TCCM Winter School LTTC 2021:
Theory and implementation of density-functional theory-based methods

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This workshop aims at illustrating how to compute exchange-correlation energies within density-functional theory via the self-consistent field Kohn-Sham method.

I. LET'S START...

To start this workshop, you have been given a `Fortran90` program called `xcDFT.f90`. At this stage, `xcDFT` does compute self-consistently the Hartree energy of atoms (there is no exchange at this stage). The first step will be to add the exact Fock exchange in order to perform self-consistent Hartree-Fock (HF) calculations. We refer the students to Ref. [1] for additional details about the self-consistent field (SCF) procedure. The algorithm of p. 146 is particularly enlightening, as the Kohn-Sham (KS) procedure used to compute exchange-correlation within density-functional theory (DFT) [2] is a straightforward modification of it. See, for example, the informative contribution of Pople and coworkers [3]. The self-consistent KS procedure will be coded in the subroutine `RKS.f90`. Below, we recall the derivation of the Roothaan-Hall equations within the HF formalism, as well as a general discussion about DFT. If you are confortable with the theory, this can be skipped but I would advise everyone to have (at least) a quick look at it.

II. HARTREE-FOCK APPROXIMATION

A. Roothaan-Hall equations

Within the LCAO (linear combination of atomic orbitals) approximation, we expand each molecular orbital (MO) as a linear combination of N atomic orbitals (AOs), such as

$$\phi_i(\mathbf{r}) = \sum_\mu c_{\mu i} \chi_\mu(\mathbf{r}). \tag{1}$$

In practice, the AOs $\chi_\mu(\mathbf{r})$ are usually chosen as cartesian Gaussian functions due to their computational convenience.

In the AO basis, we have

$$
\begin{aligned}
F_{\mu\nu} &= \langle \chi_\mu | \hat{F} | \chi_\nu \rangle \equiv \langle \mu | \hat{F} | \nu \rangle \\
&= H^c_{\mu\nu} + \sum_{\lambda\sigma} P_{\lambda\sigma} \left[\langle \mu\lambda | \nu\sigma \rangle - \frac{1}{2} \langle \mu\lambda | \sigma\nu \rangle \right],
\end{aligned} \tag{2}
$$

with

$$H^c_{\mu\nu} = \langle \mu | \hat{H}^c | \nu \rangle, \tag{3}$$

$$\langle \mu\lambda | \nu\sigma \rangle = \iint \chi_\mu(\mathbf{r}_1) \chi_\lambda(\mathbf{r}_2) r_{12}^{-1} \chi_\nu(\mathbf{r}_1) \chi_\sigma(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2, \tag{4}$$

and where the density matrix is defined as

$$P_{\mu\nu} = 2 \sum_i^{\text{occ}} c_{\mu i} c_{\nu i}. \tag{5}$$

The Hartree-Fock (HF) electronic energy of the system is then given by

$$E_{\text{HF}} = \sum_{\mu\nu} P_{\mu\nu} H^c_{\mu\nu} + \frac{1}{2} \sum_{\mu\nu\lambda\sigma}^N P_{\mu\nu} P_{\lambda\sigma} G_{\mu\nu\lambda\sigma}. \tag{6}$$

In matrix form, the Fock matrix $\mathbf{F}$ can be decomposed as

$$\mathbf{F} = \mathbf{H}^c + \mathbf{G}, \tag{7}$$

where

$$G_{\mu\nu} = \sum_{\lambda\sigma} P_{\lambda\sigma} G_{\mu\nu\lambda\sigma}, \quad G_{\mu\nu\lambda\sigma} = \langle \mu\lambda | \nu\sigma \rangle - \frac{1}{2} \langle \mu\lambda | \sigma\nu \rangle. \tag{8}$$

