An introduction to:
Density Functional Theory (DFT)

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CECAM Tutorial
Lyon, November 2006

Outline:

- Empirical vs *ab initio* calculations
- The many-body problem
- Hartree-Fock (Exercise: the Helium atom)
- Density Functional Theory (DFT)
  - The energy is a functional of the density
  - Variational principle for the density
  - The Kohn-Sham approach and the ”eigenvalues”
  - The local density approximation (LDA)
  - Self-consistency
  - A few identified problems
- Bibliographie
- Appendix: a few practical aspects

Empirical vs *ab initio* calculations

Empirical approaches: interaction between two atoms described by an explicit function of their positions (ex: Lennard-Jones, 1922):

$$V(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^{6}]$$

where (σ, ϵ) are adjusted to reproduce experimental interatomic distances, vibrational frequencies, etc. There are also empirical approaches to the electronic problem (tight-binding, Hückel, etc.)

Question: can the same parameters describe diamond, graphite, nanotubes and fullerenes ? In the case of inaccessible systems (earth center, new materials, etc.) which parameters do we use ?

ab initio **approaches** : can we calculate structural, dynamical, electronic, response properties without any adjustable parameter ?

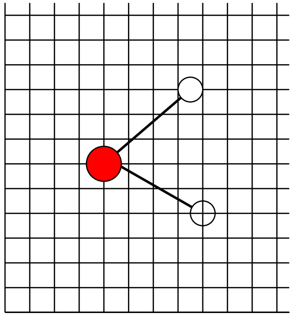
In principle, one can calculate everything from first-principles:

$$H = \sum_{i} -\frac{1}{2}\nabla_i{}^2 + \sum_{i=1}^{N} v^{ext}(r_i) + \sum_{i<j}^{N} \frac{1}{r_{ij}}, \quad v^{ext}(r_i) = -\sum_{I}^{ions} \frac{Z_I}{|R_I - r_i|}$$

Ground-state energy (without E_{ionic}): $E_0 =< \psi_0|H|\psi_0 >$ with:

- $\psi_0 = \psi_0[r_1\sigma_1, ..., r_N\sigma_N]$ antisymmetric
- $|\psi_0[r_1\sigma_1, ..., r_N\sigma_N)|^2 dr_1..dr_N$ probability of finding electron i in [r$_i$,r$_i$+dr$_i$].
- $n(r) = \rho(r) =< \psi_0| \sum_i \delta(r - r_i)|\psi_0 >$ charge density
- $\rho_2(r, r') =< \psi_0| \sum_{i\neq j} \delta(r - r_i)\delta(r' - r_j)|\psi_0 >$ density of pairs, etc.

Problem: We don't know ψ_0 ! We could use variational principle. However with $\psi = \psi[r_1\sigma_1, ..., r_N\sigma_N]$, calculating $< \psi|H|\psi >$ would require $(ngrid)^{3N} \sim 10^{30}$ operations (for small molecule). With 10^{12} flops machine $\Longrightarrow$ centuries.



Hartree-Fock: Variational approach with exact Hamiltonian but approximate wavefunction: a single Slater determinant (Pauli principle).

$$\psi(\mathbf{x_1},\mathbf{x_2},...,\mathbf{x_N}) = \frac{1}{\sqrt{N!}} \begin{bmatrix} \phi_1(\mathbf{r_1})\sigma_1 & .... & \phi_N(\mathbf{r_1})\sigma_N \\ \phi_1(\mathbf{r_2})\sigma_1 & .... & \phi_N(\mathbf{r_2})\sigma_N \\ \vdots & \ddots & \vdots \\ \phi_1(\mathbf{r_N})\sigma_1 & .... & \phi_N(\mathbf{r_N})\sigma_N \end{bmatrix}$$

$$= \frac{1}{\sqrt{N!}} \sum_P (-1)^{\epsilon(P)} \phi_{P(1)}(r_1)...\phi_{P(N)}(r_N)\sigma_{P(1)}...\sigma_{P(N)}$$

Ground-state energy: $E_0^{HF} = \sum_i \langle\phi_i| - \frac{1}{2}\nabla^2 + v^{ext}|\phi_i\rangle \; + \frac{1}{2}\sum_{i,j=1}^{N}(J_{ij} - K_{ij})$

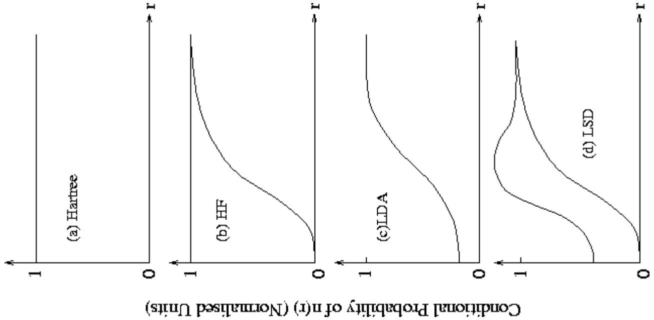
$$J_{ij} = \int d\mathbf{r}d\mathbf{r}' \; \frac{|\phi_i(\mathbf{r})|^2|\phi_j(\mathbf{r}')|^2}{|\mathbf{r}-\mathbf{r}'|} \quad \text{and } K_{ij} = \delta_{\sigma_i\sigma_j}\int d\mathbf{r}d\mathbf{r}' \; \frac{\phi_i^*(\mathbf{r})\phi_j(\mathbf{r})\phi_i(\mathbf{r}')\phi_j^*(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

with J$_{ij}$ and K$_{ij}$ the (classic) Coulomb (Hartree) and (quantum) exchange (Fock) terms. One now has N^2 integrals in $(n_{grid})^6$ dimension (instead of $(n_{grid})^{3N}$ dimension). The ϕ_i will be given by variational principle.

