# ABC of DFT



Adiabatic approximation

### Independent electrons in an effective potential

Hartree-Fock

**Density Functional Theory** 

MBPT - GW





### Density Functional Theory in a nutshell

Every observable quantity of a stationary quantum mechanical system is determined by the system ground-state density alone

The ground-state density of the interacting system of interest can be calculated as ground-state density of an auxiliary non-interacting system in an effective potential

There are prescriptions to determine the auxiliary effective potential with useful accuracy



Many Properties are within the scope of DFT...

- -Energetics, relative stability of different structures, phase diagrams;
- -Structural properties, geometry;
- -Response to external perturbations: elastic, dielectric, piezoelectric constants;
- -Vibrational properties;
- -Chemical potentials, ionization energies, electron affinities, Fermi energies;
- -Defect energetics and transport properties.

## ... and many are NOT

- -Electronic excitations (unless  $\Delta E_{GS}$  );
- -Fermi surfaces and band structures;
- -Defect induces electronic structure changes;
- -Electronic transport properties.





FIG. 1. Numbers of papers when DFT is searched as a topic in Web of Knowledge (grey), B3LYP citations (blue), and PBE citations (green, on top of blue).





Adiabatic approximation

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Adiabatic approximation

### Independent electrons in an effective potential

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### **Density Functional Theory**

- Hohenberg-Kohn theorem
- Kohn-Sham equations
- Exc functionals

MBPT - GW





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The GS density can be uses as basic variable to describe the status of a quantum many-body system.

All properties of the system are therefore functionals of the GS density.



DENSITY FUNCTIONAL THEORY the density as the basic variable (for GS properties)  $[T_{e}+V_{ee}+V] \psi_{=}^{=} E_{6s} \psi_{6s}; n(r) = \langle \psi_{6s} | \hat{n}(r) | \psi_{6s} \rangle$ Sch.eg. 42 NZ DET Hohenberg & Kohn Theorem Phy. Rev. 136 B864(1964) if  $V(r) \neq V(r) + const$  then  $n'(r) \neq n(r)$ => n(r) -> V(r)+const -> 4 -> EGS,... F[n] = <4[[n] | Te + Vee | 4[[n]>



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#### Inhomogeneous Electron Gas\*

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This paper deals with the ground state of an interacting electron gas in an external potential  $v(\mathbf{r})$ . It is proved that there exists a universal functional of the density,  $F[n(\mathbf{r})]$ , independent of  $v(\mathbf{r})$ , such that the expression  $E \equiv \int v(\mathbf{r})n(\mathbf{r})d\mathbf{r} + F[n(\mathbf{r})]$  has as its minimum value the correct ground-state energy associated with  $v(\mathbf{r})$ . The functional  $F[n(\mathbf{r})]$  is then discussed for two situations: (1)  $n(\mathbf{r}) = n_0 + \tilde{n}(\mathbf{r})$ ,  $\tilde{n}/n_0 < <1$ , and (2)  $n(\mathbf{r}) = \varphi(\mathbf{r}/r_0)$  with  $\varphi$  arbitrary and  $r_0 \rightarrow \infty$ . In both cases F can be expressed entirely in terms of the correlation energy and linear and higher order electronic polarizabilities of a uniform electron gas. This approach also sheds some light on generalized Thomas-Fermi methods and their limitations. Some new extensions of these methods are presented.



