugly...

## DFT successes

- Sometimes predicts reaction energetics with amazing accuracy
- Often predicts molecular structures of high quality
- Often predicts vibrational frequencies that agree well with experiment
- Vertical transition energies to low-lying excited states very good
- and many others...

## DFT failures

- $H_2^+$, $He_2^+$ and other odd-electron bonds: self-interaction error
- Relative alkane energies, large extended $\pi$ systems, Diels-Alder reaction, etc.
- Weak interactions due to dispersion forces (van der Waals)
- Charge-transfer excited, core-excited and Rydberg states
- Strongly-correlated systems
- and many others...

# Radial and angular quadratures

### Euler-Maclaurin quadrature

$$\int_0^\infty r^2 f(r) dr \approx \sum_{i=1}^{N_{rad}} w_i f(r_i)$$

where the roots and weights are

$$r_i = R\, i^2 (N_{rad} + 1 - i)^{-2}$$
$$w_i = 2R^3 (N_{rad} + 1) i^5 (N_{rad} + 1 - i)^{-7}$$

### Lebedev quadrature

$$\int_S g(x, y, z) d\Omega \approx \sum_{j=1}^{N_{ang}} W_j g(x_j, y_j, z_j)$$

where the roots $(x_j, y_j, z_j)$ and weights $W_j$ are chosen so that the quadrature is exact for as many low-degree spherical harmonics as possible.

## Quadrature in 3D

In typical DFT calculations, we are faced with integrals over all space

$$I = \int F(\boldsymbol{r}) d\boldsymbol{r}$$

If an atomic nucleus forms a natural origin, we can express this integral in terms of spherical polar coordinates and then estimate the radial and angular integrals using the quadratures described above, i.e.

$$I = \int_0^\infty \int_0^\pi \int_0^{2\pi} F(r, \theta, \phi) \ r^2 \sin\theta \, d\phi \, d\theta \, dr$$

$$\approx \sum_{i=1}^{N_{\text{rad}}} \sum_{j=1}^{N_{\text{ang}}} w_i W_j F(r_i, \theta_j, \phi_j)$$

## Testing the numerical quadrature

The number of electrons is given by

$$n = \int \rho(\mathbf{r})d\mathbf{r} = \int_0^\infty \int_0^\pi \int_0^{2\pi} \rho(r, \theta, \phi) \ r^2 \sin\theta \, d\phi \, d\theta \, dr$$

This can be evaluated on the quadrature grid to test the quality of the numerical integration

$$n \approx \sum_{i=1}^{N_{\text{rad}}} \sum_{j=1}^{N_{\text{ang}}} w_i W_j \, \rho(r_i, \theta_j, \phi_j)$$

If the result is far from the number of electrons, it means that your integration is inaccurate and you might want to use a larger grid

## Introduction of a basis

**Expansion in a basis**

$$\psi_i(\boldsymbol{r}) = \sum_{\mu}^{K} C_{\mu i} \phi_\mu(\boldsymbol{r}) \qquad \equiv \qquad |i\rangle = \sum_{\mu}^{K} C_{\mu i} |\mu\rangle$$

$K$ **AOs gives** $K$ **MOs:** $N/2$ are occupied MOs and $K - N/2$ are vacant/virtual MOs

**Roothaan-Hall equations**

$$f|i\rangle = \varepsilon_i |i\rangle \quad \Rightarrow \quad f\sum_{\nu} C_{\nu i} |\nu\rangle = \varepsilon_i \sum_{\nu} C_{\nu i} |\nu\rangle$$

$$\Rightarrow \quad \langle\mu| f \sum_{\nu} C_{\nu i} |\nu\rangle = \varepsilon_i \langle\mu| \sum_{\nu} C_{\nu i} |\nu\rangle$$

$$\Rightarrow \quad \sum_{\nu} C_{\nu i} \langle\mu| f |\nu\rangle = \sum_{\nu} C_{\nu i} \varepsilon_i \langle\mu|\nu\rangle \quad \Rightarrow \quad \boxed{\sum_{\nu} F_{\mu\nu} C_{\nu i} = \sum_{\nu} S_{\mu\nu} C_{\nu i} \varepsilon_i}$$

# Introduction of a basis (Take 2)

Matrix form of the Roothaan-Hall equations

$$\boxed{\mathbf{F\,C} = \mathbf{S\,C\,E} \qquad \Leftrightarrow \qquad \mathbf{F'\,C'} = \mathbf{C'\,E}}$$

$$\mathbf{F'} = \mathbf{X^\dagger\,F\,X} \qquad \mathbf{C} = \mathbf{X\,C'} \qquad \mathbf{X^\dagger\,S\,X} = \mathbb{I}$$