The exchange hole (X-hole)

Density of pairs: $\rho_2(\mathbf{x},\mathbf{x}') = \langle\psi|\sum_{i\neq j}\delta(\mathbf{x}-\mathbf{x_i})\delta(\mathbf{x}'-\mathbf{x_j})|\psi\rangle$, $\quad \mathbf{x} = (\mathbf{r},\sigma)$ gives probability to have an electron with spin σ in $\mathbf{r}$ with an electron with spin σ' in $\mathbf{r}'$. In HF, electrons with opposite spins uncorrelated $\Longrightarrow$ energy penality. Correlation energy: E^{exp}- E^{HF}=$\mathrm{E}_C < 0$

Normalized distribution function: $g(\mathbf{x},\mathbf{x}') = \rho_2(\mathbf{x},\mathbf{x}')/n(\mathbf{x})n(\mathbf{x}')$:



$$E^{ee} = \frac{1}{2}\int\frac{\rho_2(r,r')}{|r-r'|}drdr' = \frac{1}{2}\int\frac{n(r)n(r')}{|r-r'|}drdr' + \frac{1}{2}\int\frac{n(r)h_X(r,r')}{|r-r'|}drdr'$$

$h_X(r,r') = n(r')(g(r,r')-1)$ the X-hole which verifies: $\int h_X(r,r')dr' = -1$.

The helium atom: effect of correlations

Ground state: L=S=0 (singulet) symmetric through radial part $f(r_1, r_2)$. Ground-state (GS) energy: E^{exp} = -5.8075 Rydb.

Trial 1: We take $1s$ state to build GS wavefunction :

$$f(\mathbf{r_1}, \mathbf{r_2}) = \phi_a(\mathbf{r_1})\phi_a(\mathbf{r_2}), \;\; \phi_a(\mathbf{r}) = (a^{3/2}/\pi^{1/2})e^{-ar}$$

where a is a variatiobal parameter. E(a) is minimum for a_0=(2-5/16) with $E(a_0)$ = -5.695 Ry (effective ionic charge: (2- 5/16)e ← screening).

Trial 2: We provide more variational freedom:

$$f(\mathbf{r_1}, \mathbf{r_2}) = \phi_a(\mathbf{r_1})\phi_b(\mathbf{r_2}) + \phi_b(\mathbf{r_1})\phi_a(\mathbf{r_2})$$

Minimum energy (Taylor,Parr): $(a_0, b_0) = (2.183, 1.1885)$ and E(a_0, b_0) = -5.751 Ry in better agreement with experiment.

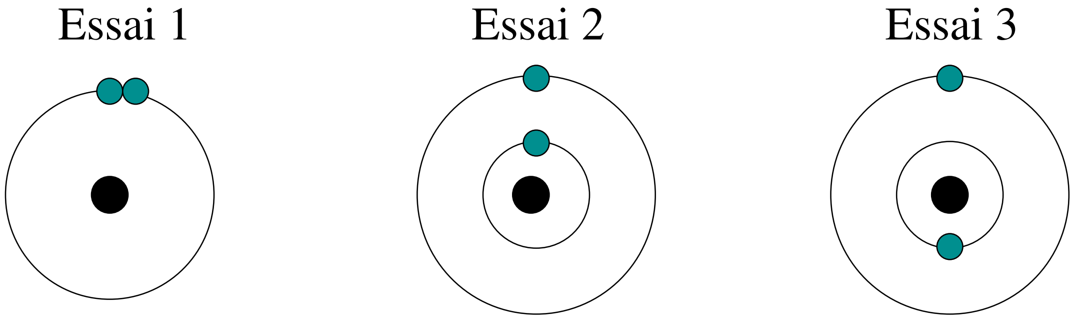
Trial 3 We include p-functions (with L=0; see Cohen-Tannoudji p.1017):

$$f(\mathbf{r_1},\mathbf{r_2}) = (1+\lambda^2)^{-1/2}\{\phi_a(\mathbf{r_1})\phi_b(\mathbf{r_2}) + \phi_b(\mathbf{r_1})\phi_a(\mathbf{r_2}) + \frac{\lambda}{\sqrt{3}}\psi_p(\mathbf{r_1},\mathbf{r_2})\}$$

$$\psi_p(\mathbf{r_1},\mathbf{r_2}) = h_{10}(r_1)h_{10}(r_2) + h_{1-1}(r_1)h_{11}(r_2)h_{1-1}(r_1)h_{11}(r_2) \quad with:$$

$$h_{1m}(\mathbf{r}) = \gamma^{5/2}/(3\pi)^{1/2} r e^{-\gamma r} Y_{1m}(\theta,\phi)$$

Minimum energy: $(a,b,\gamma,\lambda) = $ (2,176,1.201,2.475,-0.06128) and $E(a,b,\gamma,\lambda)$=-5.790 Ry



Thanks to p orbitals, the pair distribution function: P$(\mathbf{r_1},\mathbf{r_2}) = P(|\mathbf{r_1}|,|\mathbf{r_2}|,\theta)$ is angular dependant and $P(\theta=\pi) > P(\theta=0)$ (angular correlations).

