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 ρ

There is a one-to-one correspondence between ρ 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 ρ 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

$$\boxed{E_{\mathrm{KS}}[\rho] = T_{\mathrm{S}}[\rho] + E_{\mathrm{ne}}[\rho] + J[\rho] + E_{\mathrm{xc}}[\rho]}$$

where

$$\rho(\boldsymbol{r}) = \sum_{i}^{\mathrm{occ}} |\psi_i(\boldsymbol{r})|^2 \quad = \quad \text{electronic density}$$

$$T_{\mathrm{S}}[\rho] = \sum_{i}^{\mathrm{occ}} \langle \psi_i | -\frac{\nabla^2}{2} | \psi_i \rangle \quad = \quad \text{non-interacting kinetic energy}$$

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

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

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

Kohn & Sham Phys Rev 140 (1965) A1133

Density, Exchange and Correlation

The exchange-correlation energy is defined as

$$\boxed{\begin{aligned} E_{\mathrm{xc}}[\rho,\zeta] &= E_{\mathrm{x}}[\rho,\zeta] + E_{\mathrm{c}}[\rho,\zeta] \\ &= \int \rho(\boldsymbol{r}) e_{\mathrm{x}}[\rho(\boldsymbol{r}),\zeta] d\boldsymbol{r} + \int \rho(\boldsymbol{r}) e_{\mathrm{c}}[\rho(\boldsymbol{r}),\zeta] d\boldsymbol{r} \end{aligned}}$$

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

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

The correlation energy is given by

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

Density-functional approximations for exchange

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

$$\boxed{\begin{aligned} E_{\mathrm{x},\sigma} &= \int e_{\mathrm{x}}(\rho_\sigma, \nabla\rho_\sigma, \tau_\sigma, \ldots)\, \rho_\sigma \, d\boldsymbol{r} \\ &\approx \sum_i w_i \, e_{\mathrm{x}}[\rho_\sigma(\boldsymbol{r}_i), \nabla\rho_\sigma(\boldsymbol{r}_i), \tau_\sigma(\boldsymbol{r}_i), \ldots]\, \rho_\sigma(\boldsymbol{r}_i) \end{aligned}}$$

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

$$E_{\mathrm{x}}^{\mathrm{LDA}} = \int \rho(\boldsymbol{r}) e_{\mathrm{x}}^{\mathrm{LDA}}(\rho) d\boldsymbol{r} = C_{\mathrm{x}} \int \rho(\boldsymbol{r})^{4/3} d\boldsymbol{r}$$

$$\boxed{e_{\mathrm{x}}^{\mathrm{LDA}}(\rho) = C_{\mathrm{x}}\, \rho^{1/3}}$$

where

$$C_{\mathrm{x}} = -\frac{3}{2}\left(\frac{3}{4\pi}\right)^{1/3} = -0.930526\ldots$$

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,

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

where

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

The GGA exchange energy is

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

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

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

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 τ in functionals

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

or

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

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

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

$$\tau_{\mathrm{W}} = \frac{|\nabla \rho|^2}{4\,\rho}$$ is the von Weizsäcker kinetic energy density

$$\tau_{\mathrm{IUEG}} = C_{\mathrm{F}} \rho^{5/3}$$ is the kinetic energy density of the IUEG

Well thought-out MGGAs ensure that

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

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

Fashionable MGGAs

M06-L [JCP 125 (2006) 194101]

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

TPSS [PRL 91 (2003) 146401]

$$F_x^{\text{TPSS}}(x) = \text{not pretty}$$

mBEEF [JCP 140 (2014) 144107]

$$F_x^{\text{mBEEF}}(x) = \text{very ugly (64 parameters)*}$$

SCAN [PRL 115 (2015) 036402]

$$F_x^{\text{SCAN}}(x) = \text{long (constraint with “model” systems)}$$

*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	
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	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...