- Fock matrix $F_{\mu\nu} = \langle \mu | f | \nu \rangle$ and Overlap matrix $S_{\mu\nu} = \langle \mu | \nu \rangle$
- We need to determine the coefficient matrix $\mathbf{C}$ and the orbital energies $\mathbf{E}$

$$\mathbf{C} = \begin{pmatrix} C_{11} & C_{12} & \cdots & C_{1K} \\ C_{21} & C_{22} & \cdots & C_{2K} \\ \vdots & \vdots & \ddots & \vdots \\ C_{K1} & C_{K2} & \cdots & C_{KK} \end{pmatrix} \qquad \mathbf{E} = \begin{pmatrix} \varepsilon_1 & 0 & \cdots & 0 \\ 0 & \varepsilon_2 & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & \varepsilon_K \end{pmatrix}$$

Self-consistent field (SCF) procedure

$$\mathbf{F(C)\,C} = \mathbf{S\,C\,E} \quad \text{How do we solve these HF equations?}$$

# Expression of the Fock matrix in the HF case

$$F_{\mu\nu} = \langle\mu|h + \sum_j^{\text{occ}}(\mathcal{J}_j - \mathcal{K}_j)|\nu\rangle = H_{\mu\nu} + \sum_j^{\text{occ}}\langle\mu|\mathcal{J}_j - \mathcal{K}_j|\nu\rangle$$

$$= H_{\mu\nu} + \sum_j^{\text{occ}}(\langle\mu\chi_j|r_{12}^{-1}|\nu\chi_j\rangle - \langle\mu\chi_j|r_{12}^{-1}|\chi_j\nu\rangle)$$

$$= H_{\mu\nu} + \sum_j^{\text{occ}}\sum_{\lambda\sigma} C_{\lambda j}C_{\sigma j}(\langle\mu\lambda|r_{12}^{-1}|\nu\sigma\rangle - \langle\mu\lambda|r_{12}^{-1}|\sigma\nu\rangle)$$

$$= H_{\mu\nu} + \sum_{\lambda\sigma} P_{\lambda\sigma}(\langle\mu\lambda|\nu\sigma\rangle - \langle\mu\lambda|\sigma\nu\rangle)$$

$$= H_{\mu\nu} + \sum_{\lambda\sigma} P_{\lambda\sigma}\langle\mu\lambda||\nu\sigma\rangle = H_{\mu\nu} + G_{\mu\nu}$$

$$F_{\mu\nu} = H_{\mu\nu} + \sum_{\lambda\sigma} P_{\lambda\sigma}(\langle\mu\lambda|\nu\sigma\rangle - \frac{1}{2}\langle\mu\lambda|\sigma\nu\rangle) \quad \text{(closed shell)}$$

# Density matrix & Chemists vs Physicists

Density matrix **P**

$$P_{\mu\nu} = \sum_i^{\text{occ}} C_{\mu i} C_{\nu i} \qquad \text{or} \qquad P_{\mu\nu} = 2\sum_i^{N/2} C_{\mu i} C_{\nu i} \quad \text{(closed shell)}$$

Physicist's notation for two-electron integrals

$$\langle \mu\nu | \lambda\sigma \rangle = \iint \phi_\mu(1)\phi_\nu(2)\frac{1}{r_{12}}\phi_\lambda(1)\phi_\sigma(2) d\boldsymbol{r}_1 d\boldsymbol{r}_2$$

$$\langle \mu\nu || \lambda\sigma \rangle = \langle \mu\nu | \lambda\sigma \rangle - \langle \mu\nu | \sigma\lambda \rangle$$

Chemist's notation for two-electron integrals

$$(\mu\nu | \lambda\sigma) = \iint \phi_\mu(1)\phi_\nu(1)\frac{1}{r_{12}}\phi_\lambda(2)\phi_\sigma(2) d\boldsymbol{r}_1 d\boldsymbol{r}_2$$

$$(\mu\nu || \lambda\sigma) = (\mu\nu | \lambda\sigma) - (\mu\sigma | \lambda\nu)$$

