

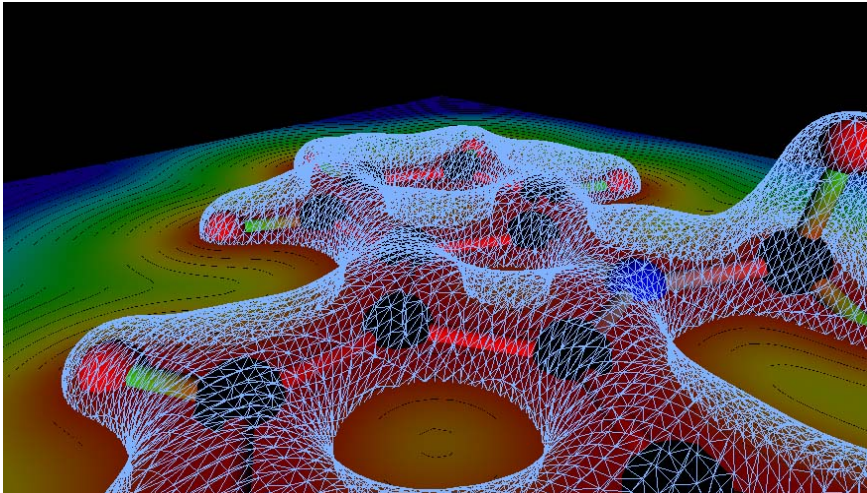


Introduction to DFT and Density Functionals

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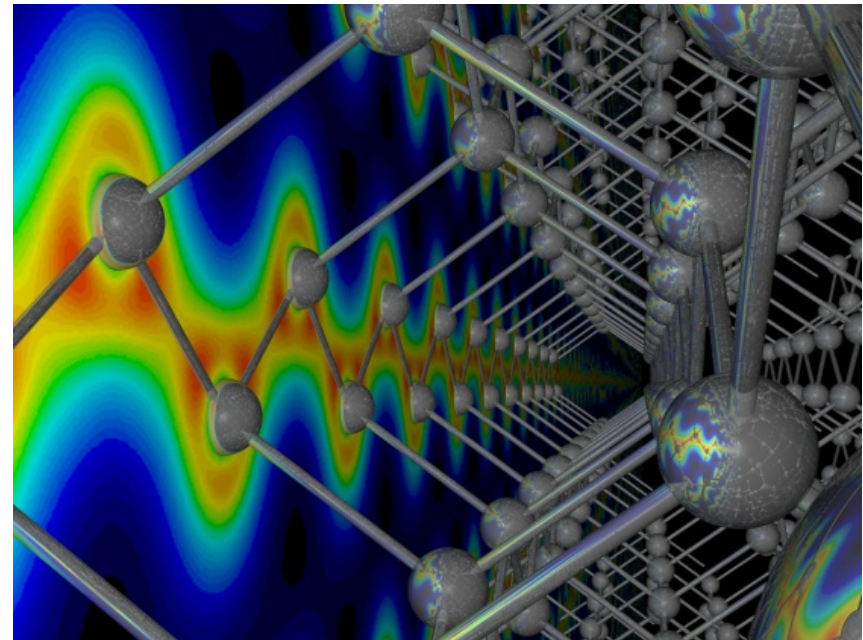
Examples

Carbazole molecule



Réf: Jean-François Brière (
[http://www.phys.umontreal.ca/
~michel_cote/Images_Scientifiques/
images.shtml](http://www.phys.umontreal.ca/~michel_cote/Images_Scientifiques/images.shtml))

Inside of diamant



Réf: Mike Towler (
<http://www.tcm.phy.cam.ac.uk/~mdt26/>)

