

Density Functional Theory (DFT)

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The Hohenberg-Kohn theorems

There are two theorems:

1. The ground state expectation value of any observable (including the total energy of the system) is a unique functional of the ground-state electron density.
2. The variational principle is applicable to the electron density i.e the true ground-state electron density minimizes the total energy functional.

Walter Kohn's reflection

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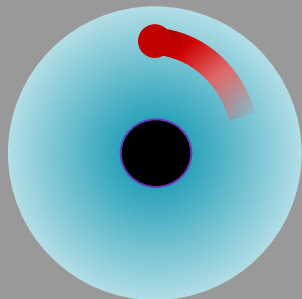


- The Hartree method gives acceptable energies.
- Thomas-Fermi theory gives a much worse description.
- The two theories are quite similar they differ primarily in their treatment of the kinetic energy term.
- Thomas-Fermi theory provides a link between electron density and potential.

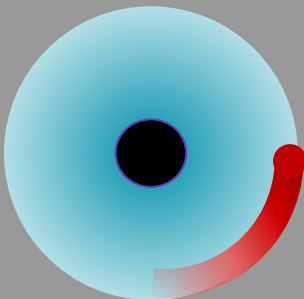
The general idea



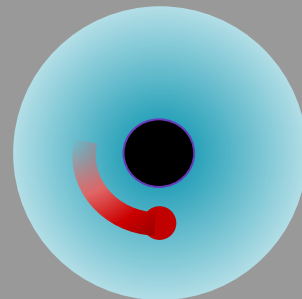
We would like to turn the complex many-electron problem into a set of one-electron problems where the electron-electron interactions are treated by an effective potential.



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Hartree vs Kohn-Sham DFT

$$F_H = -\frac{1}{2}\nabla^2 - \frac{Z}{|r-R|} + \int \frac{\rho}{|r-r'|} dr'$$

$$V_H[\rho] = \int \frac{\rho}{|r-r'|} dr'$$

In the so-called Kohn-Sham DFT, we make use of a one-electron equation that looks very similar to Hartree or Hartree-Fock. Instead of exchange operator in Hartree-Fock we have a density dependent exchange and correlation potential.

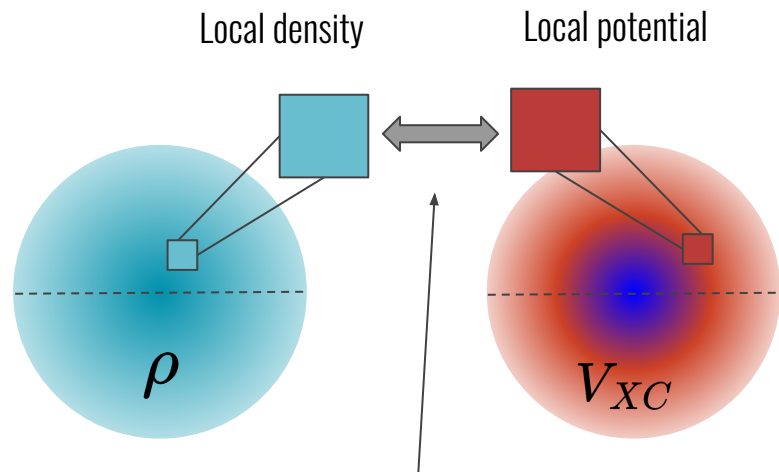
$$F_{DFT} = -\frac{1}{2}\nabla^2 - \frac{Z}{|r-R|} + V_H[\rho] + V_{XC}[\rho]$$

The ingenious thing with DFT is that it is possible to prove that the orbitals (bottom left) from the equation above can yield the true electron density of the system (bottom right). The crux is that we do not know how to write the exchange correlation functional...

$$F_{DFT}\chi_i = \epsilon_i\chi_i \qquad \rho = \sum |\chi_i|^2$$

LDA

-a simple recipe for V_{XC}

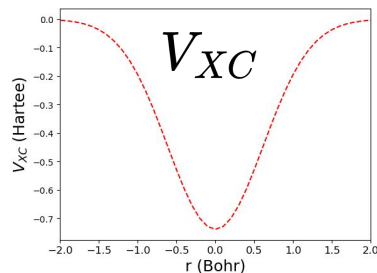
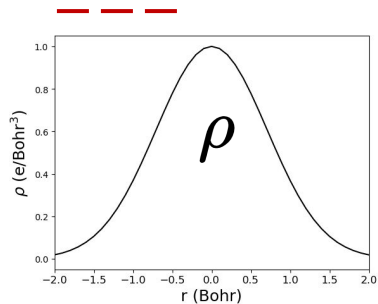


For each volume element of the density, we compute the corresponding exchange-correlation potential from the known HEG solution.