Trial 4: The Hartree-Fock solution. With the constraint S=0 for the ground-state, the only mono-determinantal solution is:

$$\psi(\mathbf{x_1},\mathbf{x_2}) = \frac{1}{\sqrt{2}} \left[\begin{array}{cc} \phi(\mathbf{r_1})\alpha(1) & \phi(\mathbf{r_2})\alpha(2) \\ \phi(\mathbf{r_1})\beta(1) & \phi(\mathbf{r_2})\beta(2) \end{array} \right] = \phi(\mathbf{r_1})\phi(\mathbf{r_2})\frac{\alpha(1)\beta(2)-\alpha(2)\beta(1)}{\sqrt{2}}$$

and we are back to the form of (Trial 1). The solution we obtain (numerically) yields: E^{HF} = -5.723 Ry in between (Trial 1) and (Trial 2). We note in particular that the wavefunction in (Trial 2) can be written as a sum of two determinants:

$$\psi(\mathbf{x_1},\mathbf{x_2}) = \frac{A}{\sqrt{2}}\{\left[\begin{array}{cc} f(\mathbf{r_1})\alpha(1) & f(\mathbf{r_2})\alpha(2) \\ g(\mathbf{r_1})\beta(1) & g(\mathbf{r_2})\beta(2) \end{array} \right] - \left[\begin{array}{cc} f(\mathbf{r_1})\beta(1) & f(\mathbf{r_2})\beta(2) \\ g(\mathbf{r_1})\alpha(1) & g(\mathbf{r_2})\alpha(2) \end{array} \right]\}$$

$\Longrightarrow$ by including several determinants containing "excited" single-electron orbitals, one can improve the GS wavefunction and energy → quantum chemistry methods (Couple Cluster, Interaction Configurations (CI), etc.) But CI quickly expensive as well. The approach widely adopted by a large fraction of the community is DFT.

The density functional theory (DFT)

The central idea is to show that the ground-state total energy is a functional of the charge density n(r) (scalar field and physical obervable) instead of the many-body wavefunction: $E[\psi] \rightarrow E[n]$.

Reminder:
$$\begin{aligned} H &= \sum_i -\frac{1}{2}{\nabla_i}^2 + \sum_{i=1}^{N} v^{ext}(r_i) + \sum_{i<j}^{N} \frac{1}{r_{ij}} \\ v^{ext}(r_i) &= -\sum_I \frac{Z_I}{|R_I - r_i|} \Longrightarrow H \Longrightarrow \psi_0 \end{aligned}$$

Theorem HK1 Given n(r) the charge density, there exists only one external potential v^{ext}(r) (up to a constant) that can realize n(r) (the reverse statement is obvious!). By absurdum, let's assume that:

$$v_1^{ext}(r) \rightarrow \psi_1 \rightarrow n(r)$$
$$v_2^{ext}(r) \rightarrow \psi_2 \rightarrow n(r)$$

then the variational principle applied to $H_1 = T + V^{ee} + v_1^{ext}$ yields (non degenerate GS): $E_1^{GS} < \langle\psi_2|H_1|\psi_2\rangle$ with:

$$\langle\psi_2|H_1|\psi_2 >=< \psi_2|H_2 + v_1^{ext} - v_2^{ext}|\psi_2 >$$

that is: $E_1^{GS} < E_2^{GS} + \int d\mathbf{r}\ \rho(\mathbf{r})[v_1^{ext} - v_2^{ext}]$

Switching (1) and (2): $E_2^{GS} < E_1^{GS} + \int d\mathbf{r}\ \rho(\mathbf{r})[v_2^{ext} - v_1^{ext}]$
and by addition of the two inequalities:

$$E_1^{GS} + E_2^{GS} < E_2^{GS} + E_1^{GS} \quad \text{(absurd)}$$

Variational principle for E=E[n]

The density n defines in a unique way v^{ext} (and N) that is the Hamiltonian. E is therefore a fonctionnal of n.

$$
\begin{aligned}
E[\psi] &= E[n] = \int d^3 r v^{ext}(r) n(r) + F_{HK}[n] \\
F_{HK}[n] &= T[n] + V^{ee}[n]
\end{aligned}
$$

F_{HK} is a universal fonctionnal of n as does not depend on v^{ext}. **Problem: we do not know F_{HK}.**

Theorem: Given a "test" density "n$^{test}(r) \geq 0$" such that $\int n(r)dr = N$, then: $E[n^{test}] \geq E_{GS}$.
Variational principle valid for the wavefunctions. Its extension to E[n] derives from the bijection between n(r) and the GS many-body wavefunction (HK1):
$n_{GS} \Longleftrightarrow v^{ext} \Longleftrightarrow \psi_{GS}$ and $n^{test} \Longleftrightarrow v^{ext,test} \Longleftrightarrow \psi^{test}$
so that: $E[n^{test}] = E[\psi^{test}] \geq E[\psi_{GS}] = E[n_{GS}]$

DFT without orbitals: From this variational principle derives a Euler-Lagrange equation which in principle allows to find n(r) by minimization:

$$\frac{\delta}{\delta n(r)}[E[n] - \mu[\int d^3r n(r) - N]] = 0 \Longrightarrow v^{ext}(r) + \frac{\delta F_{HK}}{\delta n(r)} = \mu$$

with μ the chemical potential associated with conservation of number of particles. However, F_{HK} not known !!