The stationnarity of the energy with respect to the coefficients $c_{\mu i}$ yields the Roothaan-Hall equations:

$$\sum_\nu F_{\mu\nu} c_{\nu i} = \sum_\nu S_{\mu\nu} c_{\nu i} \varepsilon_i, \tag{9}$$

or in matrix form

$$\mathbf{F}\mathbf{C} = \mathbf{S}\mathbf{C}\boldsymbol{\varepsilon}, \tag{10}$$

where the elements of the overlap matrix $\mathbf{S}$ are given by

$$S_{\mu\nu} = \langle \mu | \nu \rangle. \tag{11}$$

The coefficient matrix $\mathbf{C}$ gathers the MO coefficients $c_{\mu i}$, while the diagonal matrix $\boldsymbol{\varepsilon}$ gathers the MO energies ε_i. We introduce the orthogonalization matrix $\mathbf{X}$ such as

$$\mathbf{X}^\dagger \mathbf{S} \mathbf{X} = \mathbf{I} \tag{12}$$

in order to work in an orthogonal AO basis (where $\mathbf{I}$ is the identity matrix). There are two main orthogonalisation methods, namely the Löwdin orthogonalisation

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for which $X = S^{-1/2}$ and the canonical orthogonalisation for which $X = Us^{-1/2}$ (where U and s are the eigenvectors of eigenvalues matrices of S, respectively). Nowadays, the usual procedure consists in performing a singular value decomposition (SVD) of the overlap matrix S. This procedure is efficient, numerically stable and allows to remove the linear dependencies which might be present in the AO basis.

Rotating the Fock matrix F into the orthogonal basis yields

$$F'C' = C'\varepsilon, \tag{13}$$

where

$$F' = X^\dagger F X. \tag{14}$$

The matrices C' and ε can be determined by a straightforward diagonalisation of Eq. (13), and the matrix C is obtained by back-transforming the eigenvectors in the original basis:

$$C = XC'. \tag{15}$$

B. Self-consistent field calculation

In order to obtain the MO coefficients C, one must diagonalise the Fock matrix F. However, this matrix does depend on the MO coefficients itself. Therefore, one must employ an iterative procedure called self-consistent field (SCF) method. The SCF algorithm is described below:

1. Obtain an estimate of the density matrix P.

2. Build the Fock matrix: $F = H^c + G$.

3. Transform the Fock matrix in the orthogonal matrix: $F' = X^\dagger F X$.

4. Diagonalize F' to obtain C' and ε.

5. Back-transform the MOs in the original basis: $C = XC'$.

6. Compute the new density matrix $P = CC^\dagger$, as well as the HF energy:

$$E_{\text{HF}} = \frac{1}{2}\text{Tr}\{P(H^c + F)\}. \tag{16}$$

7. Convergence test. If not satisfied, go back to 2.

Exercise 1: Create a `Fortran90` subroutine `fock_exchange_potential.f90` which calculates the (exact) Fock exchange matrix. You can start by copying the subroutine `hartree_coulomb.f90` into `fock_exchange_potential.f90`. It is going to give you a good start to write down your subroutine. You can check that you have done things right by checking that you can reproduce the HF energies reported in Table II. Don't forget to change the variable `rung` in the file `input/options`. Hartree calculation are performed with `rung=0` while it should be set to `rung=666` for HF.

III. DENSITY-FUNCTIONAL THEORY

Density-functional theory (DFT) is based on two theorems known as the Hohenberg-Kohn (HK) theorems [4], which states that it exists a non-interacting reference system with an electronic density $\rho(r)$ equal to the real, interaction system. The first theorem proves the existence of a one-to-one mapping between the electron density and the external potential, while the second HK theorem guarantees the existence of a variational principle for the ground-state electron density.

A. Kohn-Sham equations

Present-day DFT calculations are almost exclusively done within the so-called Kohn-Sham (KS) formalism, which corresponds to an exact dressed one-electron theory [5]. In analogy to the HF theory, the electrons are treated as independent particles moving in the average field of all others but now with exchange an correlation included by virtue of an "exchange-correlation" functional.