- The exchange-correlation potential of a homogeneous electron gas (HEG) is known.
- We can follow in the spirit of Thomas-Fermi theory and build up V_{XC} from local.
- The approach is called the local density approximation (LDA).

LDA

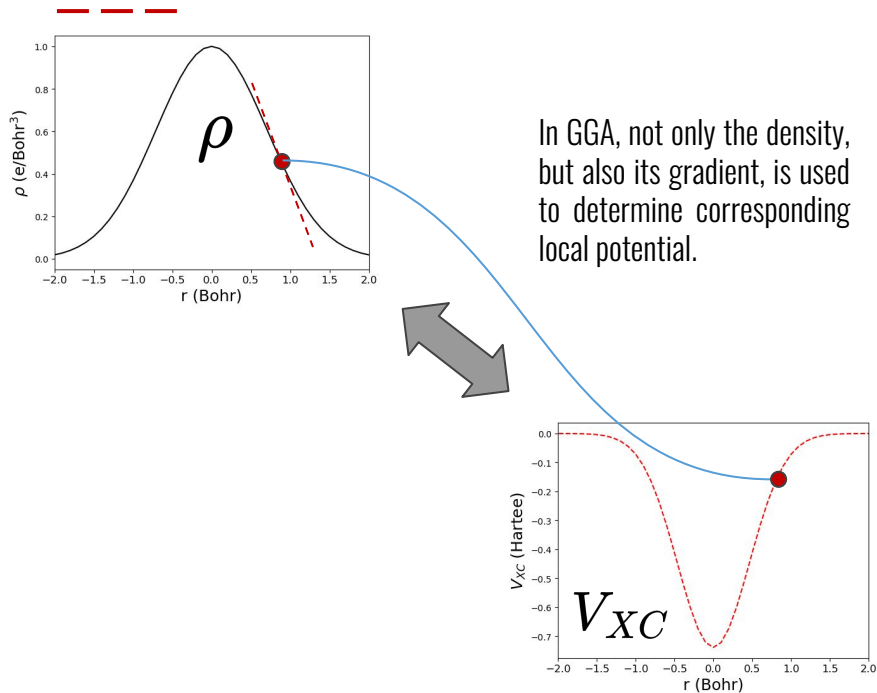
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GGA and beyond

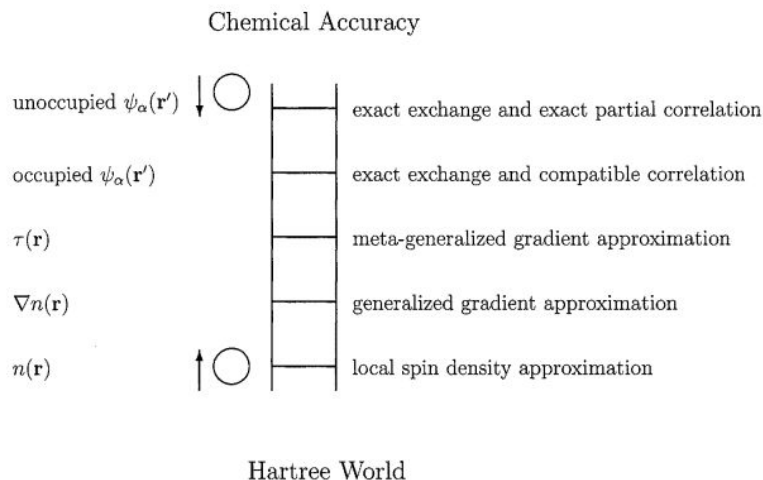
-more advanced recipes for V_{XC}



- We can improve on LDA by also taking into account the local change (gradient) of the density when deciding the value for the potential. This is called Generalized Gradient Approximation (GGA).
- We need to have reference values for each combination of density and gradient. These reference values are typically obtained from known limiting cases with empirically fitted “curves” connecting these known cases.

GGA and beyond

-more advanced recipes for V_{xc}



- We can gradually increase complexity to strive for higher accuracy.
- John Perdew summarize this using the so-called “Jacob’s ladder of density functional approximations for the exchange-correlation energy”.
- Parametrization is now more difficult.

Summary

- Useful for in principle all elements in the periodic system.
- Can be used for calculations of all bond types including Van der Waals 'Interactions if an appropriate functional is chosen.
- Less time-consuming method than Hartree-Fock. Hence large systems can be addressed ~1000 atoms.
- It is the most widely used quantum mechanical method in physics.
- Unfortunately, there is no way of systematically improving results.