

Density Functional Theory I

Nicholas M. Harrison

*Department of Chemistry, Imperial College London, &
Computational Materials Science, Daresbury Laboratory*

nicholas.harrison@ic.ac.uk

Density Functional Theory I

- The Many Electron Schrödinger Equation
- Hartree-Fock Theory
- Solving the Schrödinger Equation
- Avoiding Solving the Schrödinger Equation
- Density Matrices
- The basic ideas of DFT
- Kohn-Sham and the non-interacting system
- The local density approximation – LDA
- Conclusions
- Density Functional Theory II ...

The Schrödinger Equation for Many Electrons

Time independent, non-relativistic, Born-Oppenheimer...

$$\hat{H} \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = E \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$$

A linear equation in 3N variables

$$\hat{H} = -\frac{1}{2} \sum_i^N \nabla_i^2 + \hat{V}_{ext} + \sum_{i < j}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

Three terms – kinetic energy, external potential and electron-electron.

The External Potential

The interaction with the atomic nuclei is:

$$\hat{V}_{ext} = - \sum_a^{N_{at}} \frac{Z_a}{|\mathbf{r} - \mathbf{R}_a|}$$

The external potential and the number of electrons, N , completely determine the Hamiltonian.

The Variational Principles

For any legal wavefunction (antisymmetric, normalised)
the energy is

$$E[\Psi] = \int \Psi^* \hat{H} \Psi d\mathbf{r} \equiv \left\langle \Psi \left| \hat{H} \right| \Psi \right\rangle$$

- the energy is a *functional* of Ψ

$$E[\Psi] \geq E_0$$

- Search all Ψ to minimise $E \Rightarrow$ the ground state

Hartree Fock Theory

An ansatz for the structure of the wavefunction

$$\Psi_{HF} = \frac{1}{\sqrt{N!}} \det[\mathbf{f}_1 \mathbf{f}_2 \mathbf{f}_3 \dots \mathbf{f}_N]$$

$$\begin{aligned} E_{HF} = & \int \mathbf{f}_i^*(\mathbf{r}) \left(-\frac{1}{2} \sum_i^N \nabla_i^2 + V_{ext} \right) \mathbf{f}_i(\mathbf{r}) d\mathbf{r} \\ & + \frac{1}{2} \sum_{i,j}^N \int \frac{\mathbf{f}_i^*(\mathbf{r}_1) \mathbf{f}_i(\mathbf{r}_1) \mathbf{f}_j^*(\mathbf{r}_2) \mathbf{f}_j(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 \\ & - \frac{1}{2} \sum_{i,j}^N \int \frac{\mathbf{f}_i^*(\mathbf{r}_1) \mathbf{f}_j(\mathbf{r}_1) \mathbf{f}_i(\mathbf{r}_2) \mathbf{f}_j^*(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 \end{aligned}$$

The Hartree Fock Equations

$$\left[-\frac{1}{2}\nabla^2 + V_{ext}(\mathbf{r}) + \int \frac{r(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' \right] \mathbf{f}_i(\mathbf{r}) + \int v_X(\mathbf{r},\mathbf{r}') \mathbf{f}_i(\mathbf{r}') d\mathbf{r}' = \mathbf{e}_i \mathbf{f}_i(\mathbf{r})$$

$$\int v_X(\mathbf{r},\mathbf{r}') \mathbf{f}_i(\mathbf{r}') d\mathbf{r}' = -\sum_j^N \int \frac{\mathbf{f}_j(\mathbf{r}) \mathbf{f}_j^*(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \mathbf{f}_i(\mathbf{r}') d\mathbf{r}'$$

non-interacting electrons under the influence of a mean field potential consisting of the classical Coulomb potential and a *non-local* exchange potential.

Beyond Hartree-Fock

Many methods/approximations applicable to *small* systems.

Expensive & scaling with problem size is ferocious

Eg:

MP2, MP3, MP4 ~ N^5, N^6, N^7

CISD ~ N^6

CCSD ~ N^6

CCSD(T) ~ N^7

Avoiding Solving the Schrodinger Equation

Is it necessary to solve the Schrödinger equation and determine the $3N$ dimensional wavefunction in order to compute the ground state energy ?

..... No !