The Kohn and Sham (KS) approach

Numerous work to find T[n] and V^{ee}[n] (Thomas, Fermi, Slater, Dirac, etc.) However, the most successful approach is to come back to an "exact" expression for the kinetic energy T by re-introducing one-body orbitals. To do that, KS introduce a fictitious equivalent system of **non-interacting** electrons under the action of an effective external potential V^{eff} generating the **same density** n(r) that the real system:

$$n(r) = \int |\psi|^2 dr_1 ... dr_N \quad \Longleftrightarrow \quad n(r) = \sum_{i=1}^{N} |\phi_i(r)|^2$$

$$T[n] = ?? \quad \Longleftrightarrow \quad T_0[n] = \sum_{i=1}^{N} < \phi_i | \frac{-\nabla^2}{2} | \phi_i >$$

$$\hat{H}|\psi >= E|\psi > \quad \Longleftrightarrow \quad [\frac{-\nabla^2}{2} + V^{eff}(r)]\phi_i(r) = \epsilon_i \phi_i(r)$$

By regrouping: $F_{HK}[n] = T_0[n] + J[n] + (T - T_0 + V^{ee} - J)[n]$, the equivalence between the two systems yields:

$$V^{eff}(r) \quad = \quad v^{ext}(r) + \int \frac{n(r')dr'}{|r - r'|} + \frac{\delta E_{xc}[n]}{\delta n(r)}$$

Thanks to KS, T_0, an ”important fraction” of T[n], is calculated exactly. The unknown part: $E_{xc} = (T - T_0 + V^{ee} - J)$ is expected to be rather small.

Derivation of the "eigenvalues" equation

To connect the effective potential V^{eff} and E_{XC}, we use the variational principle: $\delta\Omega[\psi_i] = 0$, with:

$$\begin{aligned}
\Omega[\phi_i] &= E[n] - \sum_i^N \sum_j^N \epsilon_{ij} \int \phi_i^*(r)\phi_j(r)dr \\
E[n] &= T_0[n] + J[n] + E_{XC}[n] + \int v^{ext}(r)n(r)dr \\
T_0[n] &= \sum_i^N \int \phi_i^*(r)(\frac{-\nabla^2}{2})\phi_i(r)dr
\end{aligned}$$

where the (ϵ_{ij}) variables are the Lagrange parameters associated with the orthonormalization of the one-body wavefunctions (ϕ_i). This leads easily to:

$$\hat{h}^{eff}\phi_i(r) = \sum_j^N \epsilon_{ij}\phi_j(r)$$

$$
\begin{aligned}
\hat{h}^{eff} &= -\nabla^2/2 + V^{eff}(r) \\
V^{eff}(r) &= v^{ext}(r) + \int \frac{n(r')dr'}{|r-r'|} + \frac{\delta E_{xc}[n]}{\delta n(r)}
\end{aligned}
$$

Since $(\hat{h}^{eff})$ is hermitian, we can find a unitary transformation that makes (ϵ_{ij}) diagonal while preserving the charge density and thus the energy, etc. We use the notation: $v_{xc}(r) = \delta E_{xc}[n]/\delta n(r)$.

REMARK: E[n] is NOT the sum of the eigenvalues:

$$
\begin{aligned}
E &= \sum_i^N \epsilon_i - \frac{1}{2} \int \frac{n(r)n(r')}{|r-r'|} dr dr' + E_{XC}[n] - \int v_{xc} n(r) dr \\
\sum_i^N \epsilon_i &= T_0[n] + \int V^{eff}(r) n(r) dr
\end{aligned}
$$

→ difficulty to interpret the ϵ_i as electronic excitation energies.

The local density approximation (LDA)

DFT is a rigorous theory, but E_{XC} is unknown. **We need to do approximations**. The "historical" approximation still very very used is the LDA which consists in **introducing a local density of exchange and correlation (XC) energy which only depends on the value of the charge density n at r**:

$$\begin{aligned} E_{XC}[n] &= \int n(r)\varepsilon_{XC}(r)dr \quad with: \ \varepsilon_{XC}^{LDA}(r) = \varepsilon_{XC}^{LDA}(n(r)) \\ v_{XC}^{LDA}(r) &= \frac{\delta E_{XC}[n]}{\delta n(r)} = \varepsilon_{XC}(r) + n(r)\frac{\delta\varepsilon_{XC}^{LDA}(n(r))}{\delta n(r)} \end{aligned}$$

To go further, the fonction $\varepsilon_{XC}^{LDA}(n(r))$ is obtained thanks to very accurate simulations (Quantum Monte Carlo=QMC) (Ceperley, Alder, 1986) on a **homogeneous interacting electron gas** of density (uniform) n^{hom}=n(r): $\varepsilon_{XC}^{LDA}(n(r)) = \varepsilon_{XC}^{QMC}(n^{hom})$, for different values of n^{hom}.

For an homogeneous gas, $\mathrm{T}^0(\mathrm{n})$, J[n] et E_X are analytic. By subtraction to the total energy (numerical QMC values), we obtain the functional $E_C(n)$ and $\varepsilon_C^{LDA}(n)$ for the correlation energy and energy density. The QMC numerical values for are usually fitted by some analytic form which is used in the codes (e.g. Perdew+Zunger fit PRB **23** 5048 (1981))

