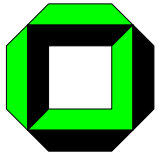

Introduction to Density Functional Theory

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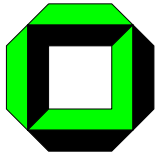
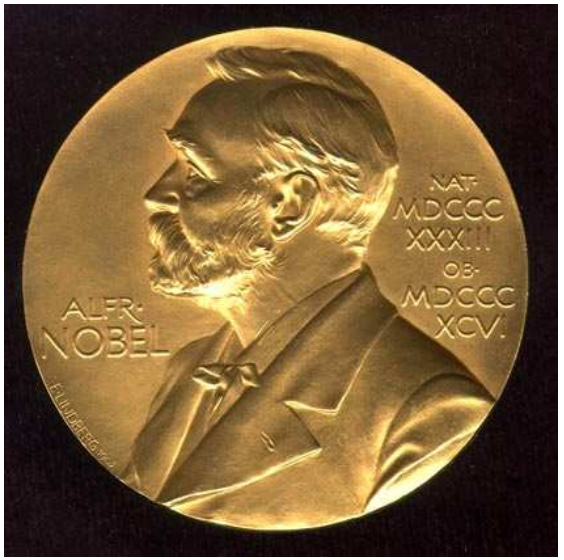
0.- Motivation I.



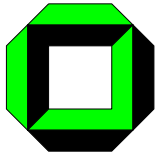
Walter Kohn was awarded with the Nobel Prize in Chemistry in 1998 for his development of the density functional theory.

Walter Kohn receiving his Nobel Prize from His Majesty the King at the Stockholm Concert Hall.



The Nobel Prize medal.

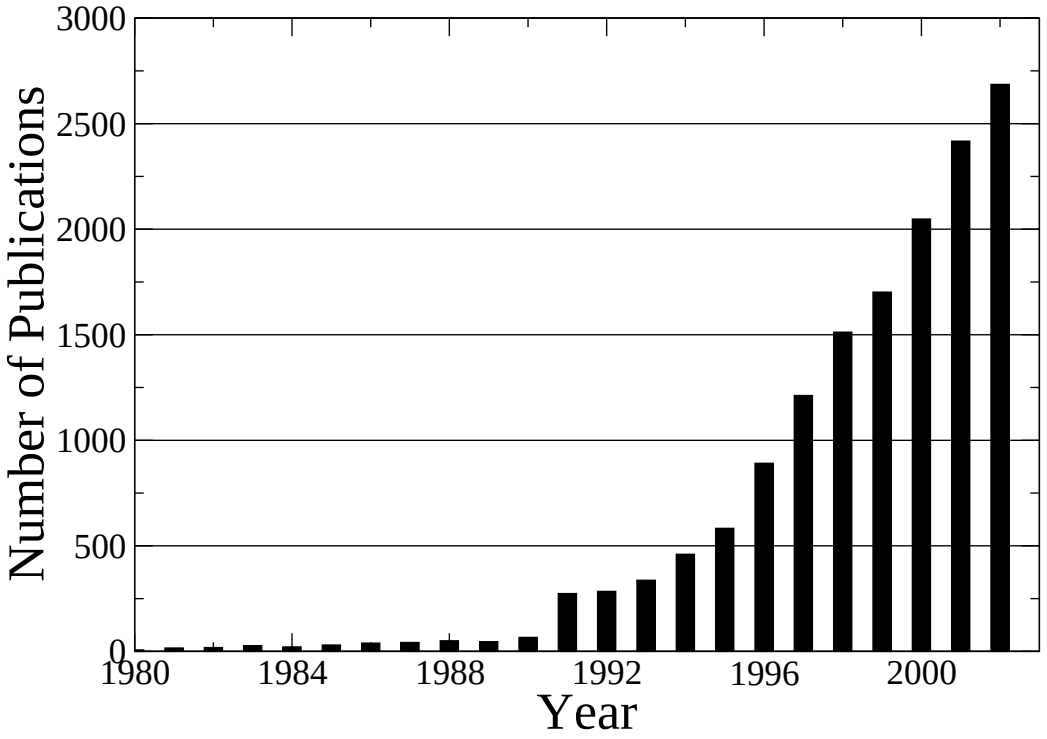
0.- Motivation II.



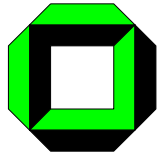
The Density Functional Theory was introduced in two seminal papers in the 60's:

1. Hohenberg-Kohn (1964): $\sim$ 4000 citations
2. Kohn-Sham (1965): $\sim$ 9000 citations

The following figure shows the number of publications where the phrase "density functional theory" appears in the title or abstract (taken from the ISI Web of Science).



0.- Motivation III.



- **The density functional theory** (DFT) is presently the most successfull (and also the most promising) approach to compute **the electronic structure of matter**.

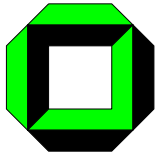
- Its **applicability** ranges from **atoms, molecules and solids** to **nuclei and quantum and classical fluids**.

- In its original formulation, the density functional theory provides **the ground state properties of a system**, and the **electron density** plays a key role.

- **An example: chemistry**. DFT predicts a great variety of molecular properties: molecular structures, vibrational frequencies, atomization energies, ionization energies, electric and magnetic properties, reaction paths, etc.

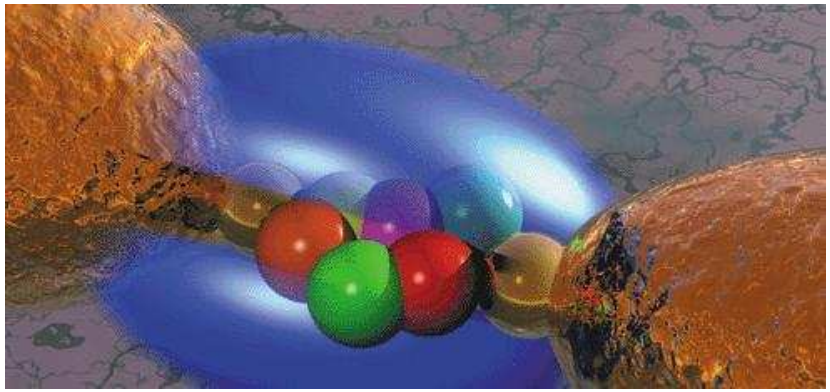
- **The original density functional theoy has been generalized** to deal with many different situations: spin polarized systems, multicomponent systems such as nuclei and electron hole droplets, free energy at finite temperatures, superconductors with electronic pairing mechanisms, relativistic electrons, time-dependent phenomena and excited states, bosons, molecular dynamics, etc.

0.- Motivation IV: Molecular Electronics.



The possibility of manipulating single molecules has created a new field:

MOLECULAR ELECTRONICS



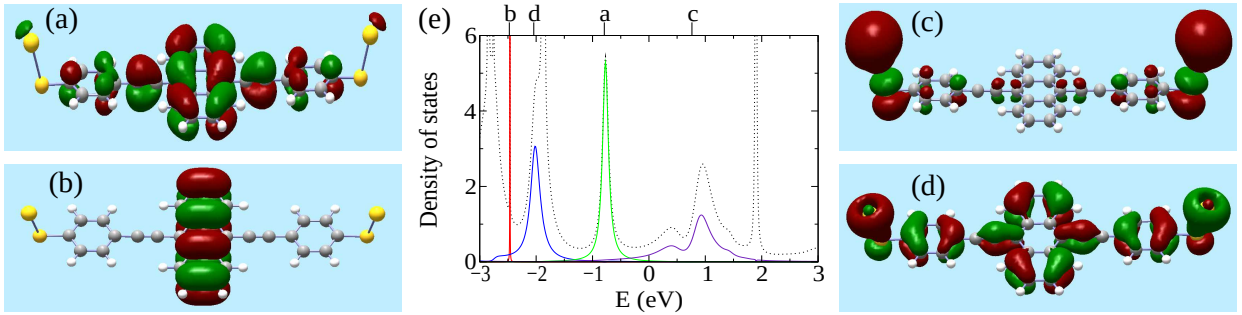
Goal: understanding of the transport at the molecular scale.

Method: *ab initio* quantum chemistry (DFT) and Green function techniques.

- **First step:** Understanding of the relation between conduction channels and molecular orbitals.

$$G = \frac{2e^2}{h} \sum_i T_i$$

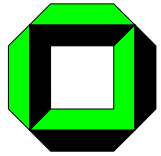
Landauer formula



Heurich, Cuevas, Wenzel and Schön, PRL (2002)

REVIEW: Cuevas, Heurich, Pauly, Wenzel and Schön, Nanotechnology **14**, 29 (2003).

0.- Literature.



The goal of this lecture is to give an elementary introduction to density functional theory. For those who want to get deeper into the subtleties and performance of this theory, the following entry points in the literature are strongly adviced:

Original papers

- *Inhomogeneous Electron Gas*, P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).
- *Self Consistent Equations Including Exchange and Correlation Effects*, W. Kohn and L.J. Sham, Phys. Rev. **140**, A1133 (1965).

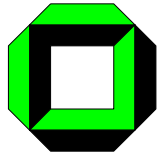
Review Articles

- *Nobel Lecture: Electronic structure of matter–wave functions and density functionals*, W. Kohn, Rev. Mod. Phys. **71**, 1253 (1998).
- *The density functional formalism, its applications and prospects*, R.O. Jones and O. Gunnarsson, Rev. Mod. Phys. **61**, 689 (1989).

Books

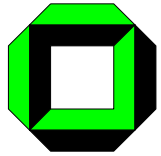
- *Density-Functional Theory of Atoms and Molecules*, R.G Parr and W. Yang, Oxford University Press, New York (1989).
- *A Chemist's Guide to Density Functional Theory*, W. Koch and M.C. Holthausen, WILEY-VCH (2001).