The Pair Density

The second order density matrix is defined as

$$P_2(\mathbf{r}'_1, \mathbf{r}'_2; \mathbf{r}_1, \mathbf{r}_2) = \frac{N(N-1)}{2} \int \Psi^*(\mathbf{r}'_1, \mathbf{r}'_2, \dots, \mathbf{r}'_N) \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) d\mathbf{r}_3 d\mathbf{r}_4 \dots d\mathbf{r}_N$$

The diagonal elements are the *two particle density matrix* or *pair density function*,

$$P_2(\mathbf{r}_1, \mathbf{r}_2) = P_2(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_1, \mathbf{r}_2)$$

This object in 6 dimensions is all we need to compute the exact total energy !

The Energy and the Density Matrices

The first order density matrix is

$$P_1(\mathbf{r}'_1; \mathbf{r}_1) = \frac{2}{N-1} \int P_2(\mathbf{r}'_1, \mathbf{r}_2; \mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2$$

H only contains one-electron and two-electron operators
- the energy can be written exactly in terms of P_1 and P_2

$$E = \int \left[\left(-\frac{1}{2} \nabla_1^2 - \sum_a \frac{Z_a}{|\mathbf{r}_1 - \mathbf{R}_a|} \right) P_1(\mathbf{r}'_1, \mathbf{r}_1) \right]_{\mathbf{r}_1 = \mathbf{r}'_1} d\mathbf{r}_1 + \int \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} P_2(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2$$

The energy is a functional of P_2 : $E[P_2]$

Perhaps solve using by minimising $E[P_2]$?

Very difficult problem –

A legal P_2 must be constructible from an antisymmetric Ψ .

Applying this constraint in practice is non trivial.

Life would be much easier if there was a way of doing it!

Do we really need to know P_2 ?

No ...

To find the exact total energy knowledge of the charge density $\rho(\mathbf{r})$ is enough !

DFT – the theorems

Theorem 1.

The external potential is uniquely determined by the density - $\rho(\mathbf{r})$
- so the total energy is a unique functional of the density - $E[\rho]$!

Theorem 2.

The density which minimises the energy is the ground state density and the minimum energy is the ground state energy.

$$\text{Min}_{\mathbf{r}} E[\mathbf{r}] = E_0$$

Hohenburg-Kohn – 1964

Mel Levy

E B Wilson

Theorem 1 – Wilson's proof

The charge density has a cusp at the nucleus of any atom such that,

$$Z_a = \frac{-1}{2\bar{r}(0)} \left[\frac{\partial \bar{r}(r_a)}{\partial r_a} \right]_{r_a=0}$$

The charge density uniquely determines the Hamiltonian, thus the wavefunction and all material properties !!!

Density Functional Theory

The fundamental statement of DFT is

$$d \left[E[\mathbf{r}] - m \left(\int \mathbf{r}(\mathbf{r}) d\mathbf{r} - N \right) \right] = 0$$

there is a *universal* functional $E[\rho]$ which could be inserted into the above equation and minimised to obtain the *exact* ground state density and energy.

What is the functional ?

There are three terms in the Hamiltonian...

$$E[\mathbf{r}] = T[\mathbf{r}] + V_{ext}[\mathbf{r}] + V_{ee}[\mathbf{r}]$$

$V_{ext}[\rho]$ is trivial

$$V_{ext}[\mathbf{r}] = \int \hat{V}_{ext}(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r}$$

T and V_{ee} are very difficult to approximate !

$E_{xc}[r]$ - Properties

- Does not depend on V_{ext} (the specific system): it is a ‘universal’ functional.
- The exact dependence on $\rho(r)$ is unknown
- $E_{(x)c}$ can be exactly determined for any specific density, but the effort is greater than for usual many-body calculations

$E_{(x)c}$ must be approximated in applications

The Homogeneous Electron Gas

For the non-interacting gas the kinetic and exchange energy per particle can be computed – the single particle wavefunctions are simply plane waves.

Perhaps integrate these energy densities for an inhomogeneous system ?

$$T[\mathbf{r}] = 2.87 \int \mathbf{r}^{5/3}(\mathbf{r}) d\mathbf{r}$$

..... No chemical bonding !

$$E_x = 0.74 \int \mathbf{r}^{4/3}(\mathbf{r}) d\mathbf{r}$$

E_x is OK but what about T ?