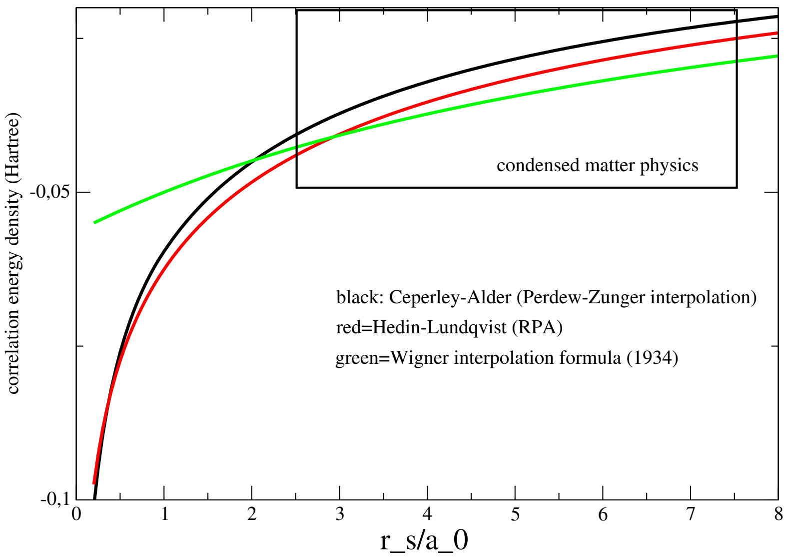
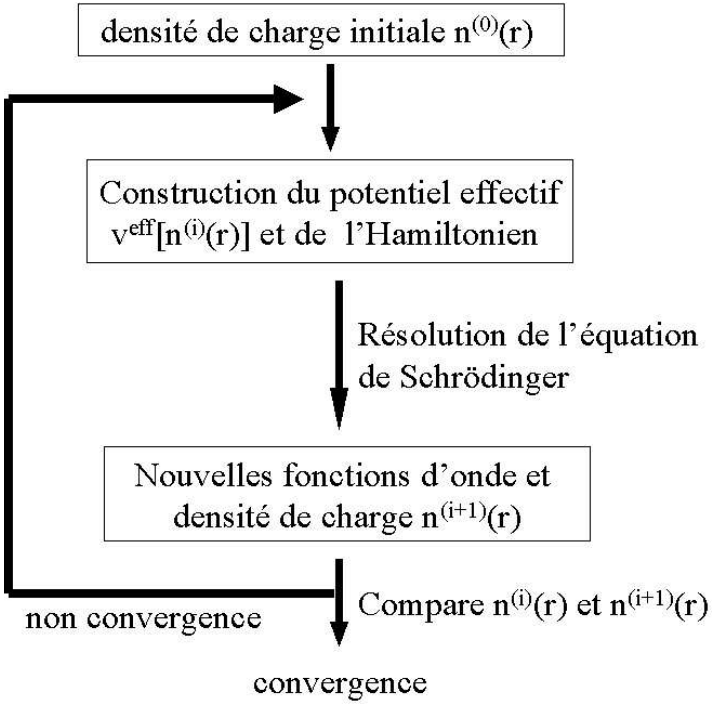


Figure: Density of correlation energy ϵ_C as a function of the reduced Wigner radius r_s/a_0, r_s such that $1/n_e = (4/3)\pi r_s^3$, n_e average electron density.

Self-consistency

H depends on n(r) that is on the unknown $\phi_i(r)$: needs self-consistency.

Resolution goes in general through construction of Hamiltonian matrix $H_{\alpha,\beta} =< \alpha|H|\beta >$ on a basis $\{\alpha\}$ (planewaves, atomic orbitals etc.). Diagonalization of $H_{\alpha,\beta}$ yields $\{\epsilon_i, \phi_i\}$ (Kohn-Sham) that is a new density n(r) and potentiel V^{eff}, etc.



densité de charge initiale $n^{(0)}(r)$

Construction du potentiel effectif $v^{eff}[n^{(i)}(r)]$ et de l'Hamiltonien

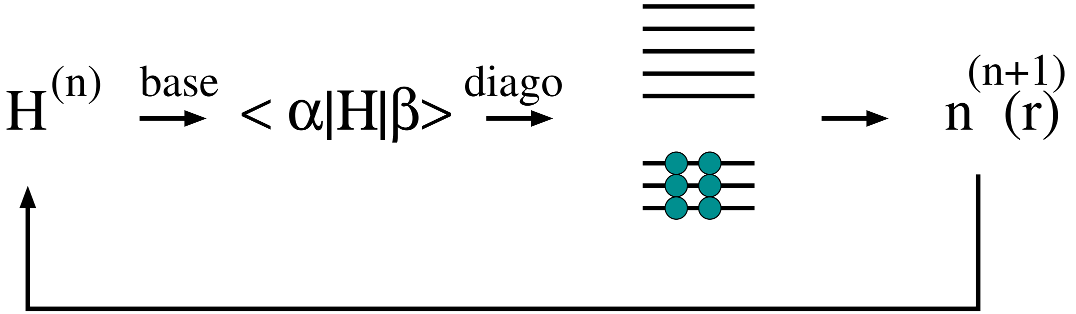
Résolution de l'équation de Schrödinger

Nouvelles fonctions d'onde et densité de charge $n^{(i+1)}(r)$

Compare $n^{(i)}(r)$ et $n^{(i+1)}(r)$

non convergence

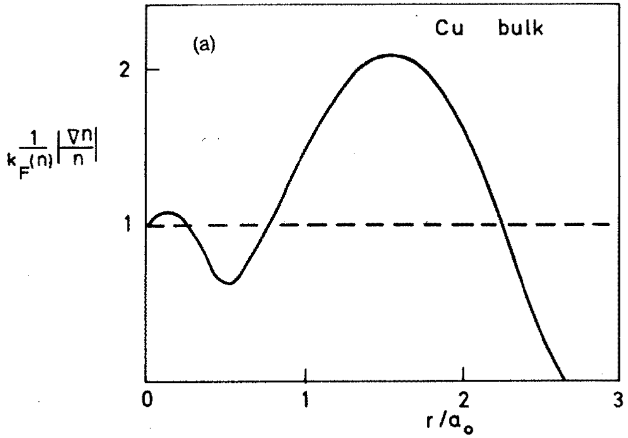
convergence



$H^{(n)} \xrightarrow{\text{base}} <\alpha|H|\beta> \xrightarrow{\text{diago}} \quad \longrightarrow n^{(n+1)}(r)$

Why LDA "is not so bad" ?