#### 1. The Density as Basic Variable

We shall be considering a collection of an arbitrary number of electrons, enclosed in a large box and moving under the influence of an external potential  $v(\mathbf{r})$  and the mutual Coulomb repulsion. The Hamiltonian has the form

$$H = T + V + U, \tag{1}$$

where<sup>10</sup>

$$T = \frac{1}{2} \int \nabla \psi^*(\mathbf{r}) \nabla \psi(\mathbf{r}) d\mathbf{r}, \qquad (2)$$

$$V \equiv \int v(\mathbf{r}) \psi^*(\mathbf{r}) \psi(\mathbf{r}) d\mathbf{r}, \qquad (3)$$

$$U = \frac{1}{2} \int \frac{1}{|\mathbf{r} - \mathbf{r}'|} \psi^*(\mathbf{r}) \psi^*(\mathbf{r}') \psi(\mathbf{r}') \psi(\mathbf{r}) d\mathbf{r} d\mathbf{r}'.$$
(4)

We shall in all that follows assume for simplicity that we are only dealing with situations in which the ground state is nondegenerate. We denote the electronic density in the ground state  $\Psi$  by

$$n(\mathbf{r}) \equiv (\Psi, \psi^*(\mathbf{r})\psi(\mathbf{r})\Psi), \qquad (5)$$

which is clearly a functional of  $v(\mathbf{r})$ .

We shall now show that conversely  $v(\mathbf{r})$  is a unique functional of  $n(\mathbf{r})$ , apart from a trivial additive constant.

The proof proceeds by reductio ad absurdum. Assume that another potential  $v'(\mathbf{r})$ , with ground state  $\Psi'$  gives rise to the same density  $n(\mathbf{r})$ . Now clearly [unless  $v'(\mathbf{r})-v(\mathbf{r})=\text{const}$ ]  $\Psi'$  cannot be equal to  $\Psi$ since they satisfy different Schrödinger equations. Hence, if we denote the Hamiltonian and ground-state energies associated with  $\Psi$  and  $\Psi'$  by H, H' and E, E', we have by the minimal property of the ground state,

$$E' = (\Psi', H'\Psi') < (\Psi, H'\Psi) = (\Psi, (H+V'-V)\Psi),$$

so that

$$E' < E + \int [v'(\mathbf{r}) - v(\mathbf{r})] n(\mathbf{r}) d\mathbf{r}.$$
 (6)

Interchanging primed and unprimed quantities, we find in exactly the same way that

$$E < E' + \int [v(\mathbf{r}) - v'(\mathbf{r})] n(\mathbf{r}) d\mathbf{r}.$$
(7)

Addition of (6) and (7) leads to the inconsistency

$$E + E' < E + E'. \tag{8}$$

Thus  $v(\mathbf{r})$  is (to within a constant) a unique functional of  $n(\mathbf{r})$ ; since, in turn,  $v(\mathbf{r})$  fixes H we see that the full many-particle ground state is a unique functional of  $n(\mathbf{r})$ .



Levy's constrained search formulation of DFT M Levy PNAS 76, 6062 (1979); M Levy, PRA 26, 1200 (1982)

The original HK theorem was obtained for densities that are (non degenerate) GS densities of some potential V ... These density are named *V*-representable

But ... what are they ? How can we define the domain of definition for the HK theorem ?

It can be shown that very reasonable densities *are not* V-representable

The extension

$$\begin{split} n(\mathbf{r}) &\longrightarrow F[n] = \inf_{\Psi \to n} \langle \Psi | T_e + W_{ee} | \Psi \rangle \\ \text{is defined for all $N$-representable densities} \\ i.e. \ \forall \ n(\mathbf{r}) > 0, \ \int n(\mathbf{r}) d\mathbf{r} = N, \ \int \left( \nabla \sqrt{n(\mathbf{r})} \right)^2 d\mathbf{r} < +\infty \end{split}$$



An analogy with a well known case...