Condensed Matter

Schrödinger's equation:

$$i\hbar \frac{\partial}{\partial t} |\Psi\rangle = H |\Psi\rangle$$

Hamiltonian for electrons and atoms with coulomb interaction:

$$H = -\sum_j^{Ne} \frac{\hbar^2}{2m} \nabla_j^2 - \sum_\alpha^{Ni} \frac{\hbar^2}{2M_\alpha} \nabla_\alpha^2 \\ - \sum_j^{Ne} \sum_\alpha^{Ni} \frac{Z_\alpha e^2}{|r_j - R_\alpha|} + \sum_{j < k}^{Ne} \frac{e^2}{|r_j - r_k|} + \sum_{\alpha < \beta}^{Ni} \frac{Z_\alpha Z_\beta e^2}{|R_\alpha - R_\beta|}$$

Electrons

Using the Born-Oppenheimer approximation:

$$H\Psi = \underbrace{\frac{-\hbar^2}{2m} \sum_{l=1}^N \nabla_l^2 \Psi}_{\text{Kinetic energy}} + \underbrace{\sum_{l=1}^N U_{\text{ion}}(\vec{r}_l) \Psi}_{\text{Potential energy}} + \underbrace{\frac{1}{2} \sum_{l,l'=1}^N \frac{e^2}{|\vec{r}_l - \vec{r}_{l'}|} \Psi}_{\text{Interaction energy}} = E\Psi$$

We are looking for a solution of the type of a wave function for many electrons:

$$\Psi(x_1, x_2, \dots, x_N)$$

The problem is easy to write down ...but the solution ...

Electrons system

$$\Psi(x_1, x_2, \dots, x_N)$$

Storage required:

$$x \rightarrow 10 \times 10 \times 10 = 1000 \text{ data}$$

$$\begin{aligned} 10 \text{ electrons} &\rightarrow 1000^{10} \text{ data} \rightarrow 10^{30} \times 16 \text{ bytes} \\ &= 16 \times 10^{21} \text{ Gb} \end{aligned}$$

Impracticable!!!

Dirac's quote (1929)

« The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble »

Réf: *Quantum mechanics of many-electron systems*, Proceedings of the Royal Society of London, pp.714. (1929)

Wavefunction approach: Hartree method

$$\Psi(x_1, x_2, \dots, x_N) = \phi_1(x_1)\phi_2(x_2) \cdots \phi_N(x_N) = \prod_{l=1}^N \phi_l(x_l)$$

$$n(x) = \sum_{l=1}^N \phi_l^*(x)\phi_l(x)$$

$$E = \langle \Psi | H | \Psi \rangle - \sum_{l=1}^N \lambda_l \langle \phi_l | \phi_l \rangle$$

Lagrange multipliers to assure that the ϕ_l remain orthogonal

$$\frac{\partial E}{\partial \phi_l^*(x)} = \left[\frac{-\hbar^2}{2m} \nabla^2 + U_{\text{ion}}(x) + e^2 \int dx' \frac{n(x')}{|x-x'|} \right] \phi_l(x) - \lambda_l \phi_l(x) = 0$$

$$\left[\frac{-\hbar^2}{2m} \nabla^2 + U_{\text{ion}}(x) + V_H(x) \right] \phi_l(x) = \lambda_l \phi_l(x) \quad \begin{array}{l} \text{Same equation} \\ \text{for all } \phi_l \end{array}$$

Hartree-Fock method

$$\Psi(x_1, x_2, \dots, x_N) = \frac{1}{\sqrt{N!}} \sum_P (-1)^P \prod_{l=1}^N \phi_{Pl}(x_l) = \Phi_0(x_1, x_2, \dots, x_N)$$
$$= \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(x_1) & \phi_1(x_2) & \cdots & \phi_1(x_N) \\ \phi_2(x_1) & \phi_2(x_2) & \cdots & \phi_2(x_N) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_N(x_1) & \phi_N(x_2) & \cdots & \phi_N(x_N) \end{vmatrix}$$

Slater determinant

Particles are not independent, change the position of one and all the others are affected.

Pauli exclusion principle is respected.

Hartree-Fock method

$$\left[\frac{-\hbar^2}{2m} \nabla^2 + U_{\text{ion}}(x) + V_H(x) \right] \phi_l(x) - \underbrace{\sum_{j=1}^N \delta_{ss'} \phi_j(x) \int dx' \frac{\phi_j^*(x') \phi_l(x')}{|x - x'|}}_{\text{Exchange energy}} = \lambda_l \phi_l(x)$$

Because of the exchange term, the problem is much harder to resolve.