# How to perform a HF or KS calculation in practice?

## The SCF algorithm

1. Specify molecule $\{R_A\}$ and $\{Z_A\}$ and basis set $\{\phi_\mu\}$
2. Calculate integrals $S_{\mu\nu}$, $H_{\mu\nu}$ and $\langle \mu\nu|\lambda\sigma \rangle$
3. Diagonalize $\mathbf{S}$ and compute $\mathbf{X}$
4. Obtain guess density matrix for $\mathbf{P}$
    1. Calculate $\mathbf{G}$ and then $\mathbf{F} = \mathbf{H} + \mathbf{G}$
    2. Compute $\mathbf{F}' = \mathbf{X}^\dagger \mathbf{F} \mathbf{X}$
    3. Diagonalize $\mathbf{F}'$ to obtain $\mathbf{C}'$ and $\mathbf{E}$
    4. Calculate $\mathbf{C} = \mathbf{X} \mathbf{C}'$
    5. Form a new density matrix $\mathbf{P} = \mathbf{C} \mathbf{C}^\dagger$
    6. Am I converged? If not go back to 1.
5. Calculate stuff that you want, like $E_{\mathrm{HF}}$ for example

# How to calculate **X**?

Different orthogonalizations

1. Symmetric orthogonalization

$$\mathbf{X} = \mathbf{S}^{-1/2} = \mathbf{U}\,\mathbf{s}^{-1/2}\,\mathbf{U}^{\dagger}$$

   Is it working?

$$\mathbf{X}^{\dagger}\,\mathbf{S}\,\mathbf{X} = \mathbf{S}^{-1/2}\,\mathbf{S}\,\mathbf{S}^{-1/2} = \mathbf{I}$$

2. Canonical orthogonalization (when you have linear dependencies)

$$\mathbf{X} = \mathbf{U}\,\mathbf{s}^{-1/2}$$

   Is it working?

$$\mathbf{X}^{\dagger}\,\mathbf{S}\,\mathbf{X} = \mathbf{s}^{-1/2}\,\mathbf{U}^{\dagger}\,\mathbf{S}\,\mathbf{U}\,\mathbf{s}^{-1/2} = \mathbf{s}^{-1/2}\,\mathbf{s}\,\mathbf{s}^{-1/2} = \mathbf{I}$$

3. Gram-Schmidt orthogonalization

# How to obtain a good guess for the MOs or density matrix?

Possible initial density matrix

1. We can set $\mathbf{P} = \mathbf{0} \Rightarrow \mathbf{F} = \mathbf{H}$ (core Hamiltonian approximation):
   $\Rightarrow$ Usually a poor guess but easy to implement

2. Use EHT or semi-empirical methods (cf previous lectures):
   $\Rightarrow$ Out of fashion

3. Using tabulated atomic densities:
   $\Rightarrow$ "SAD" guess in QChem/IQmol

4. Read the MOs of a previous calculation:
   $\Rightarrow$ Very common and very useful

# How do I know I have converged (or not)?

## Convergence in SCF calculations

1. You can check the energy and/or the density matrix:
   $\Rightarrow$ The energy/density **should not** change at convergence

2. You can check the commutator $\boldsymbol{F} \boldsymbol{P} \boldsymbol{S} - \boldsymbol{S} \boldsymbol{P} \boldsymbol{F}$:
   $\Rightarrow$ At convergence, we have $\boldsymbol{F} \boldsymbol{P} \boldsymbol{S} - \boldsymbol{S} \boldsymbol{P} \boldsymbol{F} = \boldsymbol{0}$

3. The DIIS (direct inversion in the iterative subspace) method is usually used to speed up convergence:
   $\Rightarrow$ Extrapolation of the Fock matrix using previous iterations

$$\boldsymbol{F}_{m+1} = \sum_{i=m-k}^{m} c_i \, \boldsymbol{F}_i$$

## Expression of the HF energy

$$E_{\text{HF}} = \sum_i h_i + \frac{1}{2} \sum_{ij} (\mathcal{J}_{ij} - \mathcal{K}_{ij}) \quad \text{(cf few slides ago)}$$

$$= \sum_i \langle \sum_\mu c_{\mu i} \phi_\mu | h | \sum_\nu c_{\nu i} \phi_\nu \rangle$$

$$+ \frac{1}{2} \sum_{ij} \langle (\sum_\mu c_{\mu i} \phi_\mu)(\sum_\lambda c_{\lambda j} \phi_\lambda) || (\sum_\nu c_{\nu i} \phi_\nu)(\sum_\sigma c_{\sigma j} \phi_\sigma) \rangle$$

$$= \sum_{\mu\nu} P_{\mu\nu} \left[ H_{\mu\nu} + \frac{1}{2} \sum_{\lambda\sigma} P_{\lambda\sigma} \langle \mu\lambda || \nu\sigma \rangle \right]$$

$$\boxed{E_{\text{HF}} = \frac{1}{2} \text{Tr}[\mathbf{P}\,(\mathbf{H} + \mathbf{F})]}$$