Consider the structural stability problem:  $E(V) = \min_{\mathbf{R} \to V} E(\mathbf{R})$ 

Volume V and pressure P are equally legitimate variables to describe the status of the system, each with its own thermodynamic potential, linked by a Legendre transform

$$H(P) = \min_{V} \{E(V) + PV\}, \qquad \frac{\partial H}{\partial P} = V$$

 $\cap \mathbf{T}$ 

$$E(V) = \max_{P} \left\{ H(P) - PV \right\}, \qquad \frac{\partial E}{\partial V} = -P$$



In QM potential V(r) determines the GS density n(r)

$$E_{GS}[V] = \min_{\Psi} \langle \Psi | [T_e + W_{ee} + V | \Psi \rangle + W_D(\mathbf{R})$$



In QM potential V(r) determines the GS density n(r)

$$E_{GS}[V] = \min_{\Psi} \langle \Psi | [T_e + W_{ee} + V | \Psi \rangle$$
$$V(\mathbf{r}) \implies \Psi \implies n(\mathbf{r}) = \langle \Psi | \hat{n} | \Psi \rangle = \frac{\delta E_{GS}}{\delta V(\mathbf{r})}$$

Performing a Legendre transform we obtain

$$F[n] = \max_{V} \left\{ E_{GS}[V] - \int V(\mathbf{r})n(\mathbf{r})d\mathbf{r} \right\}$$
$$= \min_{\Psi \to n} \langle \Psi | T_e + W_{ee} | \Psi \rangle$$
$$n(\mathbf{r}) \implies \Psi \implies V(\mathbf{r}) = -\frac{\delta F[n]}{\delta n(\mathbf{r})}$$

The GS density n(r) determines the potential V(r)

## **DFT variational principle**

 $[T_e + W_{eI} + W_{ee} + W_{II}] \Phi_{\nu}(\mathbf{r}|\mathbf{R}) = E_{\nu}(\mathbf{R})\Phi_{\nu}(\mathbf{r}|\mathbf{R})$ 

HK: 
$$n(\mathbf{r}) \longrightarrow F[n] = \min_{\Psi \to n} \langle \Psi | T_e + W_{ee} | \Psi \rangle$$

 $E_{GS}(\mathbf{R})$  depends only on the GS density  $n(\mathbf{r})$ (3D function) and satisfies the variational principle [Hohenberg and Kohn, 1964]

$$E_{GS}(\mathbf{R}) = \min_{n} \left\{ F[n(\mathbf{r})] + \int V_{ext}(\mathbf{r}, \mathbf{R}) n(\mathbf{r}) d\mathbf{r} \right\}$$
$$+ W_{II}(\mathbf{R})$$



# Kohn - Sham equations



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LuJ



n(r) is a smooth and simple function of r, so...



FIG. 1. Spherically averaged density n(r) in ground state of carbon atom as a function of distance r from nucleus.



... F[n] is a very non trivial functional of n(r) !



FIG. 1. Spherically averaged density n(r) in ground state of carbon atom as a function of distance r from nucleus.



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#### Self-Consistent Equations Including Exchange and Correlation Effects\*

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From a theory of Hohenberg and Kohn, approximation methods for treating an inhomogeneous system of interacting electrons are developed. These methods are exact for systems of slowly varying or high density. For the ground state, they lead to self-consistent equations analogous to the Hartree and Hartree-Fock equations, respectively. In these equations the exchange and correlation portions of the chemical potential of a uniform electron gas appear as additional effective potentials. (The exchange portion of our effective potential differs from that due to Slater by a factor of  $\frac{2}{3}$ .) Electronic systems at finite temperatures and in magnetic fields are also treated by similar methods. An appendix deals with a further correction for systems with short-wavelength density oscillations.



HK: 
$$n(\mathbf{r}) \longrightarrow F[n] = \min_{\Psi \to n} \langle \Psi | T_e + W_{ee} | \Psi \rangle$$

It is useful to introduce a ficticious system of non-interacting electrons

KS: 
$$n(\mathbf{r}) \longrightarrow T_s[n] = \min_{\Psi \to n} \langle \Psi | T_e | \Psi \rangle$$

$$F[n] = T_s[n] + E_H[n] + E_{xc}[n]$$
 This defines  $E_{xc}$ 

### The energy becomes

$$E[n] = T_s[n] + E_H[n] + E_{xc}[n] + \int V_{ext}(\mathbf{r})n(\mathbf{r})d\mathbf{r}$$