Results are better than those of the Hartree method but still not very satisfying.

Configuration Interaction method

$$\Psi(x_1, x_2, \dots, x_N) = \sum_i C_i \Phi_i(x_1, x_2, \dots, x_N)$$

Sum of Slater determinants
(configurations)

Must find the coefficients C_i

CI = configuration interaction

CIS = CI with single excitations only

CISD = CI with single and double excitations only

Correlation energy: contribution over that of Hartree-Fock

Wavefunction methods

Advantages:

- Control approximations
- Systematic approach (H, HF, CIS, ...)
- Upper bound (variational principle)

Disadvantages:

- Very costly numerically
(up to 20-30 electrons, forget solids!)

Progress in theoretical methods



John A. Pople

Nobel Prize 1998 in Chemistry:

"for his development of computational methods in quantum chemistry"



Walter Kohn

"for his development of the density-functional theory"

- efficient
- flexible
- precise
- parameter free

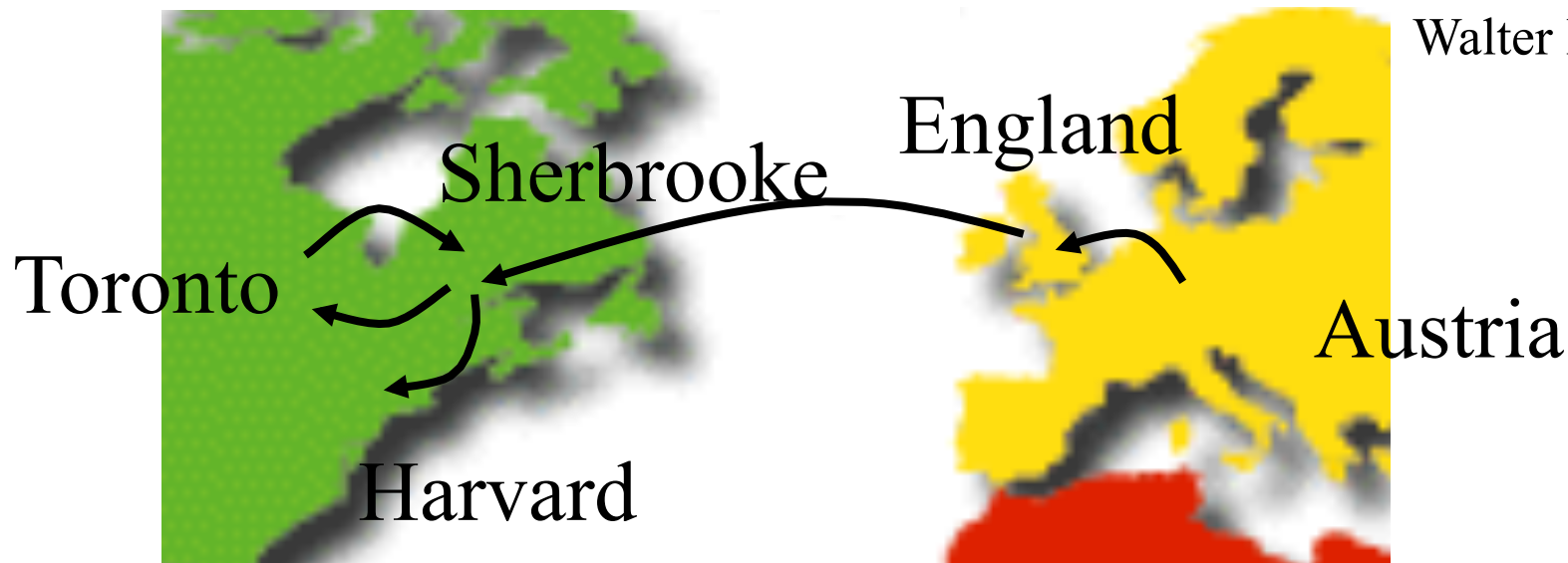
Walter Kohn and Canada

Nobel Prize in 1998 for Chemistry:
Development of *ab initio* methods

Density Functional Theory (WK)
(efficient, flexible, precise, parameters free)