Outline of the lecture.



- **0.- Motivation and literature.**
- **1.- Elementary quantum mechanics:**
  - 1.1 The Schrödinger equation.
  - 1.2 The variational principle.
  - 1.3 The Hartree-Fock approximation.
- **2.- Early density functional theories:**
  - 2.1 The electron density.
  - 2.2 The Thomas-Fermi model.
- **3.- The Hohenberg-Kohn theorems:**
  - 3.1 The first Hohenberg-Kohn theorem.
  - 3.2 The second Hohenberg-Kohn theorem.
- **4.- The Kohn-Sham approach:**
  - 4.1 The Kohn-Sham equations.
- **5.- The exchange-correlation functionals:**
  - 5.1 LDA approximation.
  - 5.2 The generalized gradient approximation.
- **6.- The basic machinary of DFT:**
  - 6.1 The LCAO Ansatz in the KS equations.
  - 6.2 Basis sets.
- **7.- DFT applications:**
  - 7.1 Applications in quantum chemistry.
  - 7.2 Applications in solid state physics.
  - 7.3 DFT in Molecular Electronics.

1.1 The Schrödinger equation.



The ultimate goal of most appproaches in solid state physics and quantum chemistry is the solution of the time-independent, non-relativistic Schrödinger equation

$$\hat{H}\Psi_i(\vec{x}_1, \vec{x}_2, ..., \vec{x}_N, \vec{R}_1, \vec{R}_2, ..., \vec{R}_M) = E_i\Psi_i(\vec{x}_1, \vec{x}_2, ..., \vec{x}_N, \vec{R}_1, \vec{R}_2, ..., \vec{R}_M) \quad (1)$$

$\hat{H}$ is the Hamiltonian for a system consisting of M nuclei and N electrons.

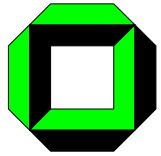
$$\hat{H} = -\frac{1}{2}\sum_{i=1}^{N}\nabla_i^2 - \frac{1}{2}\sum_{A=1}^{M}\frac{1}{M_A}\nabla_A^2 - \sum_{i=1}^{N}\sum_{A=1}^{M}\frac{Z_A}{r_{iA}} + \sum_{i=1}^{N}\sum_{j>i}^{N}\frac{1}{r_{ij}} + \sum_{A=1}^{M}\sum_{B>A}^{M}\frac{Z_A Z_B}{R_{AB}} \quad (2)$$

Here, A and B run over the M nuclei while i and j denote the N electrons in the system.

The first two terms describe the kinetic energy of the electrons and nuclei. The other three terms represent the attractive electrostatic interaction between the nuclei and the electrons and repulsive potential due to the electron-electron and nucleus-nucleus interactions.

Note: throughout this talk atomic units are used.

1.1 The Schrödinger equation.



Born-Oppenheimer approximation: due to their masses the nuclei move much slower than the electrons $\Longrightarrow$ we can consider the electrons as moving in the field of fixed nuclei $\Longrightarrow$ the nuclear kinetic energy is zero and their potential energy is merely a constant. Thus, the electronic Hamiltonian reduces to

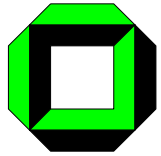
$$\hat{H}_{elec} = -\frac{1}{2}\sum_{i=1}^{N}\nabla_i^2 - \sum_{i=1}^{N}\sum_{A=1}^{M}\frac{Z_A}{r_{iA}} + \sum_{i=1}^{N}\sum_{j>i}^{N}\frac{1}{r_{ij}} = \hat{T} + \hat{V}_{Ne} + \hat{V}_{ee} \tag{3}$$

The solution of the Schrödinger equation with $\hat{H}_{elec}$ is the electronic wave function Ψ_{elec} and the electronic energy E_{elec}. The total energy E_{tot} is then the sum of E_{elec} and the constant nuclear repulsion term E_{nuc}.

$$\hat{H}_{elec}\Psi_{elec} = E_{elec}\Psi_{elec} \tag{4}$$

$$E_{tot} = E_{elec} + E_{nuc} \qquad \text{where} \quad E_{nuc} = \sum_{A=1}^{M}\sum_{B>A}^{M}\frac{Z_A Z_B}{R_{AB}} \tag{5}$$

1.2 The variational principle for the ground state.



When a system is in the state Ψ, the expectation value of the energy is given by

$$E[\Psi] = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} \text{ where } \langle \Psi | \hat{H} | \Psi \rangle = \int \Psi^* \hat{H} \Psi d\vec{x} \tag{6}$$

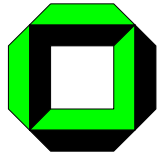
The variational principle states that **the energy computed from a guessed Ψ is an upper bound to the true ground-state energy** E_0. Full minimization of the functional $E[\Psi]$ with respect to all allowed N-electrons wave functions will give the true ground state Ψ_0 and energy $E[\Psi_0] = E_0$; that is

$$E_0 = \min_{\Psi \to N} E[\Psi] = \min_{\Psi \to N} \langle \Psi | \hat{T} + \hat{V}_{Ne} + \hat{V}_{ee} | \Psi \rangle \tag{7}$$

For a system of N electrons and given nuclear potential V_{ext}, the variational principle defines a procedure to determine the ground-state wave function Ψ_0, the ground-state energy $E_0[N, V_{ext}]$, and other properties of interest. In other words, **the ground state energy is a functional of the number of electrons N and the nuclear potential V_{ext}**:

$$E_0 = E[N, V_{ext}] \tag{8}$$

1.3 The Hartree-Fock approximation.



Suppose that Ψ_0 (the ground state wave function) is approximated as an antisymmetrized product of N orthonormal spin orbitals $\psi_i(\vec{x})$, each a product of a spatial orbital $\phi_k(\vec{r})$ and a spin function $\sigma(s) = \alpha(s)$ or $\beta(s)$, the **Slater determinant**

$$\Psi_0 \approx \Psi_{HF} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\vec{x}_1) & \psi_2(\vec{x}_1) & \dots & \psi_N(\vec{x}_1) \\ \psi_1(\vec{x}_2) & \psi_2(\vec{x}_2) & \dots & \psi_N(\vec{x}_2) \\ \vdots & \vdots & & \vdots \\ \psi_1(\vec{x}_N) & \psi_2(\vec{x}_N) & \dots & \psi_N(\vec{x}_N) \end{vmatrix} \tag{9}$$

The Hartree-Fock approximation is the method whereby the orthogonal orbitals ψ_i are found that minimize the energy for this determinantal form of Ψ_0:

$$E_{HF} = \min_{(\Psi_{HF} \to N)} E\left[\Psi_{HF}\right] \tag{10}$$

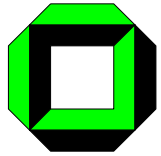
The expectation value of the Hamiltonian operator with Ψ_{HF} is given by

$$E_{HF} = \langle \Psi_{HF} | \hat{H} | \Psi_{HF} \rangle = \sum_{i=1}^{N} H_i + \frac{1}{2} \sum_{i,j=1}^{N} (J_{ij} - K_{ij}) \tag{11}$$

$$H_i \equiv \int \psi_i^*(\vec{x}) \left[-\frac{1}{2}\nabla^2 - V_{ext}(\vec{x}) \right] \psi_i(\vec{x}) \, d\vec{x} \tag{12}$$

defines the contribution due to the kinetic energy and the electron-nucleus attraction and

1.3 The Hartree-Fock approximation.



$$J_{ij} = \int\int \psi_i(\vec{x}_1)\psi_i^*(\vec{x}_1)\,\frac{1}{r_{12}}\,\psi_j^*(\vec{x}_2)\psi_j(\vec{x}_2)d\vec{x}_1 d\vec{x}_2 \tag{13}$$

$$K_{ij} = \int\int \psi_i^*(\vec{x}_1)\psi_j(\vec{x}_1)\,\frac{1}{r_{12}}\,\psi_i(\vec{x}_2)\psi_j^*(\vec{x}_2)d\vec{x}_1 d\vec{x}_2 \tag{14}$$

The integrals are all real, and $J_{ij} \geq K_{ij} \geq 0$. The J_{ij} are called **Coulomb integrals**, the K_{ij} are called **exchange integrals**. We have the property $J_{ii} = K_{ii}$.

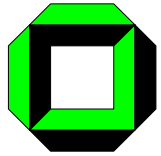
The variational freedom in the expression of the energy [Eq. (11)] is in the choice of the orbitals. The minimization of the energy functional with the normalization conditions $\int \psi_i^*(\vec{x})\psi_j(\vec{x})d\vec{x} = \delta_{ij}$ leads to **the Hartree-Fock differential equations:**

$$\hat{f}\;\psi_i = \epsilon_i\;\psi_i\;, i = 1, 2, ..., N \tag{15}$$

These N equations have the appearance of eigenvalue equations, where the Lagrangian multipliers ϵ_i are the eigenvalues of the operator $\hat{f}$. The Fock operator $\hat{f}$ is an effective one-electron operator defined as

$$\hat{f} = -\frac{1}{2}\nabla_i^2 - \sum_A^M \frac{Z_A}{r_{iA}} + V_{HF}(i) \tag{16}$$

1.3 The Hartree-Fock approximation.



The first two terms are the kinetic energy and the potential energy due to the electron-nucleus attraction. $V_{HF}(i)$ is the *Hartree-Fock potential*, the average repulsive potential experience by the i'th electron due to the remaining N-1 electrons, and it is given by

$$V_{HF}(\vec{x}_1) = \sum_{j}^{N} \left(\hat{J}_j(\vec{x}_1) - \hat{K}_j(\vec{x}_1) \right) \tag{17}$$

$$\hat{J}_j(\vec{x}_1) = \int |\psi_j(\vec{x}_2)|^2 \frac{1}{r_{12}} \, d\vec{x}_2 \tag{18}$$

The Coulomb operator $\hat{J}$ represents the potential that an electron at position $\vec{x}_1$ experiences due to the average charge distribution of another electron in spin orbital ψ_j.