Following the work of Kohn and Sham [5], we introduce KS orbitals $\psi_i(r)$, and the energy can be decomposed as

$$E_{\text{KS}}[\rho(r)] = T_{\text{s}}[\rho(r)] + E_{\text{ne}}[\rho(r)] + J[\rho(r)] + E_{\text{xc}}[\rho(r)], \tag{17}$$

where

$$T_{\text{s}}[\rho(r)] = -\frac{1}{2}\sum_i^{\text{occ}} \langle\psi_i|\nabla_i^2|\psi_i\rangle \tag{18}$$

is the non-interacting kinetic energy,

$$E_{\text{ne}}[\rho(r)] = -\sum_A^{\text{nuc}} \int \frac{Z_A\rho(r)}{|r_A - r|}dr \tag{19}$$

is the electron-nucleus attraction energy,

$$J[\rho(r)] = \frac{1}{2}\iint \frac{\rho(r_1)\rho(r_2)}{|r_1 - r_2|}dr_1 dr_2 \tag{20}$$

is the classical electronic repulsion, and the one-electron density is

$$\rho(r) = \sum_i^{\text{occ}} |\psi_i(r)|^2. \tag{21}$$

The exchange-correlation energy

$$E_{\text{xc}}[\rho(r)] = \{T[\rho(r)] - T_{\text{s}}[\rho(r)]\} + \{E_{\text{ee}}[\rho(r)] - J[\rho(r)]\} \tag{22}$$

is the sum of two terms: one coming from the difference between the exact kinetic energy $T[\rho(r)]$ and the non-interacting kinetic energy $T_{\text{s}}[\rho(r)]$, and the other one coming from the difference between the exact inter-electronic repulsion $E_{\text{ee}}[\rho(r)]$ and the classical Coulomb

repulsion $J[\rho(\boldsymbol{r})]$. Here, we will only consider the second term as the "kinetic" correlation energy is usually much smaller than its "Coulomb" counterpart. Also, as it is usually done, we will split the exchange-correlation energy as a sum of an exchange and correlation components, i.e.

$$E_{\text{xc}}[\rho(\boldsymbol{r})] = E_{\text{x}}[\rho(\boldsymbol{r})] + E_{\text{c}}[\rho(\boldsymbol{r})]. \quad (23)$$

Similarly to the Roothaan-Hall equations, the condition of stationarity of the KS energy with respect to the electron density

$$\frac{\delta E\left[\rho(\mathbf{r})\right]}{\delta \rho(\mathbf{r})} = 0 \quad (24)$$

yields the KS equations

$$\left[-\frac{\nabla_{\boldsymbol{r}}^2}{2} - \sum_{A}^{\text{nuc}} \frac{Z_A}{|\boldsymbol{r} - \boldsymbol{r}_A|} + \int \frac{\rho(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|} d\boldsymbol{r}' + \frac{\delta E_{\text{xc}}[\rho(\boldsymbol{r})]}{\delta \rho(\boldsymbol{r})} \right] \psi_i(\boldsymbol{r}) = \varepsilon_i \psi_i(\boldsymbol{r}), \quad (25)$$

which can be re-written as

$$\hat{F}_{\text{KS}} \psi_i(\boldsymbol{r}) = \varepsilon_i \psi_i(\boldsymbol{r}). \quad (26)$$

These equations are solved iteratively, just like the HF equations, by expanding the KS MOs in a AO basis, yielding

$$\boldsymbol{F}_{\text{KS}} \boldsymbol{C} = \boldsymbol{S} \boldsymbol{C} \boldsymbol{\varepsilon}. \quad (27)$$

B. Exchange-correlation functionals

Due to its moderate computational cost and its reasonable accuracy, KS DFT [4, 5] has become the workhorse of electronic structure calculations for atoms, molecules and solids [2]. To obtain accurate results within DFT, one only requires the exchange and correlation functionals, which can be classified in various families depending on their physical input quantities [6, 7]. These various types of functionals are classified by the Jacob's ladder of DFT [8, 9] (see Fig. 1).

- The local-density approximation (LDA) sits on the first rung of the Jacob's ladder and only uses as input the electron density ρ. The oldest and probably most famous LDA functional is the Dirac exchange functional (D30) [10] based on the uniform electron gas (UEG) [11]. Based on the work of Ceperley and Alder who used quantum Monte Carlo calculations (see below) to determine the correlation energy of the UEG with respect to the density [12], Vosko, Wilk and Nusair (VWN) proposed a LDA correlation functional by fitting their data [13].

