Make your own DFT program in Matlab – extension and analysis

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Abstract

Extend and perform some analysis with the DFT Matlab script:

- Change it so that you use an exponential mesh instead of a linear one. Discuss and analyze.
- Analyze how the correlation part affects the solution
- Find an alternative expression for the correlation, plug it in, and analyze.

1 Introduction

The global energy minimum determines the geometry of the molecule, the lattice structure of solids, vibrations and rotations. In the Density functional theory (DFT) we are looking for the ground state density and energy. Hohenberg-Kohn theorems tell us that ground state energy functional is minimized by ground state density and at this point it has global minimum [3]. In the DFT approach every property of the system can be viewed as a functional of the ground state electron density:

$$n(\mathbf{r}) = \sum_{n=1}^{N} |\psi(\mathbf{r})|^2.$$

Kohn-Sham (KS) approach assumes that density of the original interacting system is equal to the density of some chosen non-interacting system. It reduced many-body problem to one-particle equations with all hard many-body terms incorporated into the exchange-correlation functional.

Kohn-Sham (KS) equations:

$$\left(-\frac{1}{2}\nabla^2 + V_{eff}(\mathbf{r})\right)\psi(\mathbf{r}) = \varepsilon\psi(\mathbf{r}),$$

where the first term is kinetic energy of non-interacting electrons and second term is effective potential:

$$V_{eff}(\mathbf{r}) = V(\mathbf{r}) + \int \frac{n(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + V_{xc}(\mathbf{r}).$$

Here the first term is external potential, second term is Hartree potential which represents the electron repulsion (Coulomb's law) and third term is exchange-correlation potential.

KS equations are nonlinear and has to be solved iteratively. Firtly one is guessing density and form KS equations by evaluating all the potentials for this density. By solving KS equation one obtain new density and repeat the procedure till self-consistency (old and new density are almost equal) is reached.

DFT in principal is exact theory if we know exchange-correlation energy exactly. But here arises a problem, exact form of this functional is not known. Therefore exchange-correlation energy is a limiting factor of DFT. There was introduced various approximations of it, and probably one of the most used is *local density approximation (LDA)*.

LDA assumes that density at each point is the same as that of the homogeneous electron gas. Exchange-correlation energy in LDA is a sum of contributions from each point in space. It depends only upon the density at each point and do not take into accout density in other points:

$$E_{xc}[n] = \int d^3r \, n(\mathbf{r}) \epsilon_{xc}^{hom}(n(\mathbf{r})), \qquad (1)$$

where $\epsilon_{xc}^{hom}(n(\mathbf{r}))$ is the exchange-correlation energy per electron of the homogenious electron gas.

The corresponding exchange-correlation potential is obtained from the functional derivative of the energy

$$V_{xc}(\mathbf{r}) = \frac{\partial}{\partial n} E_{xc}[n].$$
⁽²⁾

The exchange-correlation energy can be separated onto an exchange and a correlation parts. The exchange part is evaluated exactly for the homogenious gas

$$\epsilon_x(n) = -\frac{3}{4} \left(\frac{3}{\pi}\right)^{\frac{1}{3}} n^{\frac{1}{3}}.$$
(3)

The correlation part can be computed by various methods. Later we will consider a few of them. All the computations will be performed using DFT program in MATLAB on the example of Helium atom [5].

2 Solving differential equations

During self-consistent iterations one need to solve boundary value problem for two differencial equations: Poisson equation for Hartree potential and Kohn-Sham equation. It can be done using finite difference method. Grid generation is very important for such problems. The non-uniform grid is preferable because it allows to solve accurately certain part of domain while keeping total amount of points small. The larger oscillation of wave function will occur near the nucleus due to Coulomb potential, therefore it is preferable to use grid which has larger density near origin and smaller density far from origin:

$$x_i = r_{max} + (r_{max} - r_{min}) \frac{\mathrm{e}^{i\delta} - 1}{\mathrm{e}^{N_{max}\delta} - 1},\tag{4}$$

the step size is $h_i = x_i - x_{i-1}$.

Parameter $\delta > 0$ determines how much grid will be compressed near nucleus with respect to larger distances. The smallest step size will be h_1 , so lets consider haw δ influences it:

$$h_1 = x_1 - x_0 = (r_{max} - r_{min}) \frac{e^{\delta} - 1}{e^{N_{max}\delta} - 1}$$



Figure 1: Uniform and non-uniform grids with 100 points. The horizontal axis represents distance from the nucleus.

$$\lim_{\delta \to 0} h_1 = (r_{max} - r_{min}) \frac{1}{N_{max}},$$
(5)

so it will approach uniform grid. Also

$$\lim_{\delta \to \infty} h_1 = 0 \text{ for } N_{max} \ge 2.$$
(6)

With increasing δ grid compressed near nucleus very rapidly. Already for very small values of δ (near 1) step size h_1 is very small and matrices became almost singular and therefore very ill-conditioned. On Figure 1 one can see both uniform and non-uniform grids with 100 points.