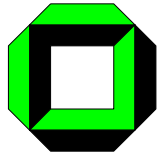
The second term in Eq. (17) is the exchange contribution to the HF potential. It has no classical analog and it is defined through its effect when operating on a spin orbital:

$$\hat{K}_j(\vec{x}_1) \; \psi_i(\vec{x}_1) = \int \psi_j^*(\vec{x}_2) \frac{1}{r_{12}} \psi_i(\vec{x}_2) \; d\vec{x}_2 \; \psi_j(\vec{x}_1) \tag{19}$$

- The HF potential is *non-local* and it depends on the spin orbitals. Thus, the HF equations must be solved *self-consistently*.

- The Koopman's theorem (1934) provides a physical interpretation of the orbital energies: it states that *the orbital energy ϵ_i is an approximation of minus the ionization energy associated with the removal of an electron from the orbital ψ_i*, i.e. $\epsilon_i \approx E_N - E_{N-1}^i = -IE(i)$.

2.1 The electron density.



The electron density is the central quantity in DFT. It is defined as the integral over the spin coordinates of all electrons and over all but one of the spatial variables ($\vec{x} \equiv \vec{r}, s$)

$$\rho(\vec{r}) = N \int ... \int |\Psi(\vec{x}_1, \vec{x}_2, ..., \vec{x}_N)|^2 ds_1 d\vec{x}_2 ... d\vec{x}_N. \tag{20}$$

$\rho(\vec{r})$ determines the probability of finding any of the N electrons within volumen element $d\vec{r}$.

Some properties of the electron density:

- $\rho(\vec{r})$ is a non-negative function of only the three spatial variables which vanishes at infinity and integrates to the total number of electrons:

$$\rho(\vec{r} \to \infty) = 0 \qquad \int \rho(\vec{r}) d\vec{r} = N \tag{21}$$

- $\rho(\vec{r})$ is an observable and can be measured experimentally, e.g. by X-ray diffraction.

- At any position of an atom, the gradient of $\rho(\vec{r})$ has a discontinuity and a *cusp* results:

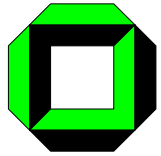
$$\lim_{r_i A \to 0} \left[\nabla_r + 2Z_A\right] \bar{\rho}(\vec{r}) = 0 \tag{22}$$

  where Z is the nuclear charge and $\bar{\rho}(\vec{r})$ is the spherical average of $\rho(\vec{r})$.

- The asymptotic exponential decay for large distances from all nuclei:

$$\rho(\vec{r}) \sim \exp\left[-2\sqrt{2I}|\vec{r}|\right] \qquad I \text{ is the exact ionization energy} \tag{23}$$

2.2 The Thomas-Fermi model.



The conventional approaches use the wave function Ψ as the central quantity, since Ψ contains the full information of a system. However, Ψ is a very complicated quantity that cannot be probed experimentally and that depends on $4N$ variables, N being the number of electrons.

The Thomas-Fermi model: the first density functional theory (1927).

- Based on the uniform electron gas, they proposed the following functional for the kinetic energy:

$$T_{TF}\left[\rho(\vec{r})\right] = \frac{3}{10}(3\pi^2)^{2/3}\int \rho^{5/3}(\vec{r})d\vec{r}. \tag{24}$$

- The energy of an atom is finally obtained using the classical expression for the nuclear-nuclear potential and the electron-electron potential:

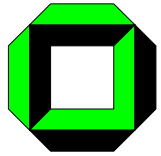
$$E_{TF}\left[\rho(\vec{r})\right] = \frac{3}{10}(3\pi^2)^{2/3}\int \rho^{5/3}(\vec{r})d\vec{r} - Z\int \frac{\rho(\vec{r})}{r}d\vec{r} + \frac{1}{2}\int\int \frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{r_{12}}d\vec{r}_1 d\vec{r}_2. \tag{25}$$

The energy is given completely in terms of the electron density!!!

- In order to determine the correct density to be included in Eq. (25), they employed a *variational principle*. They *assumed* that the ground state of the system is connected to the $\rho(\vec{r})$ for which the energy is minimized under the constraint of $\int \rho(\vec{r})d\vec{r} = N$.

Does this variational principle make sense?

3.1 The first Hohenberg-Kohn theorem.



The first Hohenberg-Kohn theorem demonstrates that the electron density uniquely determines the Hamiltonian operator and thus all the properties of the system.

This first theorem states that **the external potential $V_{ext}(\vec{r})$ is (to within a constant) a unique functional of $\rho(\vec{r})$; since, in turn $V_{ext}(\vec{r})$ fixes $\hat{H}$ we see that the full many particle ground state is a unique functional of $\rho(\vec{r})$.**

Proof: let us assume that there were two external potential $V_{ext}(\vec{r})$ and $V'_{ext}(\vec{r})$ differing by more than a constant, each giving the same $\rho(\vec{r})$ for its ground state, we would have two Hamiltonians $\hat{H}$ and $\hat{H}'$ whose ground-state densities were the same although the normalized wave functions Ψ and Ψ' would be different. Taking Ψ' as a trial wave function for the $\hat{H}$ problem

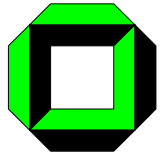
$$E_0 < \langle \Psi' | \hat{H} | \Psi' \rangle = \langle \Psi' | \hat{H}' | \Psi' \rangle + \langle \Psi' | \hat{H} - \hat{H}' | \Psi' \rangle = E'_0 + \int \rho(\vec{r}) \left[V_{ext}(\vec{r}) - V'_{ext}(\vec{r}) \right] d\vec{r}, \tag{26}$$

where E_0 and E'_0 are the ground-state energies for $\hat{H}$ and $\hat{H}'$, respectively. Similarly, taking Ψ as a trial function for the $\hat{H}'$ problem,

$$E'_0 < \langle \Psi | \hat{H}' | \Psi \rangle = \langle \Psi | \hat{H} | \Psi \rangle + \langle \Psi | \hat{H}' - \hat{H} | \Psi \rangle = E_0 + \int \rho(\vec{r}) \left[V_{ext}(\vec{r}) - V'_{ext}(\vec{r}) \right] d\vec{r}, \tag{27}$$

Adding Eq. (26) and Eq. (27), we would obtain $E_0 + E'_0 < E'_0 + E_0$, a contradiction, and so there cannot be two different $V_{ext}(\vec{r})$ that give the same $\rho(\vec{r})$ for their ground state.

3.1 The first Hohenberg-Kohn theorem.



Thus, $\rho(\vec{r})$ determines N and $V_{ext}(\vec{r})$ and hence all the properties of the ground state, for example the kinetic energy $T[\rho]$, the potential energy $V[\rho]$, and the total energy $E[\rho]$. Now, we can write the total energy as

$$E[\rho] = E_{Ne}[\rho] + T[\rho] + E_{ee}[\rho] = \int \rho(\vec{r}) V_{Ne}(\vec{r}) d\vec{r} + F_{HK}[\rho], \tag{28}$$

$$F_{HK}[\rho] = T[\rho] + E_{ee}. \tag{29}$$

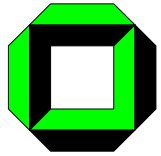
This functional $F_{HK}[\rho]$ is the holy grail of density functional theory. If it were known we would have solved the Schrödinger equation exactly! And, since it is an universal functional completely independent of the system at hand, it applies equally well to the hydrogen atom as to gigantic molecules such as, say, DNA! $F_{HK}[\rho]$ contains the functional for the kinetic energy $T[\rho]$ and that for the electron-electron interaction, $E_{ee}[\rho]$. The explicit form of both these functional lies completely in the dark. However, from the latter we can extract at least the classical part $J[\rho]$,

$$E_{ee}[\rho] = \frac{1}{2} \int \int \frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{r_{12}} d\vec{r}_1 d\vec{r}_2 + E_{ncl} = J[\rho] + E_{ncl}[\rho]. \tag{30}$$

E_{ncl} is the *non-classical* contribution to the electron-electron interaction: self-interaction correction, exchange and Coulomb correlation.

The explicit form of the functionals $T[\rho]$ and $E_{ncl}[\rho]$ is the major challange of DFT.

3.2 The second Hohenberg-Kohn theorem.



How can we be sure that a certain density is the ground-state density that we are looking for?

The second H-K theorem states that $F_{HK}[\rho]$, **the functional that delivers the ground state energy of the system, delivers the lowest energy if and only if the input density is the true ground state density.** This is nothing but the variational principle:

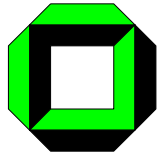
$$E_0 \leq E[\tilde{\rho}] = T[\tilde{\rho}] + E_{Ne}[\tilde{\rho}] + E_{ee}[\tilde{\rho}] \tag{31}$$

In other words this means that for any trial density $\tilde{\rho}(\vec{r})$, which satisfies the necessary boundary conditions such as $\tilde{\rho}(\vec{r}) \geq 0$, $\int \tilde{\rho}(\vec{r})d\vec{r} = N$, and which is associated with some external potential $\tilde{V}_{ext}$, the energy obtained from the functional of Eq. (28) represents an upper bound to the true ground state energy E_0. E_0 results if and only if the exact ground state density is inserted in Eq. (24).

