# Density functional theory

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**Density functional theory (DFT)** is a quantum mechanical method used in physics and chemistry to investigate the electronic structure of many-body systems, in particular molecules and the condensed phases. DFT is among the most popular and versatile methods available in condensed matter physics (computational physics) and computational chemistry.

## Contents

# Description of the theory

Traditional methods in electronic structure theory, in particular Hartree-Fock theory and its descendants, are based on the complicated many-electron wavefunction. The main objective of density functional theory is to replace the many-body electronic wavefunction with the electronic density as the basic quantity. Whereas the many-body wavefunction is dependent on $3N$ variables, three spatial variables for each of the $N$ electrons, the density is only a function of three variables and is a simpler quantity to deal with both conceptually and practically.

Although density functional theory has its conceptual roots in the Thomas-Fermi model, DFT was not put on a firm theoretical footing until the Hohenberg-Kohn theorems (HK). The first of these demonstrates the existence of a one-to-one mapping between the ground state electron density and the ground state wavefunction of a many-particle system. Further, the second HK theorem proves that the ground state density minimizes the total electronic energy of the system. The original HK theorems held only for the ground state in the absence of magnetic field, although they have since been generalized. The first Hohenberg-Kohn theorem is only an existence theorem, stating that the mapping exists, but does not provide any such exact mapping. It is in these mappings that approximations are made.

(The theorems can be extended to the time-dependent domain (TDDFT), which can be also used to determine excited states [6].)

The most common implementation of density functional theory is through the Kohn-Sham method. Within the framework of Kohn-Sham DFT, the intractable many-body problem of interacting electrons in a static external potential is reduced to a tractable problem of non-interacting electrons moving in an effective potential. The effective potential includes the external potential and the effects of the Coulomb interactions between the electrons, e.g. the exchange and correlation interactions. Modeling the latter two interactions becomes the difficulty within KS DFT. The simplest approximation is the local-density approximation (LDA), which is based upon exact exchange energy for a uniform electron gas, which can be obtained from the Thomas-Fermi model, and from fits to the correlation energy for a uniform electron gas.

DFT has been very popular for calculations in solid state physics since the 1970s. In many cases DFT with the local-density approximation gives quite satisfactory results, for solid-state calculations, in comparison to experimental data at relatively low computational costs when compared to other ways of solving the quantum mechanical many-body problem. However, it was not considered accurate enough for calculations in quantum chemistry until the 1990s, when the approximations used in the theory were greatly refined to better model the exchange and correlation interactions. DFT is now a leading method for electronic structure calculations in both fields. Despite the improvements in DFT, there are still difficulties in using density functional theory to properly describe intermolecular interactions, especially van der Waals forces (dispersion), or in calculations of the band gap in semiconductors. Its poor treatment of dispersion renders DFT unsuitable (at least when used alone) for the treatment of systems which are dominated by dispersion (e.g. interacting noble gas atoms) or where dispersion competes significantly with other effects (e.g. in biomolecules). The development of new DFT methods designed to overcome this problem, by alterations to the functional or by the inclusion of additive terms, is a current research topic.

# The Thomas-Fermi model

The predecessor to density functional theory was the *Thomas-Fermi* model, developed by Thomas and Fermi in 1927. They calculated the energy of an atom by representing its kinetic energy as a functional of the electron density, combining this with the classical expressions for the nuclear-electron and electron-electron interactions (which can both also be represented in terms of the electron density).

Although this was an important first step, the Thomas-Fermi equation's accuracy was limited because it did not attempt to represent the exchange energy of an atom predicted by Hartree-Fock theory. An exchange energy functional was added by Dirac in 1928.

However, the Thomas-Fermi-Dirac theory remained rather inaccurate for most applications. The largest source of error was in the representation of the kinetic energy, followed by the errors in the exchange energy, and due to the complete neglect of electron correlation.