Walter Kohn



Milestones : first-principles approach

Precursor : Thomas-Fermi approximation (1927)

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. Sham, Phys. Rev. **140**, A1133 (1965)

Ceperley, Alder (1980); Perdew, Zunger (1981) : computation and parametrization of the exchange and correlation energy needed in the local density approximation

Most cited papers

Papers published in APS journals (PRL, PRA, PRB, .. RMP),
most cited by papers published in APS journals

Table 1. <i>Physical Review</i> Articles with more than 1000 Citations Through June 2003				
Publication	# cites	Av. age	Title	Author(s)
PR 140, A1133 (1965)	3227	26.7	Self-Consistent Equations Including Exchange and Correlation Effects	W. Kohn, L. J. Sham
PR 136, B864 (1964)	2460	28.7	Inhomogeneous Electron Gas	P. Hohenberg, W. Kohn
PRB 23, 5048 (1981)	2079	14.4	Self-Interaction Correction to Density-Functional Approximations for Many-Electron Systems	J. P. Perdew, A. Zunger
PRL 45, 566 (1980)	1781	15.4	Ground State of the Electron Gas by a Stochastic Method	D. M. Ceperley, B. J. Alder
PR 108, 1175 (1957)	1364	20.2	Theory of Superconductivity	J. Bardeen, L. N. Cooper, J. R. Schrieffer
PRL 19, 1264 (1967)	1306	15.5	A Model of Leptons	S. Weinberg
PRB 12, 3060 (1975)	1259	18.4	Linear Methods in Band Theory	O. K. Anderson
PR 124, 1866 (1961)	1178	28.0	Effects of Configuration Interaction of Intensities and Phase Shifts	U. Fano
RMP 57, 287 (1985)	1055	9.2	Disordered Electronic Systems	P. A. Lee, T. V. Ramakrishnan
RMP 54, 437 (1982)	1045	10.8	Electronic Properties of Two-Dimensional Systems	T. Ando, A. B. Fowler, F. Stern
PRB 13, 5188 (1976)	1023	20.8	Special Points for Brillouin-Zone Integrations	H. J. Monkhorst, J. D. Pack
PR, <i>Physical Review</i> ; PRB, <i>Physical Review B</i> ; PRL, <i>Physical Review Letters</i> ; RMP, <i>Reviews of Modern Physics</i> .				