The XC hole h_{xc} scales as $1/\mathrm{k}_F$. One may expect that LDA works if: $\nabla n/k_F n < 1$. Actually, this condition usually does not hold and still LDA "works". Why ??



A) The XC hole satisfies the sum rule that: $\int h_{XC}^{LDA}(r,r')dr' = -1$

B) The XC enrgy depends on the spherical average of h_{XC}.

$$\begin{aligned}
E^{XC}[n] &= \frac{1}{2}\int \frac{n(r)h_{XC}(r,r')}{|r-r'|}drdr' \\
&= \frac{1}{2}\int n(r)dr \int_0^\infty dR\, 4\pi\, h_{XC}^{SA}(r;R) \\
h_{XC}^{SA}(r;R) &= \frac{1}{4\pi}\int_{\Omega:|r-r'|=R} h_{XC}(r,r')dr'
\end{aligned}$$

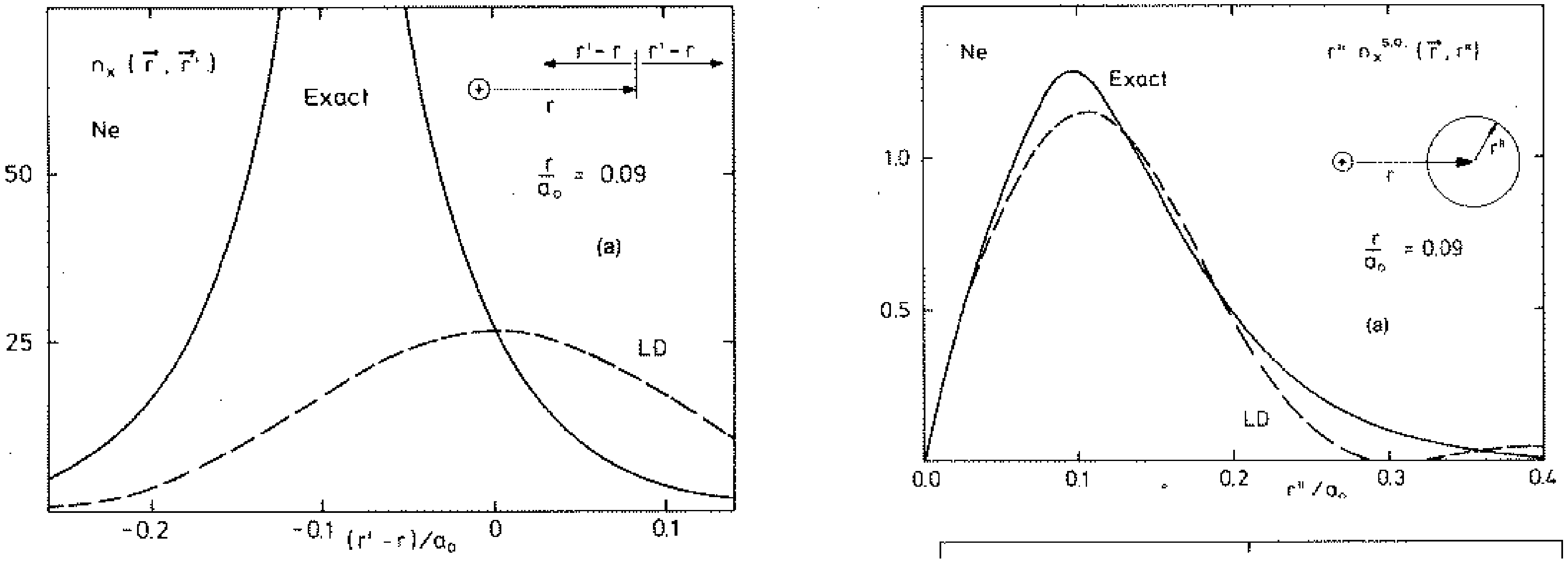


Figure: X-hole in a Ne-atom. (Left) n(**r**,**r**') plotted as a function of the $|\mathbf{r} - \mathbf{r}'|$ distance (exact and LDA). (Right) The spherical average as a function of relative distance (see: Gunnarsson et al., PRB 20 **3136**, 1979).

Known problems with LDA (amongst others)

The self-interaction (SI) problem

In LDA, an electron interacts with itself (cf. hydrogen). This effect is strong for localized states (pushed up in energy). This problem does not exist in HF (SI cancellation between J et K, i.e. $J_{ii} = K_{ii}$).
$\Longrightarrow$ there exists fonctionals E_{XC} corrected to remove this interaction (SIC: self-interaction correction). These functionals lead to a v_{XC} which is "orbital dependant" $\Longrightarrow$ N^4 scaling (expensive).

XC potential in the vacuum; Van der Waals interactions

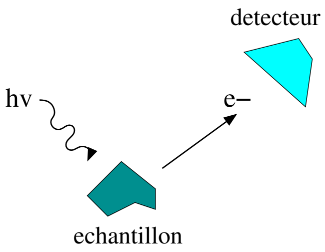
The XC potential in the vacuum must decay as 1/z (z distance to surface, molecule; cf. charge image). In LDA, it decays exponentially (as the charge density). In particular, dispersive interactions (van der Waals, etc.) between molecules are inexistant within LDA.