# Derivation and formalism

As usual in many-body electronic structure calculations, the nuclei of the treated molecules or clusters are seen as fixed (the Born-Oppenheimer approximation), generating a static external potential $V$ in which the electrons are moving. A stationary electronic state is then described by a wave function $\Psi(\vec{r}_1, \ldots, \vec{r}_N)$ fulfilling the many-electron Schrödinger equation

$$H\Psi = [T + V + U]\,\Psi = \left[\sum_i^N -\frac{\hbar^2}{2m}\nabla_i^2 + \sum_i^N V(\vec{r}_i) + \sum_{i<j} U(\vec{r}_i, \vec{r}_j)\right]\Psi = E\Psi$$

where $H$ is the electronic molecular Hamiltonian, $N$ is the number of electrons and $U$ is the electron-electron interaction. The operators $T$ and $U$ are so-called universal operators as they are the same for any system, while $V$ is system dependent or non-universal. As one can see, the actual difference between a single-particle problem and the much more complicated many-particle problem just arises from the interaction term $U$. There are many sophisticated methods for solving the many-body Schrödinger equation based on the expansion of the wave function in Slater determinants. While the simplest one is the Hartree-Fock method, more sophisticated approaches are usually categorized as post-Hartree-Fock methods. However, the problem with these methods is the huge computational effort, which makes it virtually impossible to apply them efficiently to larger, more complex systems.

Here DFT provides an appealing alternative, being much more versatile as it provides a way to systematically map the many-body problem, with $U$, onto a single-body problem without $U$. In DFT the key variable is the particle density $n(\vec{r})$ which is given by

$$n(\vec{r}) = N \int \mathrm{d}^3 r_2 \int \mathrm{d}^3 r_3 \cdots \int \mathrm{d}^3 r_N \, \Psi^*(\vec{r}, \vec{r}_2, \ldots, \vec{r}_N)\Psi(\vec{r}, \vec{r}_2, \ldots, \vec{r}_N).$$

Hohenberg and Kohn proved in 1964 [1] that the relation expressed above can be reversed, i.e. to a given ground state density $n_0(\vec{r})$ it is in principle possible to calculate the corresponding ground state wavefunction $\Psi_0(\vec{r}_1, \ldots, \vec{r}_N)$. In other words, $\Psi_0$ is a unique functional of $n_0$, i.e.

$$\Psi_0 = \Psi_0[n_0]$$

and consequently all other ground state observables $O$ are also functionals of $n_0$

$$\langle O \rangle [n_0] = \langle \Psi_0[n_0] | O | \Psi_0[n_0] \rangle .$$

From this follows, in particular, that also the ground state energy is a functional of $n_0$

$$E_0 = E[n_0] = \langle \Psi_0[n_0] | T + V + U | \Psi_0[n_0] \rangle ,$$

where the contribution of the external potential $\langle \Psi_0[n_0] | V | \Psi_0[n_0] \rangle$ can be written explicitly in terms of the

density

$$V[n] = \int V(\vec{r}) n(\vec{r}) d^3 r.$$

The functionals $T[n]$ and $U[n]$ are called universal functionals while $V[n]$ is obviously non-universal, as it depends on the system under study. Having specified a system, i.e. $V$ is known, one then has to minimise the functional

$$E[n] = T[n] + U[n] + \int V(\vec{r}) n(\vec{r}) d^3 r$$

with respect to $n(\vec{r})$, assuming one has got reliable expressions for $T[n]$ and $U[n]$. A successful minimisation of the energy functional will yield the ground state density $n_0$ and thus all other ground state observables.

The variational problem of minimising the energy functional $E[n]$ can be solved by applying the Lagrangian method of undetermined multipliers, which was done by Kohn and Sham in 1965 [2]. Hereby, one uses the fact that the functional in the equation above can be written as a fictitious density functional of a non-interacting system

$$E_s[n] = \langle \Psi_s[n] | T_s + V_s | \Psi_s[n] \rangle \, ,$$

where $T_s$ denotes the non-interacting kinetic energy and $V_s$ is an external effective potential in which the particles are moving. Obviously, $n_s(\vec{r}) \equiv n(\vec{r})$ if $V_s$ is chosen to be

$$V_s = V + U + (T - T_s) \, .$$

Thus, one can solve the so-called Kohn-Sham equations of this auxiliary non-interacting system

$$\left[ -\frac{\hbar^2}{2m} \nabla^2 + V_s(\vec{r}) \right] \phi_i(\vec{r}) = \epsilon_i \phi_i(\vec{r}),$$