Proof: the proof of Eq. (31) makes use of the variational principle established for wave functions. We recall that any trial density $\tilde{\rho}$ defines its own Hamiltonian $\tilde{\hat{H}}$ and hence its own wave function $\tilde{\Psi}$. This wave function can now be taken as the trial wave function for the Hamiltonian generated from the true external potential V_{ext}. Thus,

$$\langle\tilde{\Psi}|\hat{H}|\tilde{\Psi}\rangle = T[\tilde{\rho}] + E_{ee}[\tilde{\rho}] + \int \tilde{\rho}(\vec{r})V_{ext}d\vec{r} = E[\tilde{\rho}] \geq E_0[\rho] = \langle\tilde{\Psi}_0|\hat{H}|\tilde{\Psi}_0\rangle. \tag{32}$$

What have we learned so far?



Let us summarize what we have shown so far:

- All the properties of a system defined by an external potential V_{ext} are determined by the ground state density. In particular, the ground state energy associated with a density ρ is avaible through the functional

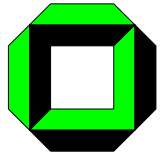
$$\int \rho(\vec{r}) V_{ext} d\vec{r} + F_{HK}[\rho]. \tag{33}$$

- This functional attains its minimum value with respect to all allowed densities if and only if the input density is the true ground state density, i.e. for $\tilde{\rho}(\vec{r}) \equiv \rho(\vec{r})$.

- The applicability of the varational principle is limited to the ground state. Hence, we cannot easily transfer this strategy to the problem of excited states.

- **The explicit form of the functional $F_{HK}[\rho]$ is the major challange of DFT.**

4.1 The Kohn-Sham equations.



We have seen that the ground state energy of a system can be written as

$$E_0 = \min_{\rho \to N} \left(F[\rho] + \int \rho(\vec{r}) V_{Ne} d\vec{r} \right) \tag{34}$$

where the universal functional $F[\rho]$ contains the contributions of the kinetic energy, the classical Coulomb interaction and the non-classical portion:

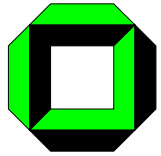
$$F[\rho] = T[\rho] + J[\rho] + E_{ncl}[\rho] \tag{35}$$

Of these, only $J[\rho]$ is known. The main problem is to find the expressions for $T[\rho]$ and $E_{ncl}[\rho]$.

The Thomas-Fermi model of section 2.2 provides an example of density functional theory. However, its performance is really bad due to the poor approximation of the kinetic energy. To solve this problem Kohn and Sham proposed in 1965 the approach described below.

They suggested to calculate the exact kinetic energy of a non-interacting reference system with the same density as the real, interacting one

$$T_S = -\frac{1}{2} \sum_i^N \langle \psi_i | \nabla^2 | \psi_i \rangle \qquad \rho_S(\vec{r}) = \sum_i^N \sum_s |\psi_i(\vec{r}, s)|^2 = \rho(\vec{r}) \tag{36}$$



where the ψ_i are the orbitals of the non-interacting system. Of course, T_S is not equal to the true kinetic energy of the system. Kohn and Sham accounted for that by introducing the following separation of the functional $F[\rho]$

$$F[\rho] = T_S[\rho] + J[\rho] + E_{XC}[\rho], \tag{37}$$

where E_{XC}, the so-called *exchange-correlation energy* is defined through Eq. (37) as

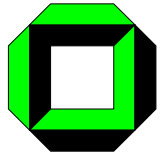
$$E_{XC}[\rho] \equiv (T[\rho] - T_S[\rho]) + (E_{ee}[\rho] - J[\rho])\,. \tag{38}$$

The exchange and correlation energy E_{XC} is the functional that contains everything that is unknown.

Now the question is: how can we uniquely determine the orbitals in our non-interacting reference system? In other words, how can we define a potential V_S such that it provides us with a Slater determinant which is characterized by the same density as our real system? To solve this problem, we write down the expression for the energy of the interacting system in terms of the separation described in Eq. (37)

$$E[\rho] = T_S[\rho] + J[\rho] + E_{XC}[\rho] + E_{Ne}[\rho] \tag{39}$$

4.1 The Kohn-Sham equations.



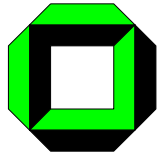
$$E[\rho] = T_S[\rho] + \frac{1}{2}\int\int \frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{r_{12}} d\vec{r}_1 d\vec{r}_2 + E_{XC}[\rho] + \int V_{Ne}\rho(\vec{r}) d\vec{r} =$$
$$-\frac{1}{2}\sum_i^N \langle\psi_i|\nabla^2|\psi_i\rangle + \frac{1}{2}\sum_i^N\sum_j^N \int\int |\psi_i(\vec{r}_1)|^2 \frac{1}{r_12}|\psi_j(\vec{r}_2)|^2 d\vec{r}_1 d\vec{r}_2 + E_{XC}[\rho] -$$
$$-\sum_i^N \int \sum_A^M \frac{Z_A}{r_{1A}}|\psi_i(\vec{r}_1)|^2 d\vec{r}_1. \tag{40}$$

The only term for which no explicit form can be given is E_{XC}. We now apply the variational principle and ask: what condition must the orbitals $\{\psi_i\}$ fulfill in order to minimize this energy expression under the usual constraint $\langle\psi_i|\psi_j\rangle = \delta_{ij}$? The resulting equations are the **Kohn-Sham equations**:

$$\left(-\frac{1}{2}\nabla^2 + \left[\int \frac{\rho(\vec{r}_2)}{r_{12}} + V_{XC}(\vec{r}_1) - \sum_A^M \frac{Z_A}{r_{1A}}\right]\right)\psi_i = \left(-\frac{1}{2}\nabla^2 + V_S(\vec{r}_1)\right)\psi_i = \epsilon_i\psi_i \tag{41}$$

$$V_S(\vec{r}_1) = \int \frac{\rho(\vec{r}_2)}{r_{12}} d\vec{r}_2 + V_{XC}(\vec{r}_1) - \sum_A^M \frac{Z_A}{r_{1A}} \tag{42}$$

4.1 The Kohn-Sham equations.



Some comments:

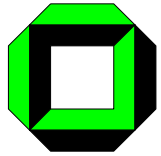
- Once we know the various contributions in Eqs. (41-42) we have a grip on the potential V_S which we need to insert into the one-particle equations, which in turn determine the orbitals and hence the ground state density and the ground state energy employing Eq. (40). Notice that V_S depends on the density, and therefore the Kohn-Sham equations have to be solved iteratively.

- The exchange-correlation potential, V_{XC} is defined as the functional derivative of E_{XC} with respect to ρ, i.e. $V_{XC} = \delta E_{XC}/\delta\rho$.

- It is very important to realize that if the exact forms of E_{XC} and V_{XC} were known, the Kohn-Sham strategy would lead to the exact energy!!

- Do the Kohn-Sham orbitals mean anything? Strictly speaking, these orbitals have no physical significance, except the highest occupied orbital, ϵ_{max}, which equals the negative of the exact ionization energy.

5.1 The local density approximation (LDA).



The *local density approximation* (LDA) is the basis of all approximate exchange-correlation functionals. At the center of this model is the idea of an *uniform electron gas*. This is a system in which electrons move on a positive background charge distribution such that the total ensemble is neutral.

The central idea of LDA is the assumption that we can write E_{XC} in the following form

$$E_{XC}^{LDA}[\rho] = \int \rho(\vec{r})\epsilon_{XC}\left(\rho(\vec{r})\right)\ d\vec{r} \tag{43}$$

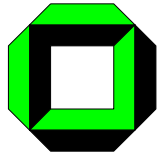
Here, $\epsilon_{XC}(\rho(\vec{r}))$ is the exchange-correlation energy per particle of an uniform electron gas of density $\rho(\vec{r})$. This energy per particle is weighted with the probability $\rho(\vec{r})$ that there is an electron at this position. The quantity $\epsilon_{XC}(\rho(\vec{r}))$ can be further split into exchange and correlation contributions,

$$\epsilon_{XC}(\rho(\vec{r})) = \epsilon_X(\rho(\vec{r})) + \epsilon_C(\rho(\vec{r})). \tag{44}$$

The exchange part, ϵ_X, which represents the exchange energy of an electron in a uniform electron gas of a particular density, was originally derived by Bloch and Dirac in the late 1920's

$$\epsilon_X = -\frac{3}{4}\left(\frac{3\rho(\vec{r})}{\pi}\right)^{1/3} \tag{45}$$

5.1 The local density approximation (LDA).



No such explicit expression is known for the correlation part, ϵ_C. However, highly accurate numerical quantum Monte-Carlo simulations of the homogeneous electron gas are available (Ceperly-Alder, 1980).

Some comments:

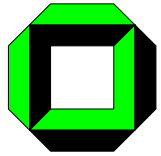
- The accuracy of the LDA for the exchange energy is typically within 10%, while the normally much smaller correlation energy is generally overstimated by up to a factor 2. The two errors typically cancle partially.

- Experience has shown that the LDA gives ionization energies of atoms, dissociation energies of molecules and cohesive energies with a fair accuracy of typically 10-20%. However, the LDA gives bond lengths of molecules and solids typically with an astonishing accuracy of $\sim 2\%$.

- This moderate accuracy that LDA delivers is certainly insufficient for most applications in chemistry.

- LDA can also fail in systems, like heavy fermions, so dominated by electron-electron interaction effects.