### Thomas-Fermi approximation to Ts

$$E[n] = T_s[n] + E_H[n] + E_{xc}[n] + \int V_{ext}(\mathbf{r})n(\mathbf{r})d\mathbf{r}$$

$$T_s[n] \approx \int \varepsilon_{kin}^{hom}(n(\mathbf{r}))n(\mathbf{r})d\mathbf{r} = \int \frac{3}{5} \frac{\hbar^2}{2m} k_F^2(\mathbf{r})n(\mathbf{r})d\mathbf{r}$$





EH Lieb, Rev Mod Phys **53**, 605 (1981) Thomas-Fermi and related theories of atoms and molecules Simple approximations for Ts are only qualitative

$$E[n] = T_s[n] + E_H[n] + E_{xc}[n] + \int V_{ext}(\mathbf{r})n(\mathbf{r})d\mathbf{r}$$



FIG. 4. Relative magnitudes of contributions to total valence energy of Mn atom (in eV).



Kohn - Sham equations  
the minimum condition for the interacting  
system is  

$$S[F[n] + \int V(r) n(r) d^{2}r - \mu (\int n(r) d^{2}r - N)] = 0$$
  
 $\frac{\delta F[n]}{\delta n(r)} + V_{\delta}(r) - \mu = 0$   
 $\frac{\delta T_{\delta}[n]}{\delta n(r)} + \frac{e^{2} (n(r')) d^{2}r^{1}}{\delta n(r)} + \frac{\delta E[n]}{\delta n(r)} + V_{\delta}(r) - \mu = 0$   
let  $V_{ks}$  be the potential of the NON-interacting  
system that gives  $v(r)$ 

## Kohn-Sham equations

- interacting system

$$E[n] = T_s[n] + E_H[n] + E_{xc}[n] + \int V_{ext}(\mathbf{r})n(\mathbf{r})d\mathbf{r} -\mu \left(\int n(\mathbf{r})d\mathbf{r} - N\right) = \frac{\delta E[n]}{\delta n(\mathbf{r})} = \frac{\delta T_s[n]}{\delta n(\mathbf{r})} + \frac{\delta E_H[n]}{\delta n(\mathbf{r})} + \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})} + V_{ext}(\mathbf{r})$$

- non-interacting system

$$E_{KS}[n] = T_s[n] + \int V_{KS}(\mathbf{r})n(\mathbf{r})d\mathbf{r} -\mu' \left(\int n(\mathbf{r})d\mathbf{r} - N\right)$$
$$\iota' = \frac{\delta E_{KS}[n]}{\delta n(\mathbf{r})} = \frac{\delta T_s[n]}{\delta n(\mathbf{r})} + V_{KS}(\mathbf{r})$$



 $\mu$ 

$$Kohh = -Sham = equations$$

$$\begin{bmatrix} -\frac{h^2}{2m} \nabla^2 + V_{KS}^{(r)} \\ -\frac{h^2}{2m} \nabla^2 + V_{KS}^{(r)} \end{bmatrix} q_i(r) = \varepsilon_i q_i(r)$$

$$q_i(r_i) = \cdots q_i(r_p)$$

$$\frac{q_i(r_i) - \cdots - q_p(r_p)}{q_p(r_i) - \cdots - q_p(r_p)}$$

$$n(r) = \sum |q_i(r)|^2$$

$$S \begin{bmatrix} T_b [n] + \int V_{KS}^{(r)} n(r) d^2r - \mu(\int u(r) d^3r - N) \end{bmatrix} = 0$$

$$\frac{d T_s}{d u(r)} + V_{KS}^{(r)} - \mu = 0$$

$$V_{KS}^{(r)} = V_0(r) + \varepsilon^2 \int \frac{n(r)}{|r-r|} d^3r^2 + \frac{\int \varepsilon_{KS}^{rm}}{\int n(r)}$$

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Self-consistent equations [Kohn-Sham, 1965]

$$V_{KS}(\mathbf{r}, \mathbf{R}) = V_{ext}(\mathbf{r}, \mathbf{R}) + e^2 \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})}$$