which yields the orbitals $\phi_i$ that reproduce the density $n(\vec{r})$ of the original many-body system

$$n(\vec{r}) \equiv n_s(\vec{r}) = \sum_i^N |\phi_i(\vec{r})|^2 \, .$$

The effective single-particle potential $V_s$ can be written in more detail as

$$V_s = V + \int \frac{e^2 n_s(\vec{r}')}{|\vec{r} - \vec{r}'|} d^3 r' + V_{\mathrm{XC}}[n_s(\vec{r})],$$

where the second term denotes the so-called Hartree term describing the electron-electron Coulomb repulsion, while the last term $V_{\mathrm{XC}}$ is called the exchange correlation potential. Here, $V_{\mathrm{XC}}$ includes all the many-particle

interactions. Since the Hartree term and $V_{\mathrm{XC}}$ depend on $n(\vec{r})$, which depends on the $\phi_i$, which in turn depend on $V_s$, the problem of solving the Kohn-Sham equation has to be done in a self-consistent (i.e. iterative) way. Usually one starts with an initial guess for $n(\vec{r})$, then calculates the corresponding $V_s$ and solves the Kohn-Sham equations for the $\phi_i$. From these one calculates a new density and starts again. This procedure is then repeated until convergence is reached.

# Approximations

The major problem with DFT is that the exact functionals for exchange and correlation are not known except for the free electron gas. However, approximations exist which permit the calculation of certain physical quantities quite accurately. In physics the most widely used approximation is the local-density approximation (LDA), where the functional depends only on the density at the coordinate where the functional is evaluated:

$$E_{XC}[n] = \int \epsilon_{XC}(n)n(r)\mathrm{d}^3r.$$

The local spin-density approximation (LSDA) is a straightforward generalization of the LDA to include electron spin:

$$E_{XC}[n_\uparrow, n_\downarrow] = \int \epsilon_{XC}(n_\uparrow, n_\downarrow)\mathrm{d}^3r.$$

Highly accurate formulae for the exchange-correlation energy density $\epsilon_{XC}(n_\uparrow, n_\downarrow)$ have been constructed from Quantum Monte Carlo simulations of a free-electron gas.

Generalized gradient approximations (GGA) are still local but also take into account the gradient of the density at the same coordinate:

$$E_{XC}[n_\uparrow, n_\downarrow] = \int \epsilon_{XC}(n_\uparrow, n_\downarrow, \vec{\nabla}n_\uparrow, \vec{\nabla}n_\downarrow)\mathrm{d}^3r.$$

Using the latter (GGA) very good results for molecular geometries and ground state energies have been achieved. Many further incremental improvements have been made to DFT by developing better representations of the functionals.

# Generalizations to include magnetic fields

The DFT formalism above breaks down in the presence of a vector potential, i.e. a magnetic field. In such a case, the one-to-one mapping between electron density and external potential breaks down. Generalizations to include the effects of magnetic fields have led to two different theories: current density functional theory and magnetic field functional theory. In both these theories, the functional used for the exchange and correlation must be generalized to include more than just the electron density. In current density functional theory, developed by Vignale and Rasolt, the

functionals become dependent on both the electron density and the current density. In magnetic field density functional theory, developed by Salsbury, Grayce and Harris, the functionals depend on the electron density and the magnetic field, and the functional form can depend on the form of the magnetic field. In both of these theories it has been difficult to develop functionals beyond their equivalent to LDA, which are also readily implementable computationally.

# Applications

In practice, Kohn-Sham theory can be applied in several distinct ways depending on what is being investigated. In solid state calculations, the local density approximations are still commonly used along with plane wave basis sets, as an electron gas approach is more appropriate for an infinite solid. In molecular calculations, however, more sophisticated functionals are needed, and a huge variety of exchange-correlation functionals have been developed for chemical applications. Some of these are inconsistent with the uniform electron gas approximation, however, they must reduce to LDA in the electron gas limit. Among physicists, probably the most widely used functional is the revised Perdew-Burke-Enzerhof exchange model (a direct generalized-gradient parametrization of the free electron gas with no free parameters); however, this is not sufficiently calorimetrically accurate for gas-phase molecular calculations. In the chemistry community, one popular functional is known as BLYP (from the names Becke, Lee, Yang and Parr); but even more widely used is B3LYP [3-5] which is a hybrid method in which the DFT exchange functional, in this case from BLYP, is combined with the exact exchange functional from Hartree-Fock theory. These hybrid functionals carry adjustable parameters which are generally fitted to a 'training set' of molecules. Unfortunately, although the results obtained with these functionals are usually sufficiently accurate for most applications, there is no systematic way of improving them (in contrast to some of the traditional wavefunction-based methods like configuration interaction or coupled cluster theory). Hence in the current DFT approach it is not possible to estimate the error of the calculations without comparing them to other methods or experiment.