- The generalized-gradient approximation (GGA) corresponds to the second rung and adds the gradient of the electron density $\nabla \rho$ as an extra ingredient. The well-known B88, G96, PW91 and PBE exchange functionals are examples of GGA exchange functionals [14–17]. Probably the most famous GGA correlation functional is LYP [18], which gave birth to the GGA exchange-correlation functional BLYP [19] by combination with B88.
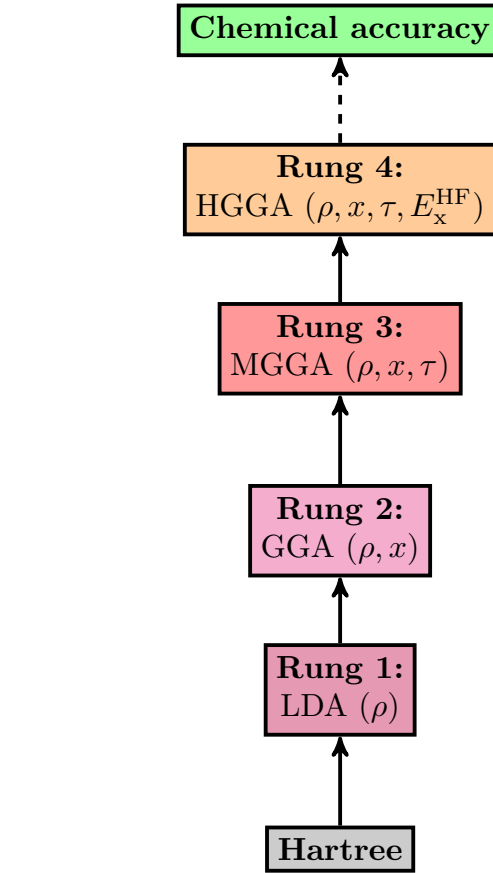

FIG. 1. Jacob's ladder of DFT. ρ, x, τ and E_{x}^{HF} are the electron density, the reduced gradient, the kinetic energy density, and the HF exchange energy, respectively.

- The third rung is composed by the so-called meta-GGA (MGGA) functionals [20] which uses, in addition to ρ and $\nabla \rho$, the kinetic energy density

$$\tau = \sum_{i}^{\text{occ}} |\nabla \psi_i|^2. \quad (28)$$

The M06-L functional from Zhao and Truhlar [21], the mBEEF functional from Wellendorff et al. [22]

and the SCAN [23] and MS [24, 25] family of functionals from Sun et al. are examples of widely-used MGGA functionals.

- The fourth rung (hyper-GGAs or HGGAs) includes the widely-used hybrid functionals, introduced by Becke in 1993 [26], which add a certain percentage of HF exchange. Example of such functionals are B3LYP [26], B3PW91 [26–28], BH&HLYP [29] or PBE0 [30]. Hybrids functionals are known for their accuracy in electronic structure theory. However, they are more computationally expensive than LDA or GGA functionals due to the calculation of the costly HF exchange.

- The fifth rung includes double hybrids and RPA-like functionals but we will not be discussing such types of functionals in the present workshop.

IV.   WORKSHOP

A.   Exchange-correlation energy

As mentioned above, according to DFT [2], the exchange (x) and correlation (c) energies can be written as functionals of the electron density $\rho(\boldsymbol{r})$ of a system. In most approximate functionals, these energies are written as integrals of functions of the density, for example

$$E_x = \int e_x[\rho(\boldsymbol{r})]\,d\boldsymbol{r} \tag{29}$$

and this allows the exchange (or correlation) energy to be computed much more quickly than by other methods (e.g. Hartree-Fock theory, perturbation theory, coupled cluster theory, etc.) The not-so-good news is that the DFT estimates are approximate and, sometimes, they can be far from the true values.

In practical DFT calculations, the forms of the approximate exchange-correlation functionals used are quite complicated, such that the required integrals involving the functionals generally cannot be evaluated analytically. These integrals are usually evaluate through numerical quadrature directly applied to the exchange-correlation integrand.