5.2 The generalized gradient approximation (GGA).



The first logical step to go beyond LDA is the use of not only the information about the density $\rho(\vec{r})$ at a particular point $\vec{r}$, but to supplement the density with information about the gradient of the charge density, $\nabla\rho(\vec{r})$ in order to account for the non-homogeneity of the true electron density. Thus, we write the exchang-correlation energy in the following form termed **generalized gradient approximation (GGA)**,

$$E_{XC}^{GEA}[\rho_\alpha, \rho_\beta] = \int f(\rho_\alpha, \rho_\beta, \nabla\rho_\alpha, \nabla\rho_\beta)\, d\vec{r} \tag{46}$$

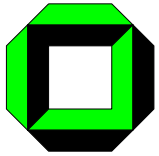
Thanks to much thoughtful work, important progress has been made in deriving successful GGA's. Their construction has made use of sum rules, general scaling properites, etc.

In another approach A. Becke introduced a successful **hybrid functional**:

$$E_{XC}^{hyb} = \alpha E_X^{KS} + (1-\alpha) E_{XC}^{GGA}, \tag{47}$$

where E_X^{KS} is the exchange calculated with the exact KS wave function, E_{XC}^{GGA} is an appropiate GGA, and α is a fitting parameter.

5.2 The generalized gradient approximation (GGA).

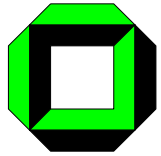


Some comments:

- GGA's and hybrid approximations has reduced the LDA errors of atomization energies of standard set of small molecules by a factor 3-5. This improved accuracy has made DFT a significant component of quantum chemistry.

- All the present functionals are inadequate for situations where the density is not a slowly varying function. Examples are (a) Wigner crystals; (b) Van der Waals energies between nonoverlapping subsystems; (c) electronic tails evanescing into the vacuum near the surfaces of bounded electronic systems. However, this does not preclude that DFT with appropiate approximations can successfully deal with such problems.

6.1 The LCAO Ansatz in the The Kohn-Sham equations.



Recall the central ingredient of the Kohn-Sham approach to density functional theory, i.e. the one-electron KS equations,

$$\left(-\frac{1}{2}\nabla^2 + \left[\sum_j^N \int \frac{|\psi_j(\vec{r}_2)|^2}{r_{12}} d\vec{r}_2 + V_{XC}(\vec{r}_1) - \sum_A^M \frac{Z_A}{r_{1A}} \right] \right) \psi_i = \epsilon_i \, \psi_i. \tag{48}$$

The term in square brackets defines the Kohn-Sham one-electron operator and Eq. (48) can be written more compactly as

$$\hat{f}^{KS} \, \psi_i = \epsilon_i \, \psi_i. \tag{49}$$

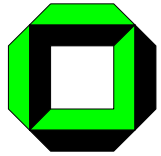
Most of the applications in chemistry of the Kohn-Sham density functional theory make use of the LCAO expansion of the Kohn-Sham orbitals. In this approach we introduce a set of L predefined basis functions $\{\eta_\mu\}$ and linearly expand the K-S orbitals as

$$\psi_i = \sum_{\mu=1}^{L} c_{\mu i} \eta_\mu. \tag{50}$$

We now insert Eq. (44) into Eq. (43) and obtain in very close analogy to the Hartree-Fock case

$$\hat{f}^{KS}(\vec{r}_1) \sum_{\nu=1}^{L} c_{\nu i} \eta_\nu(\vec{r}_1) = \epsilon_i \sum_{\nu=1}^{L} c_{\nu i} \eta_\nu(\vec{r}_1). \tag{51}$$

6.1 The LCAO Ansatz in the The Kohn-Sham equations.



If we now multiply this equation from the left with an arbitrary basis function η_μ and integrate over space we get L equations

$$\sum_{\nu=1}^{L} c_{\nu i} \int \eta_\mu(\vec{r}_1)\hat{f}^{KS}(\vec{r}_1)\eta_\nu(\vec{r}_1)d\vec{r}_1 = \epsilon_i \sum_{\nu=1}^{L} c_{\nu i} \int \eta_\mu(\vec{r}_1)\eta_\nu(\vec{r}_1)d\vec{r}_1 \quad \text{for } 1 \leq i \leq L \tag{52}$$

The integrals on both sides of this equation define a matrix:

$$F^{KS}_{\mu\nu} = \int \eta_\mu(\vec{r}_1)\hat{f}^{KS}(\vec{r}_1)\eta_\nu(\vec{r}_1)d\vec{r}_1 \qquad S_{\mu\nu} = \int \eta_\mu(\vec{r}_1)\eta_\nu(\vec{r}_1)d\vec{r}_1, \tag{53}$$

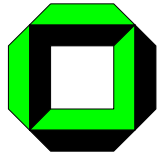
which are the elements of the *Kohn-Sham matrix* and the *overlap matrix*, respectively. Both matrices are $L \times L$ dimensional. Eqs.(52) can be rewritten compactly as a matrix equation

$$\hat{F}^{KS}\hat{C} = \hat{S}\hat{C}\hat{\epsilon}. \tag{54}$$

Hence, through the LCAO expansion we have translated the non-linear optimization problem into a linear one, which can be expressed in the language of standard algebra.

By expanding $\hat{f}^{KS}$ into its components, the individual elements of the KS matrix become

6.1 The LCAO Ansatz in the The Kohn-Sham equations.



$$F_{\mu\nu}^{KS} = \int \eta_\mu(\vec{r}_1) \left(-\frac{1}{2}\nabla^2 - \sum_A^M \frac{Z_A}{r_{1A}} + \int \frac{\rho(\vec{r}_2)}{r_{12}} d\vec{r}_2 + V_{XC}(\vec{r}_1) \right) \eta_\nu(\vec{r}_1) d\vec{r}_1 \qquad (55)$$

The first two terms describe the kinetic energy and the electron-nuclear interaction, and they are usually combined one-electron integrals

$$h_{\mu\nu} = \int \eta_\mu(\vec{r}_1) \left(-\frac{1}{2}\nabla^2 - \sum_A^M \frac{Z_A}{r_{1A}} \right) \eta_\nu(\vec{r}_1) d\vec{r}_1 \qquad (56)$$

For the third term we need the charge density ρ which takes the following form in the LCAO scheme

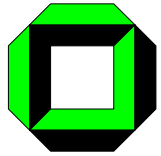
$$\rho(\vec{r}) = \sum_i^L |\psi_i(\vec{r})|^2 = \sum_i^N \sum_\mu^L \sum_{nu}^L c_{\mu i} c_{\nu i} \eta_\mu(\vec{r}) \eta_\nu(\vec{r}). \qquad (57)$$

The expansion coefficients are usually collected in the so-called *density matrix* $\hat{P}$ with elements

$$P_{\mu\nu} = \sum_i^N c_{\mu i} c_{\nu i}. \qquad (58)$$

Thus, the Coulomb contribution in Eq. (55) can be expressed as

6.1 The LCAO Ansatz in the The Kohn-Sham equations.



$$J_{\mu\nu} = \sum_{\lambda}^{L} \sum_{\sigma}^{L} P_{\lambda\sigma} \int \int \eta_{\mu}(\vec{r}_1)\eta_{\nu}(\vec{r}_1)\frac{1}{r_{12}}\eta_{\lambda}(\vec{r}_2)\eta_{\sigma}(\vec{r}_2)d\vec{r}_1 d\vec{r}_2. \tag{59}$$

Up to this point, exactly the same formulae also apply in the Hartree-Fock case. The difference is only in the exchange-correlation part. In the Kohn-Sham scheme this is represented by the integral

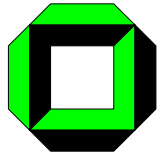
$$V_{\mu\nu}^{XC} = \int \eta_{\mu}(\vec{r}_1)V_{XC}(\vec{r}_1)\eta_{\nu}(\vec{r}_1)d\vec{r}_1, \tag{60}$$

whereas the Hartree-Fock exchange integral is given by

$$K_{\mu\nu} = \sum_{\lambda}^{L} \sum_{\sigma}^{L} P_{\lambda\sigma} \int \int \eta_{\mu}(\vec{x}_1)\eta_{\lambda}(\vec{x}_1)\frac{1}{r_{12}}\eta_{\nu}(\vec{x}_2)\eta_{\sigma}(\vec{x}_2)d\vec{x}_1 d\vec{x}_2. \tag{61}$$

The calculation of the $L^2/2$ one-electron integrals contained in $h_{\mu\nu}$ can be fairly easily computed. The computational *bottle-neck* is the calcalution of the $\sim L^4$ two-electron integrals in the Coulomb term.

6.2 Basis sets.



- **Slater-type-orbitals (STO)**: they seem to be the natural choice for basis functions. They are exponential functions that mimic the exact eigenfunctions of the hydrogen atom. A typical STO is expressed as

$$\eta^{STO} = N r^{n-1} \exp\left[-\beta r\right] Y_{lm}(\Theta, \phi). \tag{62}$$

  Here, n corresponds to the principal quantum number, the orbital exponent is termed β and Y_{lm} are the usual spherical harmonics. Unfortunately, many-center integrals are very difficult to compute with STO basis, and they do not play a major role in quantum chemistry.

- **Gaussian-type-orbitals (GTO)**: they are the usual choice in quantum chemistry. They have the following general form

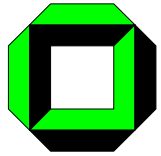
$$\eta^{GTO} = N x^l y^m z^n \exp\left[-\alpha r\right]. \tag{63}$$

  N is a normalization factor which ensures that $\langle \eta_\mu | \eta_\mu \rangle = 1$, α represents the orbital exponent. $L = l + m + n$ is used to clasify the GTO as s-functions ($L = 0$), p-functions ($L = 1$), etc.