When we are using non-uniform grid, the result matrices in general are not symmetric. In order to take advantage of symmetry we will symmetrize our matrices. Tridiagonal matrix

$$A = \begin{pmatrix} a_i & b_i & 0\\ c_i & a_{i+1} & b_{i+1}\\ 0 & c_{i+1} & a_{i+2} \end{pmatrix}$$
(7)

can be symmetrized $\hat{A} = DAD^{-1}$ by diagonal matrix D = diag(d) where vector d has elements:

$$d(1) = 1, \quad d(i+1) = d(i)\sqrt{\frac{b(i)}{c(i)}}.$$
 (8)

Then one can easily solve transformed eigenvalue problem for Schrödinger equation $(Ax = \lambda x)$:

$$\hat{A}\hat{x} = \lambda\hat{x},\tag{9}$$

$$x = D^{-1}\hat{x},\tag{10}$$

and linear system for Poisson equation (Ax = b):

 $\hat{b} = Db,$ $\hat{A}\hat{x} = \hat{b},$ $x = D^{-1}\hat{x}.$



Figure 2: Comparison of results for uniform and non-uniform grids, 30 grid points



Figure 3: Comparison of results for uniform and non-uniform grids, 70 grid points

We remind that program stops when difference between old and new energies reach some predefined accuracy. In our example of Helium atom for both grids it needed the same number of iterations. But the values of energies for non-uniform grid are more accurate. For example already for 30 point non-uniform grid gives good result, but uniform instead fails. In the Figures 2-4 presented comparison for uniform and non-uniform grids. In this section in computations we used Perdew–Zunger correlation (see Subsection 3.2).

Figure 5 present dependence error in total energy of number of grid points. From figure one can see that for $\delta = 0.01$ the optimal number of grid points is 200, bacause further increase of number of grid points does not improve result.

Error in total energy for different values of δ is presented in Figure 6. Notice logarithmic scale for x-axis. With larger δ number of point near nucleus increases, therefore accuracy becomes



Figure 4: Comparison of results for uniform and non-uniform grids, 120 grid points



Figure 5: Error in total energy for various number of points in grid for $\delta = 0.01$



Figure 6: Error in total energy for various values of δ and $N_{max} = 200$ grid points

better.

3 Correlation part

In DFT and HF electrons moved in the background of Hartree and external potentials. The exchange term in HF describes interaction of electrons with parallel spin which avoid each other because of the Pauli exclusion principle. Electrons with opposite spin do not feel this interaction. Instead in DFT, exchange-correlation term includes exchange effects like HF and correlation effects due to Coulomb repulsion. This part of energy which HF neglects is called correlation energy:

$$E_{correlation} = E_{total} - E_{exchange}.$$
 (11)

Accurate quantum Monte Carlo simulations for the energy of the homogenious electron gas have been performed for several intermediate values of the density, in turn providing accurate values of the correlation energy density. The most popular LDA to the correlation energy density interpolate these accurate values obtained from simulation. Here we will consider two of such interpolations: Perdew–Zunger [2,4] and Vosko–Wilk–Nusair [2] correlation. Gunnarsson–Lundqvist [1,2] interpolation used data obtained from computations of properties of homogenious spin-polarized electron gas.

For every method parameters are given for two extreme spin parametrizations ζ : paramagnetic($\zeta = 0$) and ferromagnetic ($\zeta = 1$). To find exchange-correlation for spin polarization between extreme value is used spin interpolation. All the computation will be performed with paramagnetic parameters. Further ϵ_c denotes correlation energy for the homogenious electron gas and V_c is a correlation potential.

Also r_s is called Seitz radius and it equals to the radius of a sphere whose volume is equal to the mean volume per electron in the homogenious electron gas:

$$r_s = \left(\frac{3}{4\pi n}\right)^{\frac{1}{3}}.$$

3.1 Gunnarsson–Lundqvist correlation

	Paramagnetic	Ferromagnetic
A	11.4	15.9
C	0.0666	0.0406

$$\begin{aligned} x &= \frac{r_s}{A}, \\ \epsilon_c &= -C\left(\left(1+x^3\right)\ln\left(1+\frac{1}{x}\right) + \frac{1}{2}x - x^2 - \frac{1}{3}\right), \\ V_c &= -C\ln\left(1+\frac{1}{x}\right). \end{aligned}$$

3.2 Perdew–Zunger correlation

	Paramagnetic	Ferromagnetic	
γ	-0.1423	-0.0843	
β_1	1.0529	1.3981	
β_2	0.3334	0.2611	
A	0.0311	0.01555	
B	-0.048	-0.0269	
C	0.0020	0.0007	
D	-0.0116	-0.0048	

Perdew–Zunger correlation energy and potential have different forms for high and small density homogenious gas.