A local function of the density

Thomas-Fermi-Dirac suggests:

$$E_{xc}[\mathbf{r}] \approx \int \mathbf{r}(\mathbf{r}) \mathbf{e}_{xc}(\mathbf{r}(\mathbf{r})) d\mathbf{r}$$

$$\mathbf{e}_{xc}(\mathbf{r}) = \mathbf{e}_x(\mathbf{r}) + \mathbf{e}_c(\mathbf{r})$$

$$\mathbf{e}_x(\mathbf{r}) = -C\mathbf{r}^{1/3}$$

J. Slater 1951

The *functional* is a local *function* of the density ...

What to do about $\epsilon_c(\rho)$?

$E[\mathbf{r}]$ – The Kohn Sham Approach

Write the density in terms of a set of N non-interacting orbitals...

$$\mathbf{r}(\mathbf{r}) = \sum_i |\mathbf{f}_i(\mathbf{r})|^2$$

The non interacting kinetic energy and the classical Coulomb interaction

$$T_s[\mathbf{r}] = -\frac{1}{2} \sum_i^N \langle \mathbf{f}_i | \nabla^2 | \mathbf{f}_i \rangle \quad V_H[\mathbf{r}] = \frac{1}{2} \int \frac{\mathbf{r}(\mathbf{r}_1) \mathbf{r}(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2$$

Allow us to recast the energy functional as:

$$E[\mathbf{r}] = T_s[\mathbf{r}] + V_{ext}[\mathbf{r}] + V_H[\mathbf{r}] + E_{xc}[\mathbf{r}]$$

Where we have introduced

$$E_{xc}[\mathbf{r}] = (T[\mathbf{r}] - T_s[\mathbf{r}]) + (V_{ee}[\mathbf{r}] - V_H[\mathbf{r}])$$

Variation Theorem => Kohn Sham Equations

Vary the energy with respect to the orbitals and

$$\left[-\frac{1}{2} \nabla^2 + V_{ext}(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + V_{xc}(\mathbf{r}) \right] \mathbf{f}_i(\mathbf{r}) = \epsilon_i \mathbf{f}_i(\mathbf{r})$$

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

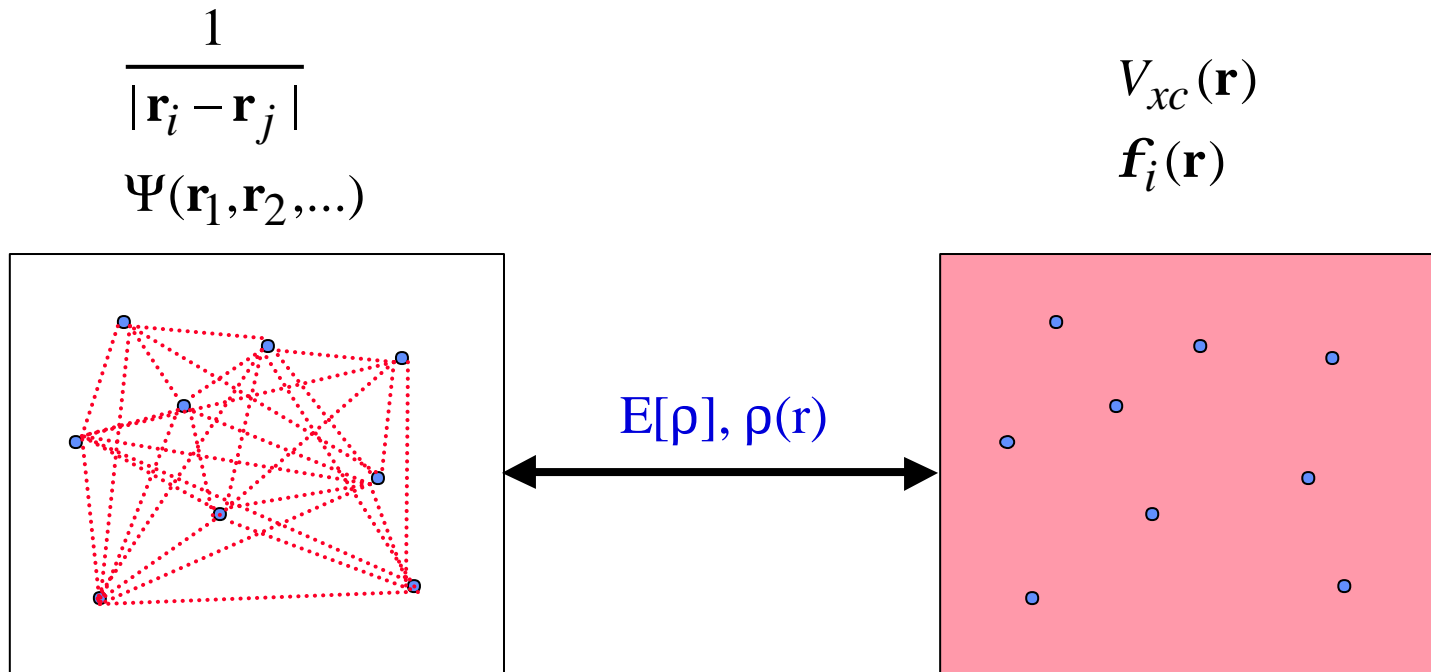
No approximations, So...