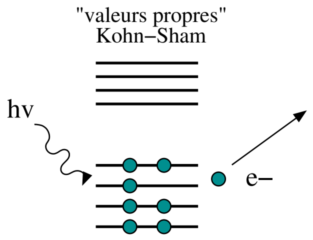
Excitation energies

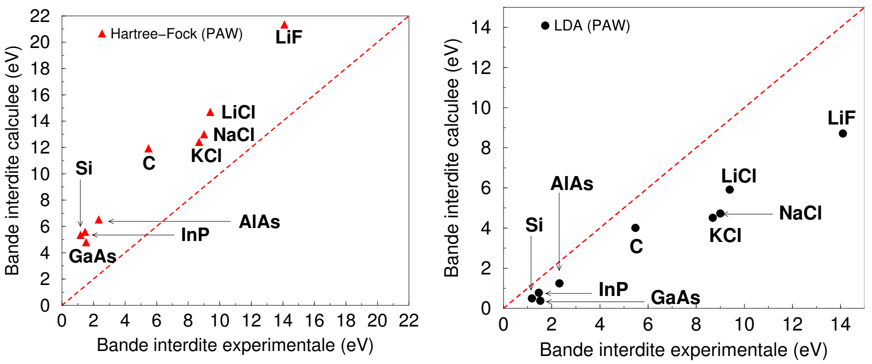
Experimentaly, the band gap, electronic affinity, ionization energy (EI) are obtained as differences of total energy, e.g.: EI = E(N)-E(N-1)

In exact DFT, one can calculate E(N) and E(N-1) (for finite size systems). What about LDA ? What is the meaning of Kohn-Sham "Lagrange parameters" ?

Figure (bottom): band gap in solids (left) HF (right) DFT-LDA. (courtesy: Brice Arnaud, Rennes, France)







Beyond the LDA: gradient corrections

In LDA, $v_{XC}(r)$ depends only on n(r) (local potential), while we know (cf. Fock term K$_{ij}$, van der Waals, etc.) that it must depend on the system at every point of space (non-locality). One step in this direction may be done by using "gradient corrected" functionals:

$$v_{XC}^{LDA}((n(r)) \Longrightarrow v_{XC}^{GGA}(n(r), s(r)), \text{ avec: } s(r) = \frac{|\nabla n(r)|}{k_F n(r)}$$

These first functionals (GEA) based on "simple" Taylor expansions were yielding worst results than LDA usually: these fonctionals did not satisfied anymore sum rules ! Several "generalized" gradient corrected functionals (GGA) have been introduced to satisfy these sum rules ... and many other nice properties (asymptotic long range behavior of v_{XC}, etc.). Are implemented in PWSCF:

- PW91 (Perdew, Wang, PRB **45**, 13244 (1992))
- PBE (Perdew, Wang, Ernzerhof, PRL **77**, 3865 (1996))

Rule of thumb: LDA tends to underestimate bond lengths, and overestimate binding energies and bulk modulus. The GGA functionals do ... the contrary! (e.g. Dal Corso et al., PRB **53**, 1180 (1996); Garcia et al., PRB **46**, 9829 (1992)).

Mainly in chemistry (with local orbitals), ”hybrid” functionals, introducing somme percentage of the non-local exchange (Fock) operator (”orbital” dependent) are used extensively (but more expensive...). A good balance between Fock energy and local exchange and correlation is ”fitted” to get good results on a large set of molecules.

LDA+U: with highly localized orbitals (e.g. $3d$ in transition metals), one can add an adjustable on-site correlation term named U which acts on the localized orbitals only. Implemented in PWSCF. Use with care ...

Other approaches aim at introducing non-local orbital-dependent functionals in a manner which is much more consistent with the DFT Kohn-Sham idea. They are known under the name ”Optimized Effective Potential” (OPE).

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Review articles:

- "The DFT, its applications and prospects", Jones, Gunnarsson, Rev. Mod. Phys. **61**, No.3, July 1989.

- ”Nobel Lecture: Electronic structure of matter-wave functions and density functionals, W. Kohn, Rev. Mod. Phys. **71**, 1253-1266 (1999).
- ”Iterative minimization techniques for ab initio total energy calculations”, Payne, Teter, Allan, Arias, Joanopoulos, Rev. Mod. Phys. **64**, No.4, octobre 1992.

Basic DFT articles:

- ”Inhomogeneous electron gaz”, Hohenberg and Kohn, Phys. Rev. **136**, B864 (1964).
- ”Self-consistent equations including exchange and correlation effects”, Kohn and Sham, Phys. Rev. **140**, A1133 (1965).
- ”Description of exchange and correlation effects in inhomogeneous electron systems”, Gunnarsson, Jonson, Lundqvist, Phys. Rev. B **20**, 3136 (1979).
- ”Self-interaction correction to density functional approximations for many-electron systems”, Perdew and Zunger, Phys. Rev. B **23**, 5048 (1981).

Appendix A: Practical aspects

A) Instead of diagonalizing the Hamiltonian matrix, one can use variational principle to minimize $E[c_i(\alpha)]$ with $c_i(\alpha)$ the coefficients of ϕ_i on the $\{\alpha\}$ basis (under the condition that the ϕ_i are orthonormal). Several techniques: conjugate gradient, newtonian techniques, damped dynamics, etc. (NOT implemented in PWSCF).