- Sometimes one uses the so-called **contracted Gaussian functions (CGF)** basis sets, in which several primitive Gaussian functions are combined in a fixed linear combination:

$$\eta_\tau^{CGF} = \sum_a^A d_{a\tau} \eta_a^{GTO}. \tag{64}$$

7.1 Applications in quantum chemistry.



Molecular structures: DFT gives the bond lengths of a large set of molecules with a precision of 1-2%. The hybrid functionals have improved the LDA results.

Bond lengths for different bonding situations [Å]:

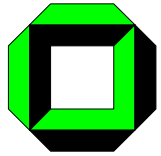
Bond		LDA	BLYP	BP86	Experiment
H-H	R_{H-H}	0.765	0.748	0.752	0.741
H_3C-CH_3	R_{C-C}	1.510	1.542	1.535	1.526
	R_{C-H}	1.101	1.100	1.102	1.088
HC≡CH	R_{C-C}	1.203	1.209	1.210	1.203
	R_{C-H}	1.073	1.068	1.072	1.061

Vibrational frequencies: DFT predicts the vibrational frequencies of a broad range of molecules within 5-10% accuracy.

Vibrational frequencies of a set of 122 molecules: method, rms deviations, proportion outside a 10% error range and listings of problematic cases (taken from Scott and Radom, 1996).

Method	RMS	10%	Problematic cases (deviations larger than 100 cm^{-1})
BP86	41	6	142(H_2), 115(HF), 106(F_2)
B3LYP	34	6	132(HF), 125(F_2), 121(H_2)

7.1 Applications in quantum chemistry.



Atomization energies: the most common way of testing the performance of new functionals is the comparison with the experimental atomization energies of well-studied sets of small molecules. These comparisons have established the following hierarchy of functionals:

$$\text{LDA} < \text{GGA} < \text{hybrid functionals}$$

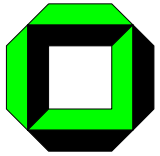
The hybrid functionals are progressively approaching the desired accuracy in the atomization energies, and in many cases they deliver results comparable with highly sophisticated post-HF methods.

Molecule	LDA	BLYP	Molecule	LDA	BLYP
CH	7	0	F_2	47	18
CH_3	31	-2	O_2	57	19
CH_4	44	-3	N_2	32	6
C_2H_2	50	-6	CO	37	1
C_2H_4	86	-6	CO_2	82	11

Deviations [kcal/mol] between computed atomization energies and experiment (taken from Johnson et al., 1993).

Ionization and affinity energies: the hybrid functionals can determined these energies with an average error of around 0.2 eV for a large variety of molecules.

7.2 Applications in solid state physics.

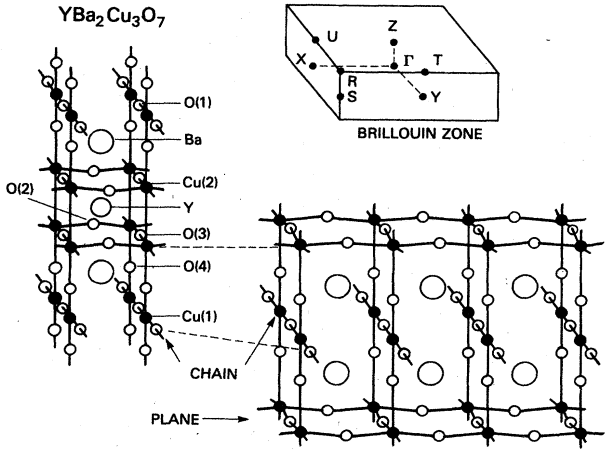


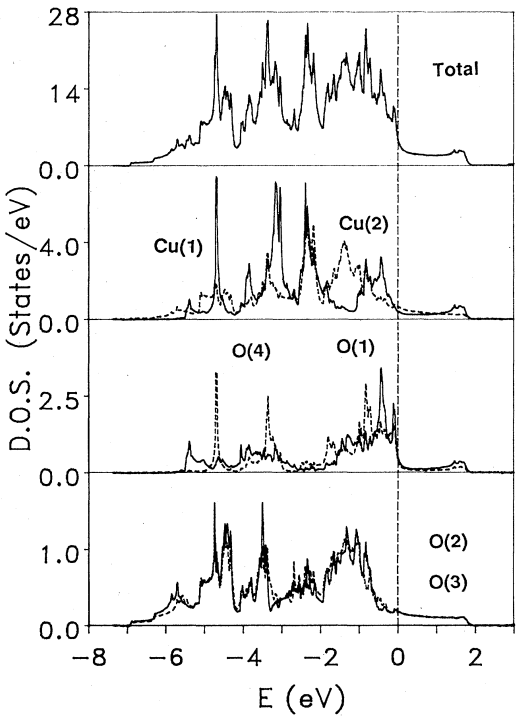
Example 1: DFT describes very accurately alkali metals. Below, the spin susceptibility of alkali metals χ/χ_0, where χ_0 is the Pauli susceptibility of a free electron gas (Vosko et al., 1975):

Metal	DFT result (LDA)	Experiment
Li	2.66	2.57
Na	1.62	1.65
K	1.79	1.70

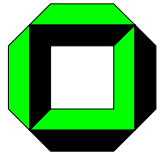
Metal	DFT result (LDA)	Experiment
Rb	1.78	1.72
Cs	2.20	2.24

Example 2: DFT fails to describe strongly correlated system such as heavy fermions or high temperature superconductors.





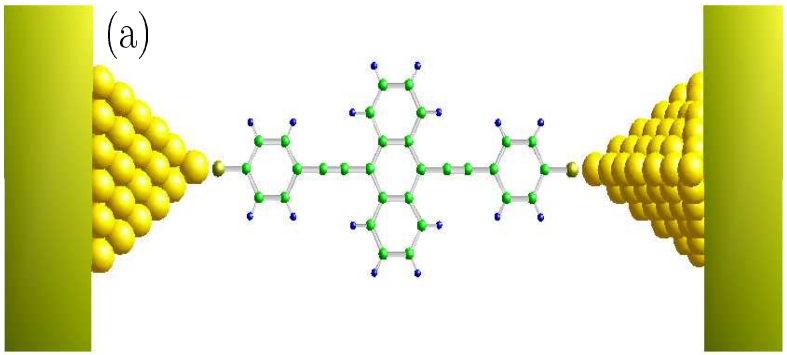
7.3 DFT in Molecular Electronics I.



[Heurich, Cuevas, Wenzel and Schön, PRL **88**, 256803 (2002).]

Three subsystems: central cluster and leads

$$\hat{H} = \hat{H}_L + \hat{H}_R + \hat{H}_C + \hat{V}$$



- **Central cluster:** Density functional calculation (DFT) $\hat{H}_C = \sum_i \epsilon_i \, \hat{d}_i^\dagger \hat{d}_i$

  $\epsilon_i \longrightarrow$ molecular levels (Kohn-Sham orbital levels)

  $\hat{d}_i^\dagger \longrightarrow$ molecular orbitals

  (a) Basis set: LANL2DZ (relativistic core pseudopotentials)

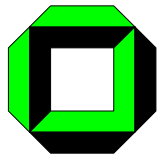
  (b) DFT calculations: B3LYP hybrid functional.

- **Leads:** The reservoirs are modeled as two perfect semi-infinite crystals using a tight-binding parameterization (Papaconstantopoulos' 86).

- **Coupling:** $\hat{V} = \sum_{ij} v_{ij} (\hat{d}_i^\dagger \hat{c}_j + h.c.)$.

  v_{ij}: hopping elements between the lead orbitals and the MOs of the central cluster (Löwdin transformation).

7.3 DFT in Molecular Electronics II.

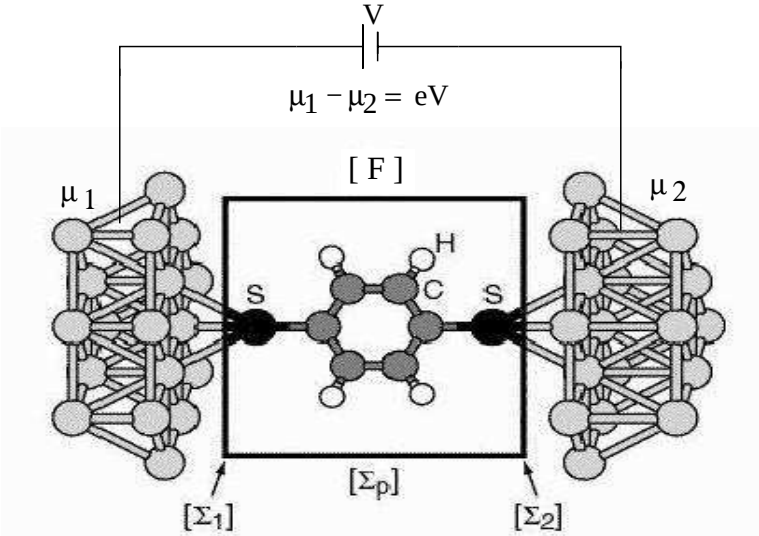


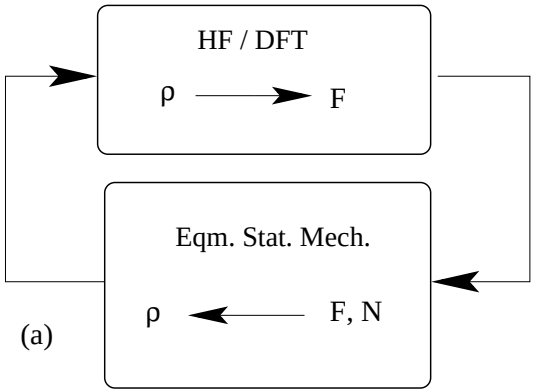
Generalization of DFT to nonequilibrium: implementation in TURBOMOLE