If we knew $E_{xc}[\rho]$ we could solve for the *exact* ground state energy and density !

Cost – N^3 In principle N .

The Non-interacting system

There exists an effective mean field potential which, when applied to a system of non-interacting fermions, will generate the exact ground state energy and charge density !!!



Hartree Fock is a density functional theory...

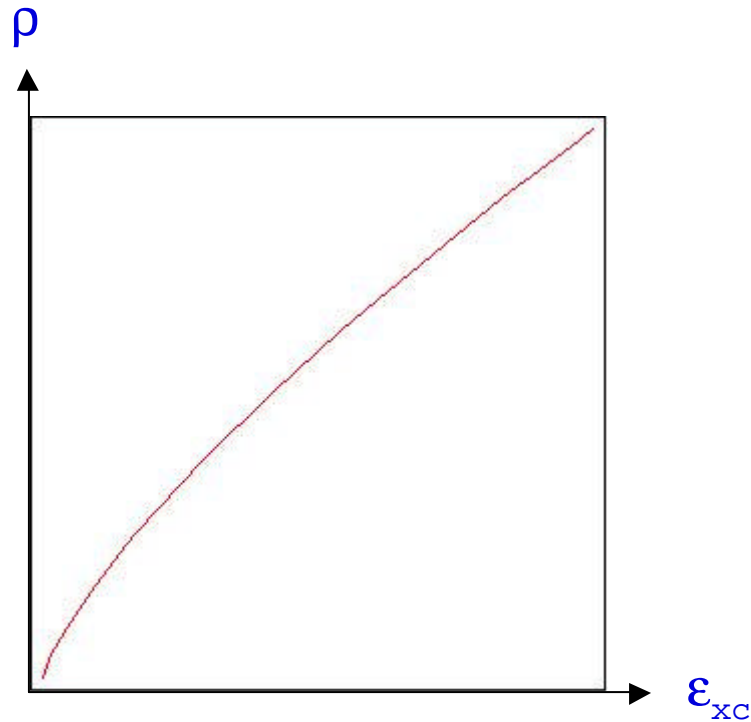
Hartree-Fock theory is a density functional theory !

- but with a non-local potential.

$$\begin{aligned} V_{xc}\mathbf{f}_i &= \int dr_2 V(\vec{r}_1, \vec{r}_2)\mathbf{f}_i(\vec{r}_2) \\ &= -\sum_j \int dr_2 \frac{\mathbf{f}_j(\vec{r}_2)\mathbf{f}_i(\vec{r}_2)\mathbf{f}_j(\vec{r}_1)}{\left|\vec{r}_1 - \vec{r}_2\right|} \end{aligned}$$

