# **Density Functional Theory**

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Automatic references and formula numbering feature are used.

# **Introduction**

In real quantum system there are many electrons and nucleuses. Electrons and nucleuses have spins and magnetic moments. Each electron has unique quantum state in such quantum system. Complicated interaction between those different electrons and nucleuses can be described by many-body Schrödinger equation [[[1]](#endnote-1)]:



where  is many-body wave function, **r***i* is position operator for electron *i*, and **H** is many-body Hamiltonian



where the first term is the kinetic energy operator,  is the potential energy operator due to Coulomb interaction of *i* electron with nucleuses,  is the potential energy operator due to electron-electron Coulomb interaction. In writing Eq. (1) and (2), we consider Born–Oppenheimer approximation, when the nuclei are fixed.

Write expressions for  and  from Eq. (2)

This quantum system may have *k* different quantum states  with energies *Ek*, which correspond to *k* solutions of Eq. . The first state, *E*1, , is the ground state, and the remaining are excited states.

In Kohn-Sham (KS) Density Functional Theory (DFT), we look only at one electron, and suppose that complicated many-body interaction with other electrons of the system, can be described by some potential, which depends on many parameters, exchange-correlation (XC) functional *VXC*.

Using *VXC* we can write the set of KS equations for one-electron wave functions , *i* = 1,...,*N*



where KS Hamiltonian



and KS potential is



KS equation is describing the ground state of the system, and , *i* = 1,…,*N* are KS energy levels.

Write expression for the total energy of the system for the ground state. Use Ref. [[[2]](#endnote-2)].

What is the difference between many-body and DFT approaches?

**Local Density Approximation**

The simplest way to approximate many-body interaction is Local Density Approximation (LDA), when we treat electrons as the homogeneous electron gas and the exchange and correlation energies depend on electron density *ρ*.

You can add here the main aspects how exchange and correlation potentials are derived in LDA.

The exchange potential in LDA has a form



The correlation potential in LDA in the form of Ceperley-Alder with Perdew-Zunger parametrization for unpolarized case has a form:



where , *A* = 0.0311, *B* = −0.048, *C* = 0.002, *D* = −0.0116, *β*1 = 1.0529, *β*2 = 0.3334, γ = −0.1423. For derivation of Eq. and see Ref. [[[3]](#endnote-3)].

There are many different approaches to approximate many-body interaction between electrons more and more accurately, for example, Generalized Gradient Approximation (GGA) when energy depends not only on charge density but also on its gradient too, or hybrid functionals, when the XC functional is the mix of two-electron Hartree-Fock potential with one-electron potential. According to Hohenberg-Kohn theorem, the ground-state density uniquely determines the potential. However, we can calculate the potential only approximately.

**Self-interaction error**

DFT approach, due to inaccuracy in accounting of many-body interaction in *VXC*, leads to uncompensated interaction of electron with itself, unphysical electron self-interaction. As a consequence, this self-interaction error causes many problems, for example, significantly underpredicts chemical reaction barriers compared with experiments because of the tendency of DFT to overstabilize transition states with stretched bonds, the eigenvalue of the highest occupied KS orbital does not correspond to the ionization potential, as it should, underestimates band gap in semiconductors.

In order to correct self-interaction error, it was developed different self-interaction corrections (SIC), or you can use many-body approaches, like, for example, GW approximation, or Møller-Plesset (MP) approach.

**Self-consistent field**

Self-consistent field (SCF) method is used to solve KS equation numerically. We can start from some initial approximation to the solution. Let us suppose, that the set of  and  is good initial guess to the solution. Using these values we can calculate KS potential and then solve KS equation with known potential. We will get new solution,  and , from which we can recalculate new KS potential, *V*1. Since using just new calculated potential *V*1 can lead to divergence of iterations, we can set some mixing parameter α and calculate the potential for next iteration as following



where . In other words, we add only some part of the new calculated potential and keep part of the previous potential in order not to change the new solution,  and , too much.

We can make several SCF iterations until we reach necessary accuracy for *εi*.

**Software for DFT**

There are available multiple DFT software with free or commercial license, written on different programming languages. These software may or may not use GPU accelerators. From physical point of view it can be written for different tasks and can use different basis set. For basis set it can be used plane waves or Bloch sums for periodic systems like crystals, 2D materials, or polymers, or can be based on local basis functions, like Slater- or Gaussian-functions, which is more suitable to study separate molecules.

The list of available DFT software can be browsed on wiki page [[[4]](#endnote-4)] and in review article [[[5]](#endnote-5)].

Check installed DFT software on your university computer cluster. The most popular DFT programs are Quantum Espresso, VASP, Abinit, Gaussian.

**Atomic units**

In atomic units, more suitable for practical calculations, we set the charge of electron *e* = 1, the mass of electron *me* = 1, and the Plank constant ℏ = 1. In this atomic units (a.u.), one a.u. of length is Bohr radius *a*0 = 0.529177210903 Å, and 1 a.u. of energy (1 Hartree) is 27.211386245988 eV.

**Literature**

1. K. Burke “The ABC of DFT” <https://dft.uci.edu/doc/g1.pdf> [↑](#endnote-ref-1)
2. Parr, R.G.; Yang, W. Density functional theory of atoms and molecules. Oxford University Press, New York, 1989 [↑](#endnote-ref-2)
3. Perdew, J.P.; Zunger, A. Self-interaction correction to density-functional approximations for many-electron systems. **Phys. Rev. B** 23, 5048, 1981 <https://doi.org/10.1103/PhysRevB.23.5048> [↑](#endnote-ref-3)
4. <https://en.wikipedia.org/wiki/List_of_quantum_chemistry_and_solid-state_physics_software> [↑](#endnote-ref-4)
5. Malyshkina, M.V.; Novikov, A.S. “Modern software for computer modeling in quantum chemistry and molecular dynamics. **Compounds** 1, 134, 2021 <https://doi.org/10.3390/compounds1030012> [↑](#endnote-ref-5)