For $r_s \geq 1$:

$$\begin{split} e_c &= \frac{\gamma}{1+\beta_1\sqrt{r_s}+\beta_2 r_s},\\ V_c &= e_c \frac{1+\frac{7}{6}\beta_1\sqrt{r_s}+\frac{4}{3}\beta_2 r_s}{1+\beta_1\sqrt{r_s}+\beta_2 r_s}, \end{split}$$

for $r_s < 1$:

$$e_c = A \ln(r_s) + B + Cr_s \ln(r_s) + Dr_s,$$

$$V_c = A \ln(r_s) + B - \frac{A}{3} + \frac{2}{3}Cr_s \ln(r_s) + \frac{1}{3}(2D - C)r_s.$$

3.3 Vosko–Wilk–Nusair correlation

	Paramagnetic	Ferromagnetic
a	0.0621814	0.0310907
b	3.72744	7.06042
c	12.9352	18.0578
b_1	9.81379	3.46791
b_2	2.82224	1.25842
b_3	0.736412	0.170393
x_0	-0.10498	-0.32500

$$X_{r_s} = r_s + b\sqrt{r_s} + c,$$

$$X_{x_0} = x_0^2 + b\sqrt{x_0^2} + c,$$

$$Q = \sqrt{4c - b^2},$$

$$\begin{split} t_2 &= \frac{Q}{2\sqrt{r_s} + b}, \\ t_1 &= \ln \frac{(\sqrt{r_s} - x_0)^2}{X_{r_s}} + \frac{2(b + 2x_0)}{Q} \arctan(t_2), \\ t &= \ln \frac{r_s}{X_{r_s}} + \frac{2b}{Q} \arctan(t_2) - \frac{bx_0 t_1}{X_{x_0}}, \end{split}$$

$$e_{c} = At,$$

$$V_{c} = e_{c} - \frac{A}{3} \frac{1 + b_{1}\sqrt{r_{s}}}{1 + b_{1}\sqrt{r_{s}} + b_{2}r_{s} + b_{3}r_{s}^{\frac{3}{2}}}.$$

3.4 Properties

Interesting to see how the correlation influences result. On the Figure 7 presented total energies computed with and without correlation for various methods. After adding correlation results are improved for every method. Also adding correlation does not influence number of iterations needed to reach self-consistency. Notice that already on the first iteration result with correlation are better.

Comparison of various methods is given on Figure 8. Densities computed with LDA are usually good and results are not differ too much. Instead total energy is underestimated for Perdew-Zunger method and underestimated for Gunnarsson-Lundqvist and Vosko-Wilk-Nusair methods. Note that for every method is needed the same number of iterations to reach selfconsistency (program stops when difference between total energies on subsequent iterations is less than 1e-7).



Figure 7: Total energy with and without correlation for various correlation methods $(N_{max} = 200, \delta = 0.01)$



Figure 8: Comparison of various correlation methods $(N_{max} = 200, \delta = 0.01)$

The exchange energy is underestimated, but this is compensated by an overestimation of correlation by 2 or 3 times, which is also 7-8 times smaller than exchange. In total overall error for total energy is only about 2-3%. In the table 1 given results of exchange, correlation and total energies for various methods. Reference values are taken from [6].

Corresponding correlation energies and absolute values of correlation potentials are given on Figure 9 as function of r_s for paramagnetics ($\zeta = 0$) and ferromagnetics ($\zeta = 1$). Correlation potentials decays almost exponentially, in real systems it decays much slower. It means that some part of self-interaction is still exists in LDA.

4 Conclusion

Introducing non-uniform grid improves results due to finer approximation near nucleus where the main activity occurs. Three correlation methods was considered on the example of Helium atom. The most accurate result was given by Vosko-Wilk-Nusair method, although it underestimates

	Gunnarsson–Lundqvist	Perdew–Zunger	Vosko–Wilk–Nusair	Exact
E_{ex}	-0.808 (21.1%)	-0.804 (21.5%)	-0.819 (20.0%)	-1.024
E_c	-0.174 (-314.2%)	-0.068 (-61.9%)	-0.140 (-233.3%)	-0.042
E_{xc}	-0.982 (7.9%)	-0.872 (18.1%)	-0.959~(10.0%)	-1.066
E_{tot}	-2.998 (-3.24%)	-2.835(2.38%)	-2.947 (-1.48%)	-2.904

Table 1: Computed energies for various methods



Figure 9: Correlation energy and potential for various correlation methods

total energy. It was showen that the LDA potential decays asymptotically with an exponential form. In general correlation energy is overestimated, but it canceled by exchange energy, that as a result total exchange-correlation energy have error 11% in average.

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