Quantum Monte Carlo Simulations

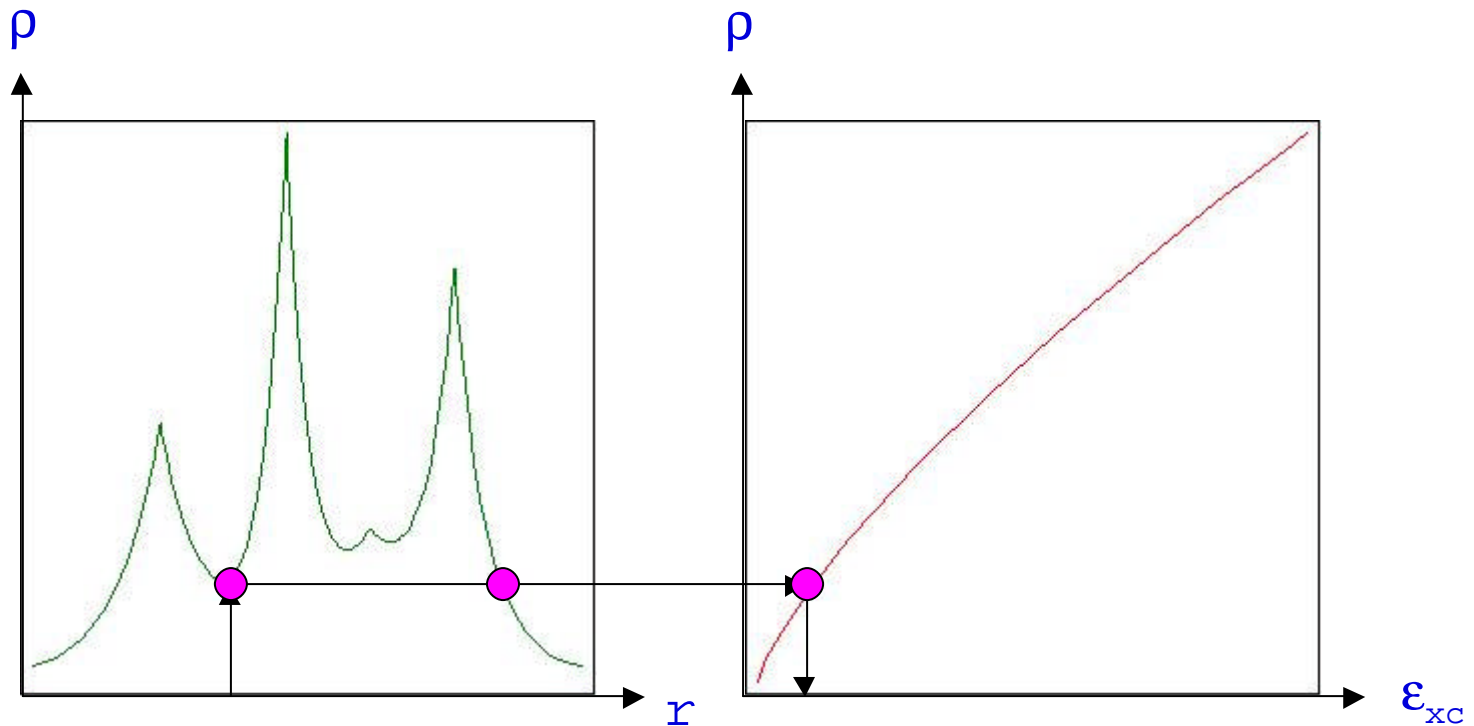
For the Homogeneous electron gas the exact dependence of $\epsilon_{xc}(\rho)$ can be computed.



Ceperley and Alder 1980

The Local Density Approximation - LDA

$$E_{xc}^{LDA}[\mathbf{r}] = \int \mathbf{r}(\mathbf{r}) \mathbf{e}_{xc}(\mathbf{r}(\mathbf{r})) d\mathbf{r}$$



Picture courtesy of Andreas Savin

Conclusions I

- For the ground state energy and density there is an exact mapping between the many body system and a fictitious non-interacting system.
 - DFT-people study the fictitious system !
- The fictitious system is subject to an unknown potential derived from the exchange-correlation functional
- The energy functional may be approximated as a local function of the density !

Density Functional Theory II

- Why does the LDA work ?
- The exchange correlation hole
- Comparison with exact exchange and correlation energy densities
- Generalised gradient approximations – GGA's
- Semi-local interactions: Meta-GGA's
- Hybrid-exchange functionals
- Performance in molecules and solids