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_{KS}(\mathbf{r},\mathbf{R})\right]\phi_i(\mathbf{r}) = \varepsilon_i\phi_i(\mathbf{r})$$

$$n(\mathbf{r}) = 2\sum_{i} |\phi_i(\mathbf{r})|^2$$



The density is exact if  $V_{KS}(\mathbf{r})$  is, however  $\{\phi_i(\mathbf{r})\}$ 's &  $\{\varepsilon_i\}$ 's are auxiliary functions w/o clear physical meaning







Self-consistent equations [Kohn-Sham, 1965]

$$V_{KS}(\mathbf{r}, \mathbf{R}) = V_{ext}(\mathbf{r}, \mathbf{R}) + e^2 \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})}$$

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_{KS}(\mathbf{r},\mathbf{R})\right]\phi_i(\mathbf{r}) = \varepsilon_i\phi_i(\mathbf{r})$$

$$n(\mathbf{r}) = 2\sum_{i} |\phi_i(\mathbf{r})|^2$$



It is as simple as a Mean-field approach but it is exact !

 $E_{xc}[n]$  is not known exactly  $\rightarrow$  approximations



### Simple approximations to Exc are possible

$$E[n] = T_s[n] + E_H[n] + E_{xc}[n] + \int V_{ext}(\mathbf{r})n(\mathbf{r})d\mathbf{r}$$



FIG. 4. Relative magnitudes of contributions to total valence energy of Mn atom (in eV).



Local Density Approximation

The simplest approximation is LDA that exploits nearsightedness of the electronic matter

W. Kohn, PRL 76,3168 (1996)

$$E_{xc}^{LDA}[n(\mathbf{r})] = \int \varepsilon_{xc}^{hom}(n(\mathbf{r}))n(\mathbf{r})d\mathbf{r}$$

Analogous to the Thomas-Fermi approximation for the Kinetic Energy term but applied to the much smaller Exchange-Correlation term



Local Density Approximation

The simplest approximation is LDA that exploits nearsightedness of the electronic matter

W. Kohn, PRL 76,3168 (1996)



$$\begin{aligned} \text{Total Energy expression in DFT} \\ E(R) &= \min_{\rho} \left[ T_s[\rho] + \frac{e^2}{2} \int \frac{\rho(r)\rho(r')}{|r - r'|} dr dr' + E_{xc}[\rho] + \int V_0(r)\rho(r)dr \right] \\ &+ W_{II}(R) \\ \rho(r) &= 2 \sum_{k,i} |\phi_{k,i}(r)|^2 \longrightarrow T_s[\rho] = 2 \sum_{k,i} \langle \phi_{k,i}| - \frac{\hbar^2}{2m} \nabla^2 |\phi_{k,i}\rangle \\ E_{xc}^{LDA}[\rho] &= \int \rho(r) \varepsilon_{xc}^{hom}(\rho(r)) dr \\ &\implies V_{xc}^{LDA}(r) = \left. \frac{d(\rho \varepsilon_{xc}^{hom}(\rho))}{d\rho} \right|_{\rho=n(r)} \end{aligned}$$

ha per seguir virtute e conoscio

## **Exchange-Correlation functionals**



FIG. 3. The alphabet soup of approximate functionals available in a code near you. Figure used with permission from Peter Elliott.

Kieron Burke, "Perspective on density functional theory" JCP 136 (2012) 150901



## Jacob's ladder of Densitv Functional Theory

Chemical Accuracy



### Hartree World

**FIGURE 1.** Jacob's ladder of density functional approximations. Any resemblance to the Tower of Babel is purely coincidental. Also shown are angels in the spherical approximation, ascending and descending. Users are free to choose the rungs appropriate to their accuracy requirements and computational resources. However, at present their safety can be guaranteed only on the two lowest rungs.



### How people in science see each other



### THE END