B.   Radial Quadrature

There are many possible ways to estimate a general radial integral from 0 to ∞. One of these is the Euler-Maclaurin quadrature developed by Boys and Handy and given by

$$\int_0^\infty r^2 f(r)dr \approx \sum_{i=1}^{N_{\mathrm{rad}}} w_i f(r_i) \tag{30}$$

where the roots and weights are

$$r_i = R\,i^2(N_{\mathrm{rad}} + 1 - i)^{-2} \tag{31}$$
$$w_i = 2R^3(N_{\mathrm{rad}} + 1)i^5(N_{\mathrm{rad}} + 1 - i)^{-7} \tag{32}$$

The parameter R is a scaling variable that allows the quadrature to be tailored to a particular integral. If it is well chosen, it can lead to more accurate results with few quadrature points. We will assume (at least initially) that $R = 1$.

Of course, the accuracy of these approximations depends on the number N_{rad} of points and the function $f(r)$. However, it has been found to be reasonably effective for many of the radial integrals that arise in DFT calculations.

You have been given a `Fortran77` subroutine called `EulMac` (see `dft_grid.f90`) which computes these roots and weights for any desired values of N_{rad} and R.

C.   Angular Quadrature

There are many possible ways to estimate a general angular integral over the surface of a unit sphere S. One of these is the quadrature developed by Lebedev, which extends the familiar octahedral 6-point rule. It is given by

$$\int_S g(x,y,z)d\Omega \approx \sum_{j=1}^{N_{\mathrm{ang}}} W_j g(x_j, y_j, z_j) \tag{33}$$

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.

Of course, the accuracy of these approximations depends on the number N_{ang} of points and the function $g(x, y, z)$. However, it has been found to be reasonably effective for many of the radial integrals that arise in DFT calculations.

You have been given a `Fortran77` subroutine called `Lebdev` which computes these roots and weights for any desired value of N_{ang}.

D.   Quadrature in 3D

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

$$I = \int F(\boldsymbol{r})d\boldsymbol{r} \tag{34}$$

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

TABLE I. Number of radial points N_{rad} and angular points N_{ang} as well as total number of points N_{grid} for the SG-n grids ($n = 0 - 3$).

SG-n grid	N_{rad}	N_{ang}	N_{grid}
0	23	170	3 910
1	50	194	97 00
2	75	302	22 650
3	99	590	58 410

the quadratures described above, i.e.

$$I = \int_0^\infty \int_0^\pi \int_0^{2\pi} F(r, \theta, \phi) \, r^2 \sin\theta \, d\phi \, d\theta \, dr \quad (35)$$

$$\approx \sum_{i=1}^{N_{\text{rad}}} \sum_{j=1}^{N_{\text{ang}}} w_i W_j F(r_i, \theta_j, \phi_j) \quad (36)$$

Usually, the electron density itself is also integrated numerically as a test of the quality of the numerical quadrature. The extent to which this numerical result differs from the number of electrons is an indication of the accuracy of the other numerical integrals.

Exercise 2: Create a Fortran90 function `electron_number.f90` which estimates the number of electrons in the helium, beryllium and neon atoms by integrating its electron density $\rho(r)$ over all space using the well-known (unpruned) SG-n grids ($n = 0, \ldots, 3$). Their characteristics are given in Table I. To do this, you will need to create first a subroutine called `density.f90` that computes the one-electron density `rho` on each grid point using the values of the AOs (variable `AO`). Explore the effects of using various numbers of radial and angular points for these three atoms. The grid can be changed in the file `input/options`.

E. Dirac–Slater exchange functional

The famous Dirac–Slater exchange functional (which is the exchange part of the LDA) is [2]

$$E_x^{\text{LDA}}[\rho(r)] = C_x \int \rho(r)^{4/3} \, dr \quad (37)$$

where

$$C_x = -\left(\frac{1}{2}\right)^{1/3} \frac{3}{2} \left(\frac{3}{4\pi}\right)^{1/3} = -0.738559 \quad (38)$$

and $\rho(r) = \rho_\alpha(r) + \rho_\beta(r)$ is the one-electron density, and $\rho_\alpha(r)$ and $\rho_\beta(r)$ are the spin-up and spin-down one-electron densities, respectively.