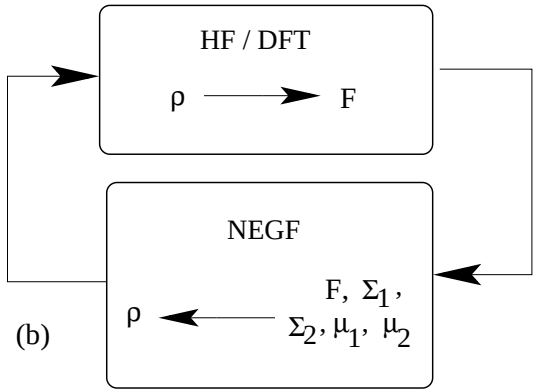
- self-consistent determination of the electrostatic profile
- inclusion of the leads in the self-consitency
- use the relations:

$$\rho = \int d\epsilon [-iG^{<}(\epsilon)/2\pi]$$

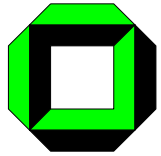
$$-iG^{<} = G(f_1\Gamma_1 + f_2\Gamma_2)G^{\dagger}$$







7.3 DFT in Molecular Electronics III.



Electrical current:

$$I = \frac{2e}{h} \int_{-\infty}^{\infty} d\epsilon \; \mathrm{Tr}\left\{\widehat{t}\widehat{t}^{\dagger}\right\} \left[f(\epsilon - eV/2) - f(\epsilon + eV/2)\right]$$

Transmission matrix:

$$\hat{t}(\epsilon, V) = 2\, \hat{\Gamma}_L^{1/2}(\epsilon - eV/2)\, \hat{G}_C^r(\epsilon, V)\, \hat{\Gamma}_R^{1/2}(\epsilon + eV/2)$$

- Scattering rates: $\hat{\Gamma}_{L,R}(\epsilon) \equiv \mathrm{Im}\left\{\hat{\Sigma}_{L,R}(\epsilon)\right\}$ ($\hat{\Sigma}$ = self-energy)

$$\hat{\Sigma}_{L,R}(\epsilon) = \hat{v}_{CL,R}\, g_{L,R}(\epsilon)\, \hat{v}_{L,RC}$$

- The central cluster Green functions $\hat{G}_C^r$ are given by:

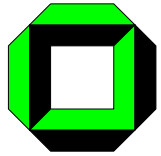
$$\hat{G}_C(\epsilon, V) = \left[\epsilon \hat{1} - \hat{H}_C - \hat{\Sigma}_L(\epsilon - eV/2) - \hat{\Sigma}_R(\epsilon + eV/2)\right]^{-1}$$

- $\mathrm{Dim}(\widehat{t}\widehat{t}^{\dagger}) = M_L \;\rightarrow$ number of molecular orbitals in the central cluster.

Linear regime: (T_i are the eigenvalues of $\widehat{t}\widehat{t}^{\dagger}$ at the Fermi level)

$$G = \frac{2e^2}{h} \sum_{i=1}^{M_L} T_i$$

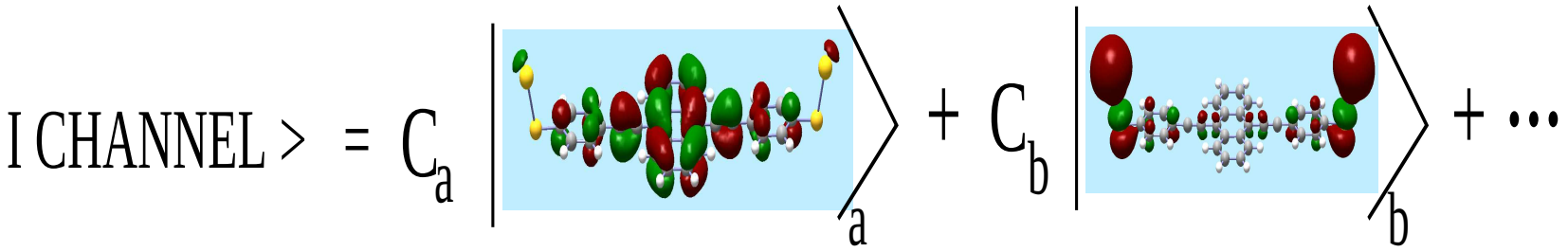
7.3 DFT in Molecular Electronics IV.



- We can analyze the current in terms of **conduction channels**, defined as eigenfunctions of $\widehat{t}\widehat{t}^{\dagger}$.

- Such analysis allows to quantify the contribution to the transport of **every individual molecular level**.

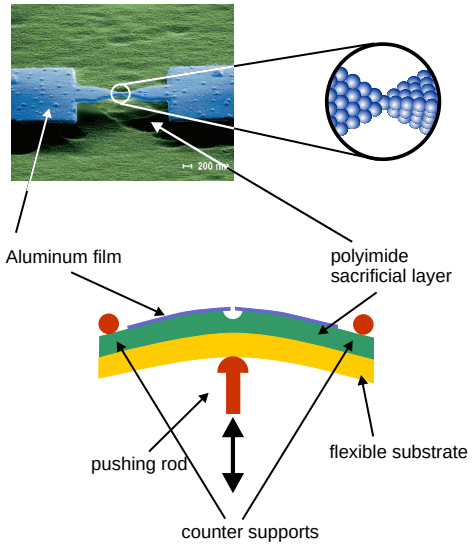
- **The channels are a linear combination of the molecular orbitals $|\phi_j\rangle$ of the central cluster**, i.e. $|c\rangle = \sum_j \alpha_{cj}|\phi_j\rangle$.

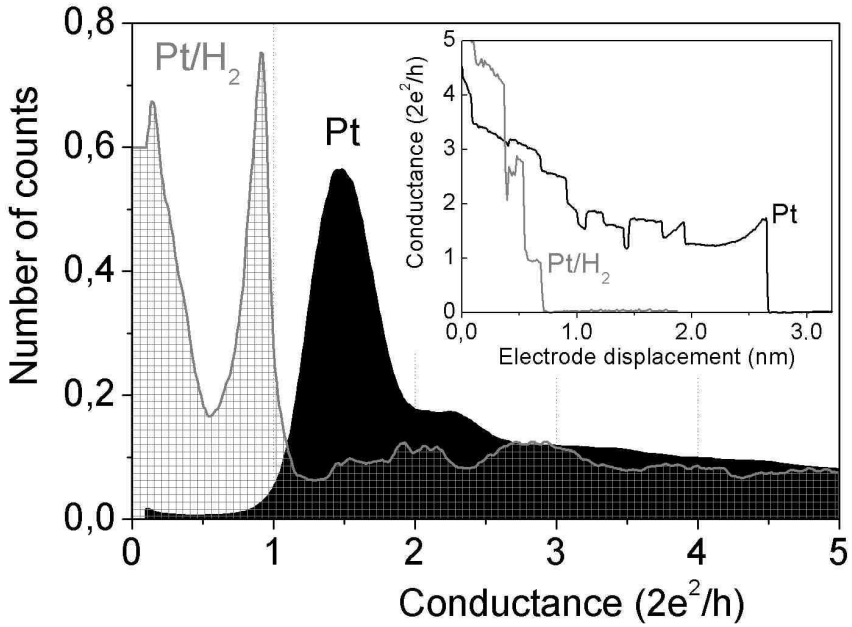


- Ultimately, this information concerning the channels can eventually be measured using superconducting electrodes or other means.

Conductance of a hydrogen molecule I.

[R.H.M. Smit et al., Nature **419**, 906 (2002).]

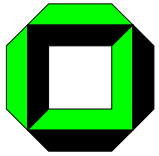




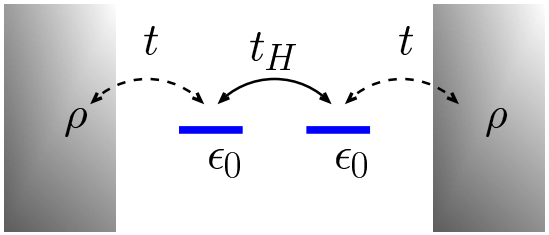
Main observations

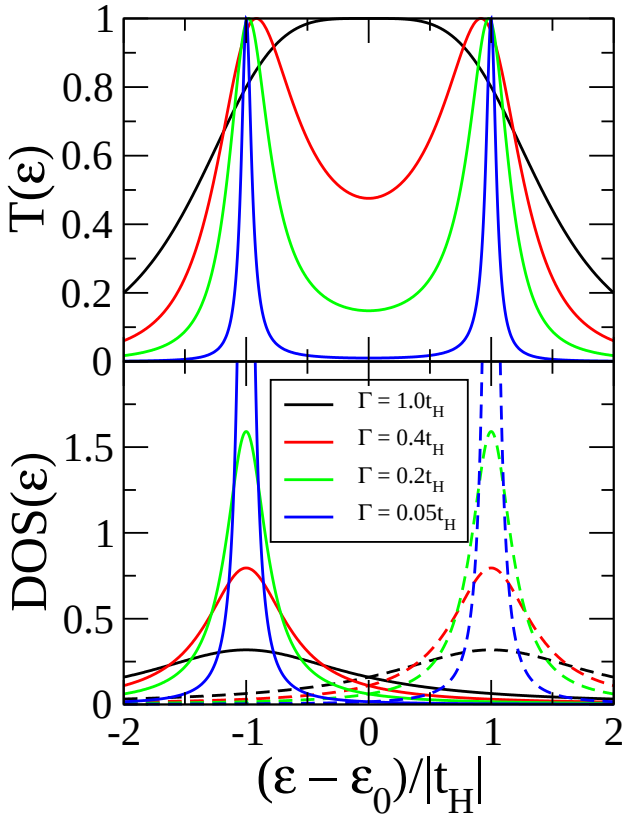
- The H_2 bridge has a nearly perfect conductance of one quantum unit, carried by a single channel.
- The presence of the molecule was identified by the analysis of its vibration modes.
- The number of channels was estimated from the analysis of the conductance fluctuations.