B) A matrix diagonalization (or the orthonormalization constraint in a minimization approach) scaled as N^3: this is the price associated with DFT calculations. For large hamiltonian matrices (e.g. in a planewave basis), one compute iteratively the lowest eigenvales and eigenstates (ϵ_i, ϕ_i) (we really need only the occupied states to build n(r)). Again several algorythms exists:

In PWSCF, Davidson, DIIS, and conjugate-gradient-like are implemented (variable "diagonalisation"). See a discussion in: Kresse and Furthmuller, PRB **54**, 11169 (1996); Štich, Car, Parrinello, Baroni, PRB **39**, 4997 (1989); etc.

C) **Self-consistency and charge density mixing:** In the self-consistent loop, instead of injecting n^i to start the (i+1) iteration, one usually uses a "mixing" of the two previous charge densities: $n^{new} = \alpha n^i + (1-\alpha) n^{i-1}$, in order to avoid energy and charge "sloshing" (the larger the system, the smaller the α usually). More sophisticated mixing have been developed (preconditioned, Pulay, etc.) In PWSCF: mixing_beta is the (1-α) variable and "mixing_mode" selects the type of mixing (plain=Broyden, TF=Thomas-Fermi, etc.)

Figure: Convergency for a W(100) surface with simple linear mixing and Broyden approach (Singh et al., PRB **34**, 8391 (1986))

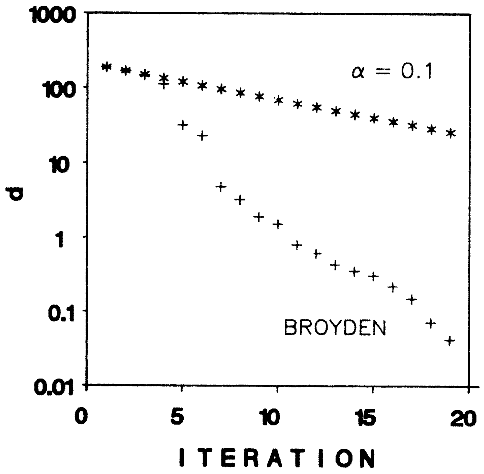

FIG. 1. The distance [in 10^{-3} electrons/a.u.^{3}, cf. Eq. (9)] between the input and output charge densities as a function of iteration number.

Planewave (PW) formalism. Bloch theorem and Fourier expansion yields:

$$\psi_{n\mathbf{k}}(\mathbf{r}) = \frac{1}{N_{cells}}\exp(i\mathbf{k}\cdot\mathbf{r})u_{n\mathbf{k}}(\mathbf{r}) \ \text{ with: } \ u_{n\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{\Omega_{cell}}}\sum_m c_{n,m}(\mathbf{k})\exp(i\mathbf{G}_\mathbf{m}\cdot\mathbf{r})$$

$$\begin{aligned} E_{tot} \quad &= \quad \sum_{n\mathbf{k}} w_{n\mathbf{k}} \left\{ \sum_{m,m'} c^*_{n,m} \left[\frac{\hbar^2}{2m_e}|\mathbf{k}+\mathbf{G}_\mathbf{m}|^2 \delta_{m,m'} + V_{ext}(\mathbf{k}+\mathbf{G}_\mathbf{m}, \mathbf{k}+\mathbf{G}_{\mathbf{m}'}) \right] c_{n,m'} \right. \\ &+ \quad \sum_{\mathbf{G}} \varepsilon_{xc}(\mathbf{G})n(\mathbf{G}) + 2\pi e^2 \sum_{\mathbf{G}\neq 0} \frac{n(\mathbf{G})^2}{G^2} + \gamma_{Ewald} + \left(\sum_s \alpha_s\right)\frac{N_e}{\Omega} \end{aligned}$$

$(\mathbf{k}, w_{n\mathbf{k}})$ related to Brillouin-zone $\mathbf{k}$-point sampling, $V_{ext}(\mathbf{k}+\mathbf{G}_\mathbf{m}, \mathbf{k}+\mathbf{G}_{\mathbf{m}'})$ the Fourier components of the non-local part of the ionic potential, $\frac{N_e}{\Omega}$ the average density,

See e.g.: Ihm, Zunger, Cohen J. Phys. C: Solid State Phys. **12**, 4409 (1979).

Planewave formalism (2):

- size of PW basis determined by maximum kinetic energy: $G \leq G_{max}$ with $E_{kin}^{max} = G_{max}^2$ (in Ryd). E_{kin}^{max} is the ecutwfn variable in PWSCF. Roughly, $2\pi/G_{max}$ sets the real-space precision for describing $\psi_{n\mathbf{k}}(\mathbf{r})$.

- if $\psi_{n\mathbf{k}}(\mathbf{r})$ have Fourier components up to G_{max}, then: $V_{ext}(\mathbf{k}+\mathbf{G}, \mathbf{K}+\mathbf{G}')$ and n($\mathbf{r}$) (product of $\psi_{n\mathbf{k}}$) must be described up to $2G_{max}$ (that is a maximum kinetic energy 4 times larger: ecutrho parameter in PWSCF).

- XC functionals are expressed in real-space => one use a Fourier transform of the charge density onto a real-space grid: $n(\mathbf{G}) \Rightarrow \mathbf{n}(\mathbf{r})$, with spacing $\Delta r \sim 2\pi/2G_{max}$. (Fast) Fourier transforms are an important issue when parallelizing codes (communication).

- The (G=0) components of the Hartree, electron-ion and ion-ion energies diverge. The divergencies cancel up to a constant (γ_{Ewald} and α terms) but still a problem of ”zero energy reference” in periodic/planewave calculations => Kohn-Sham eigenvalues are not referenced with respect to vacuum level !