# Software supporting DFT

- Abinit
- ADF
- AIMPRO
- Atomistix Toolkit
- CADPAC
- CASTEP
- CPMD
- CRYSTAL06 (http://www.crystal.unito.it/)
- DACAPO
- DALTON
- deMon2K (http://www.demon-software.com/public_html)
- DFT++ (http://dft.physics.cornell.edu/)

- DMol3 (http://www.accelrys.com/products/mstudio/modeling/quantumandcatalysis/dmol3.html)
- EXCITING
- Fireball (http://www.physics.byu.edu/research/lewis/fireball/index.htm)
- GAMESS (UK)
- GAMESS (US)
- GAUSSIAN
- JAGUAR
- MOLCAS
- MPQC
- NWChem
- OCTOPUS
- ORCA (http://ewww.mpi-muelheim.mpg.de/bac/logins/downloads_en.php)
- OpenMX (http://staff.aist.go.jp/t-ozaki/openmx/openmx.html)
- PARAGAUSS[1] (http://www.theochem.tu-muenchen.de/welcome/index.php?
  option=com_content&task=view&id=61&lang=en)
- Q-Chem
- Quantum-ESPRESSO (http://www.quantum-espresso.org/)
- SIESTA
- S/PHI/nX (http://www.sphinxlib.de)
- TURBOMOLE
- VASP
- PWscf
- WIEN2k
- Spartan (http://www.wavefun.com/products/spartan.html)
- FSatom, dozens of free and proprietary DFT programs (http://www.fsatom.org/programs.php?type=4#r)

# Books on DFT

- R. Dreizler, E. Gross, Density Functional Theory. (Plenum Press, New York, 1995).
- W. Koch, M. C. Holthausen, A Chemist's Guide to Density Functional Theory. (Wiley-VCH, Weinheim, ed. 2, 2002).
- R. G. Parr, W. Yang, Density-Functional Theory of Atoms and Molecules. (Oxford University Press, New York, 1989).

# References

1. P. Hohenberg and W. Kohn, Phys. Rev. *136* (1964) B864 (http://prola.aps.org/abstract/PR/v136/i3B/pB864_1)
2. W. Kohn and L. J. Sham, Phys. Rev. *140* (1965) A1133 (http://prola.aps.org/abstract/PR/v140/i4A/pA1133_1)
3. A. D. Becke, J. Chem. Phys. *98* (1993) 5648

4. C. Lee, W. Yang, and R. G. Parr, Phys. Rev. B *37* (1988) 785 (http://prola.aps.org/abstract/PRB/v37/i2/p785_1)
5. P. J. Stephens, F. J. Devlin, C. F. Chabalowski, and M. J. Frisch, J. Phys. Chem. *98* (1994) 11623
6. K. Burke, J. Werschnik, and E. K. U. Gross, *Time-dependent density functional theory: Past, present, and future*. J. Chem. Phys. *123*, 062206 (http://dx.doi.org/10.1063/1.1904586) (2005). OAI: arXiv.org:cond-mat/0410362 (http://arxiv.org/abs/cond-mat/0410362) .

# External links

- Walter Kohn, Nobel Laureate (http://www.vega.org.uk/video/programme/23) Freeview video interview with Walter on his work developing density functional theory by the Vega Science Trust.
- Klaus Capelle, A bird's-eye view of density-functional theory (http://arxiv.org/abs/cond-mat/0211443)
- Walter Kohn, Nobel Lecture (http://nobelprize.org/chemistry/laureates/1998/kohn-lecture.pdf)

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