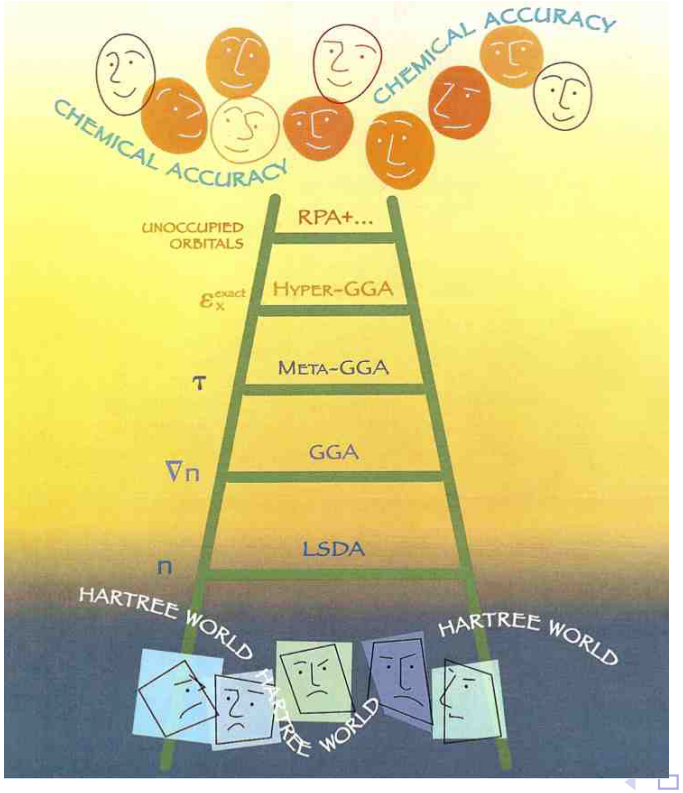
A zoo of functionals

Pick your poison...

Burke, JCP 136 (2012) 150901

Jacob's ladder of DFT

Level	Name	Variables	Examples
1	LDA	ρ	VWN,PZ81,Xα
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 π 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

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

where the roots and weights are

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

Lebedev quadrature

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

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

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

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.

$$\begin{aligned} I &= \int_0^\infty \int_0^\pi \int_0^{2\pi} F(r,\theta,\phi)\; r^2 \sin\theta \, d\phi \, d\theta \, dr \\ &\approx \sum_{i=1}^{N_{\text{rad}}} \sum_{j=1}^{N_{\text{ang}}} w_i W_j F(r_i, \theta_j, \phi_j) \end{aligned}$$

Testing the numerical quadrature

The number of electrons is given by

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

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

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

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

- 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 $\mathbf{E}$

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

Self-consistent field (SCF) procedure

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

Expression of the Fock matrix in the HF case

$$
\begin{aligned}
F_{\mu\nu} &= \langle \mu | h + \sum_j^{\text{occ}} (\mathcal{J}_j - \mathcal{K}_j) | \nu \rangle = H_{\mu\nu} + \sum_j^{\text{occ}} \langle \mu | \mathcal{J}_j - \mathcal{K}_j | \nu \rangle \\
&= H_{\mu\nu} + \sum_j^{\text{occ}} (\langle \mu\chi_j | r_{12}^{-1} | \nu\chi_j \rangle - \langle \mu\chi_j | r_{12}^{-1} | \chi_j\nu \rangle) \\
&= H_{\mu\nu} + \sum_j^{\text{occ}} \sum_{\lambda\sigma} C_{\lambda j} C_{\sigma j} (\langle \mu\lambda | r_{12}^{-1} | \nu\sigma \rangle - \langle \mu\lambda | r_{12}^{-1} | \sigma\nu \rangle) \\
&= H_{\mu\nu} + \sum_{\lambda\sigma} P_{\lambda\sigma} (\langle \mu\lambda | \nu\sigma \rangle - \langle \mu\lambda | \sigma\nu \rangle) \\
&= H_{\mu\nu} + \sum_{\lambda\sigma} P_{\lambda\sigma} \langle \mu\lambda || \nu\sigma \rangle = H_{\mu\nu} + G_{\mu\nu}
\end{aligned}
$$

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

Density matrix & Chemists vs Physicists

Density matrix **P**

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

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 $\{\boldsymbol{R}_A\}$ 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_{HF} for example

How to calculate $\mathbf{X}$?

Different orthogonalizations

1. Symmetric orthogonalization

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

Is it working?

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

2. Canonical orthogonalization (when you have linear dependencies)

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

Is it working?

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

3. Gram-Schmidt orthogonalization

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

Possible initial density matrix

1. We can set $\mathbf{P} = \mathbf{0} \Rightarrow \boldsymbol{F} = \boldsymbol{H}$ (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

$$
\begin{aligned}
E_{\mathrm{HF}} &= \sum_i h_i + \frac{1}{2}\sum_{ij}(\mathcal{J}_{ij} - \mathcal{K}_{ij}) \quad \text{(cf few slides ago)} \\
&= \sum_i \langle \sum_\mu c_{\mu i}\phi_\mu | h | \sum_\nu c_{\nu i}\phi_\nu \rangle \\
&+ \frac{1}{2}\sum_{ij}\langle (\sum_\mu c_{\mu i}\phi_\mu)(\sum_\lambda c_{\lambda j}\phi_\lambda) || (\sum_\nu c_{\nu i}\phi_\nu)(\sum_\sigma c_{\sigma j}\phi_\sigma) \rangle \\
&= \sum_{\mu\nu} P_{\mu\nu}\left[H_{\mu\nu} + \frac{1}{2}\sum_{\lambda\sigma} P_{\lambda\sigma}\langle \mu\lambda || \nu\sigma \rangle \right]
\end{aligned}
$$

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