Conductance of a hydrogen molecule II.

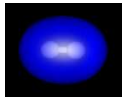
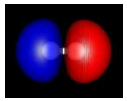


Simple model:





⇒ **Two molecular orbitals**

- bonding state at $\epsilon_0 + t$: 
- anti-bonding state at $\epsilon_0 - t$: 

Approximations:

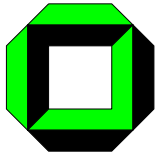
- flat DOS: $\rho(\epsilon) = \rho$
- no charge transfer

Result:

- $\Gamma = \pi t^2 \rho$. Due to the large value of $t_H \sim -7$ eV, one would expect the curve $\Gamma = 0.05 t_H$ to represent the relevant situation.

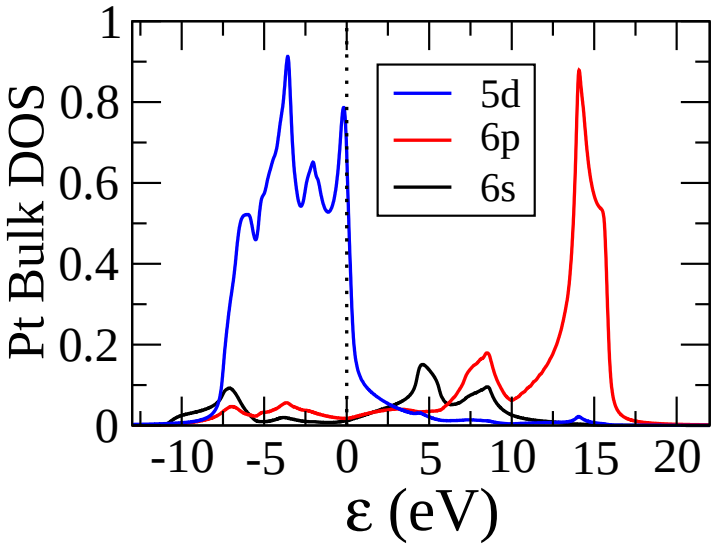
Naively, H_2 should be insulating!

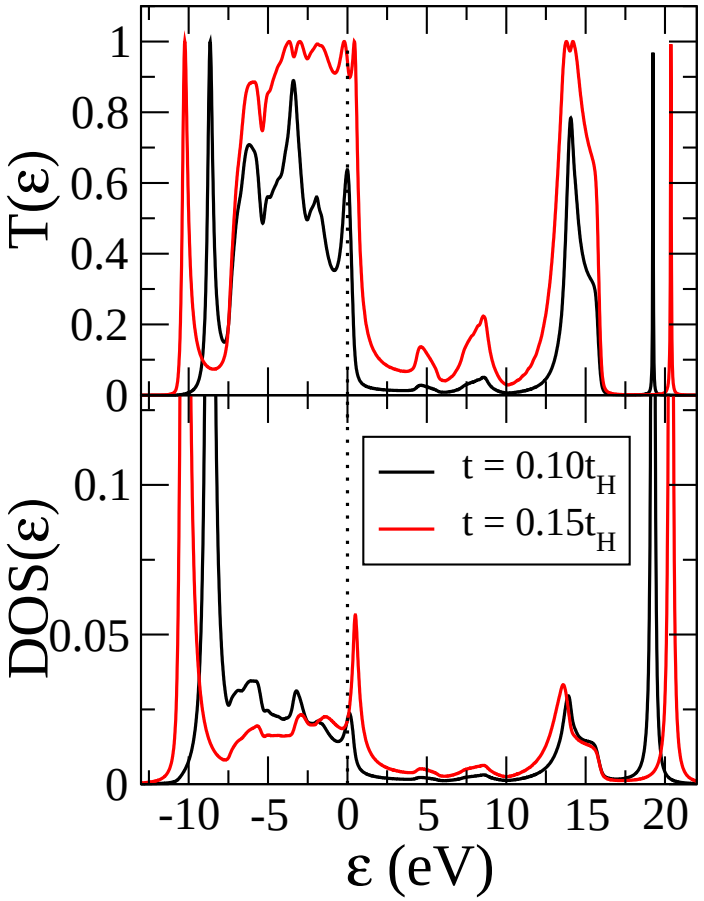
Conductance of a hydrogen molecule III.



Making the model more realistic:

- account for proper charge transfer
  DFT predicts ~ 0.1 e$^-$
  $\Rightarrow$ E_F is shifted down ~ 6 eV
- replace the flat DOS by the proper bulk Pt-Green's function





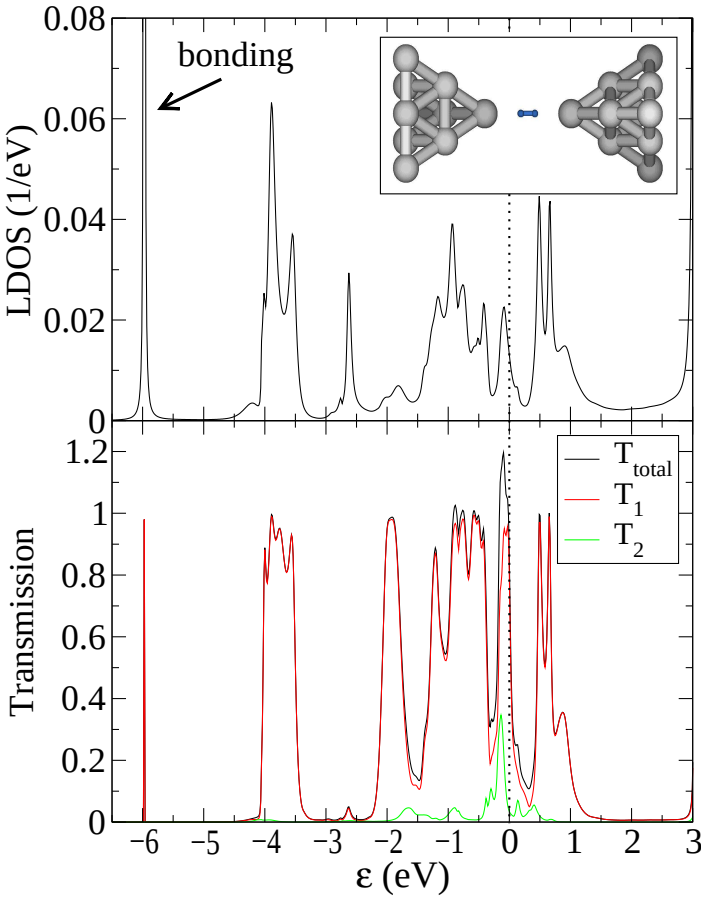
- estimate the coupling strength $\sim 1 - 2$ eV
- the simple model shows a transmission compatible with the experiment

The charge transfer and the strong hybridization with the Pt d-band make H_2 a good conductor!

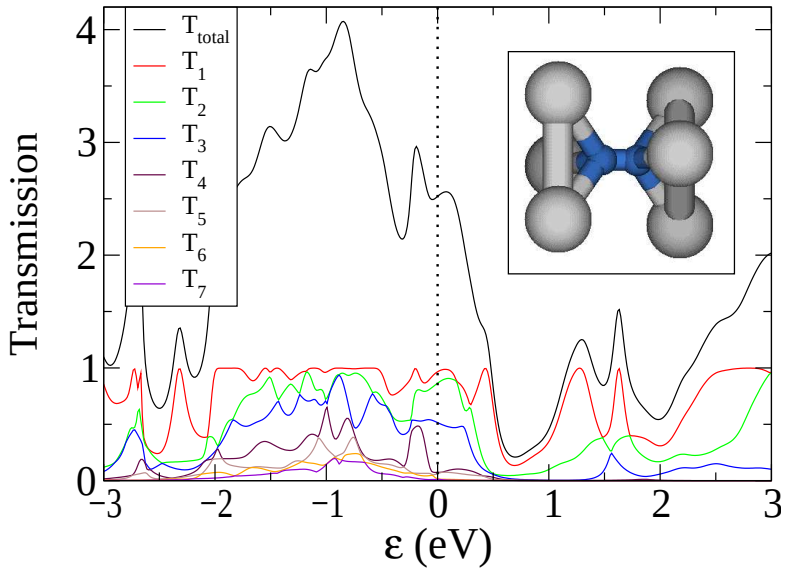
Conductance of a hydrogen molecule IV.

DFT calculations: [Cuevas, Heurich, Cuevas, Wenzel, Schön, Nanotechnology **14**, 29 (2003)]

Top position

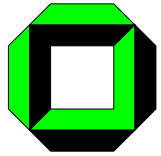


Hollow position



The DFT calculations confirm the conduction mechanism through hydrogen and provide a good description of the experimental results

Conclusions.



- **The density functional theory** (DFT) is presently the most successfull (and also the most promising) approach to compute **the electronic structure of matter**.

- Its **applicability** ranges from **atoms, molecules and solids** to **nuclei and quantum and classical fluids**.

- In its original formulation, the density functional theory provides **the ground state properties of a system**, and the **electron density** plays a key role.

- **An example: chemistry**. DFT predicts a great variety of molecular properties: molecular structures, vibrational frequencies, atomization energies, ionization energies, electric and magnetic properties, reaction paths, etc.

- **The original density functional theoy has been generalized** to deal with many different situations: spin polarized systems, multicomponent systems such as nuclei and electron hole droplets, free energy at finite temperatures, superconductors with electronic pairing mechanisms, relativistic electrons, time-dependent phenomena and excited states, bosons, molecular dynamics, etc.