Exercise 3: Modify the Fortran program xcDFT.f90 to compute the LDA exchange energy. First, you can compute the LDA energy at the end of the HF calculation. For this you can create a subroutine called `lda_exchange_energy.f90` which requires the quadrature weights and the density computed on this grid. The subroutine `lda_exchange_energy.f90` must be called in the function `exchange_energy.f90`. Second, you can try to compute the LDA exchange self-consistently by modifying the HF self-consistent process. For this, create a new subroutine called `lda_exchange_potential.f90` which is called in the subroutine `exchange_potential.f90`. Have a look at Ref. [3] to know how to modify the Fock operator to incorporate LDA exchange.

F. Wigner 38 correlation functional

The 1938 Wigner correlation functional is [31]

$$E_c^{\text{W38}}[\rho_\alpha(r), \rho_\beta(r)] =$$
$$- 4a \int \frac{\rho_\alpha(r)\rho_\beta(r)}{\rho(r)} \frac{1}{1 + d\rho(r)^{-1/3}} \, dr \quad (39)$$

where $a = 0.04918$ and $d = 0.349$.

Exercise 4: Similarly to what you have done for the exchange LDA, modify the Fortran program xcDFT.f90 to compute the LDA correlation energy. First, you can compute the LDA correlation energy at the end of the HF calculation. For this you can create a function called `lda_correlation_energy.f90` which requires the quadrature weights and the density computed on this grid. This subroutine is called in `correlation_energy.f90`. Second, you can try to compute the LDA exchange-correlation self-consistently by modifying the HF self-consistent process. The procedure is similar to what you have done for the exchange part. Again, have a look at Ref. [3] to know how to modify the Fock operator to incorporate LDA correlation.

G. Gill 96 exchange functional

The 1996 Gill exchange functional is [15]

$$E_x^{\text{G96}}[\rho_\alpha(r), x_\alpha(r)] = E_x^{\text{LDA}}[\rho_\alpha(r)]$$
$$- \beta \int \rho_\alpha(r)^{4/3} x_\alpha(r)^{3/2} \, dr \quad (40)$$

where $\beta = 1/137$ and the reduced density gradient is defined by

$$x_\alpha(r) = \frac{|\nabla \rho_\alpha(r)|}{\rho_\alpha(r)^{4/3}} \quad (41)$$

Exercise 5: Similarly to what you have done for the LDA, modify the Fortran program xcDFT.f90 to compute the GGA exchange energy. You might need to create

a subroutine `gradient_density.f90` in order to calculate the gradient of the electron density. The quantities `AO` and `dAO` computed in the subroutine `AO_values.f90` reporting the AO values and their derivatives at the grid points might be particularly useful. First, you can compute the GGA energy at the end of the HF calculation. Second, you can try to compute the GGA exchange self-consistently by modifying the HF self-consistent process. Again, have a look at Ref. [3] to know how to modify the Fock operator to incorporate GGA exchange.

Appendix A: How do I know I am right?

In Table II, you will find self-consistent KS energies I have produced for the systems studied here using the SG-1 grid and the default values of the program. Note that you may have small differences depending on the version of `LAPACK` you are using.

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TABLE II. Total energies computed with the SG-1 grid and various exchange functionals.

System	basis	E_{HF}	E_{D30}	$E_{\text{D30+W38}}$
He	cc-pVDZ	$-2.855\,160\,477$	$-2.714\,654\,148$	$-2.772\,377$
He	cc-pVTZ	$-2.861\,153\,574$	$-2.722\,731\,996$	$-2.780\,028$
Be	cc-pVDZ	$-14.572\,363\,038$	$-14.221\,555\,828$	$-14.331\,449$
Ne	cc-pVDZ	$-128.488\,866\,172$	$-127.412\,883\,672$	$-127.773\,407$