A basic reference on DFT and applications to solids

Richard M. Martin

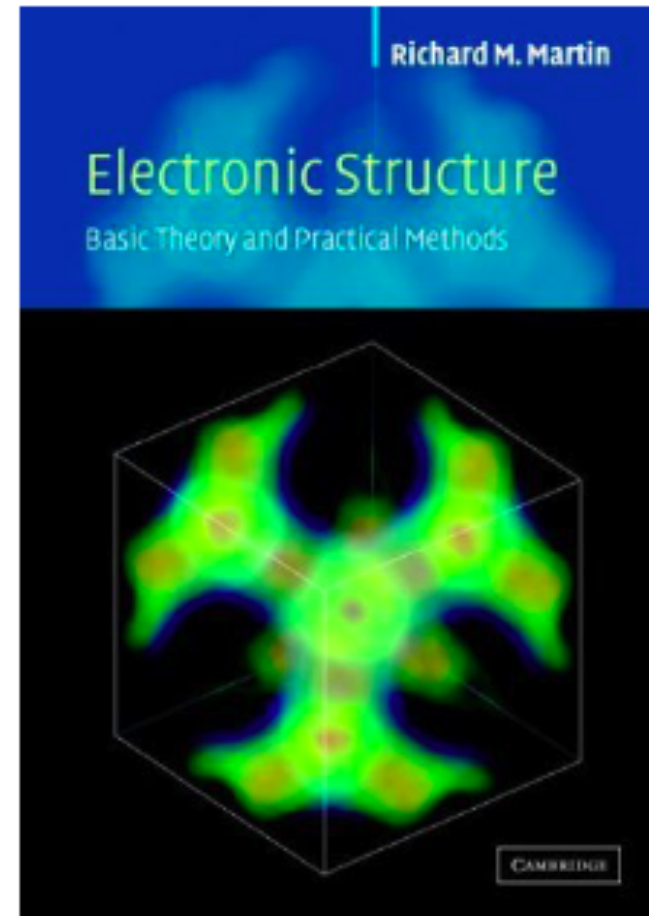
Cambridge University Press, 2004

Electronic Structure : Basic Theory and
Practical Methods

(ISBN: 0521782856)

For details, see

[http : //www.cambridge.org/uk/catalogue/catalogue.asp?isbn=0521782856](http://www.cambridge.org/uk/catalogue/catalogue.asp?isbn=0521782856)



Functionals of the density

What is a functional?

It is a quantity that depends non on a variable but on a function.

$$f(x) = Ax^2 \quad \text{function}$$

$$f[n] = \int n(x)v(x)dx \quad \text{functionnal}$$

Derivative

$$\frac{\partial f(x)}{\partial x} = \lim_{\alpha \rightarrow 0} \frac{f(x+\alpha) - f(x)}{\alpha}$$
$$\frac{\partial f[n]}{\partial n(x)} = \lim_{\alpha \rightarrow 0} \frac{f[n(x') + \alpha\delta(x'-x)] - f[n(x')]}{\alpha}$$

 function of x

Density functional theory:

First Hohenberg-Kohn theorem

Hohenberg et Kohn, Physical Review, vol 136, B864, (1964)

$$\begin{array}{l} \text{Assume:} \\ V(r) \rightarrow \Psi \rightarrow n(r) \\ V'(r) \rightarrow \Psi' \rightarrow n(r) \end{array}$$

$$E' = \langle \Psi' | H' | \Psi' \rangle < \langle \Psi | H' | \Psi \rangle = \langle \Psi | H - V(r) + V'(r) | \Psi \rangle$$

$$E' < E + \int [V'(r) - V(r)]n(r)dr$$

Something but starting from E :

$$E < E' + \int [V(r) - V'(r)]n(r)dr$$

Combine:

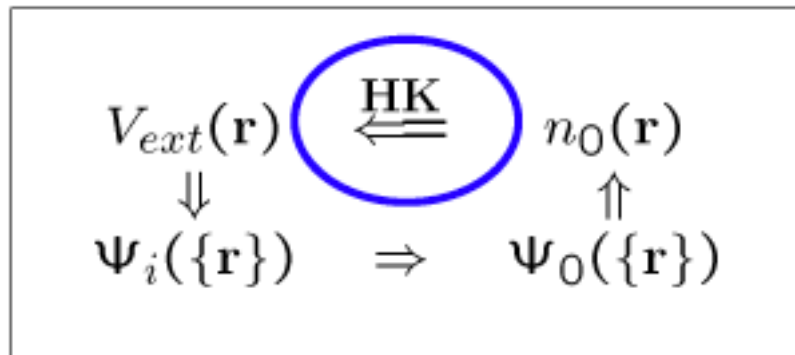
$$E' + E < E' + E \quad \text{Contradiction!!!}$$

$$n(r) \leftrightarrow V(r) \leftrightarrow \Psi$$

First Hohenberg-Kohn theorem

The ground state density $n(\mathbf{r})$ of a many-electron system determines uniquely the external potential $V(\mathbf{r})$, modulo one global constant.

Consequence : **formally**, the density can be considered as the fundamental variable of the formalism, instead of the potential.



No need for wavefunctions
or Schrödinger equation !

The constrained-search approach to DFT

M. Levy, Proc. Nat. Acad. Sci. USA, 76, 6062 (1979)

Use the extremal principle of QM.

$$\begin{aligned} E_V &= \min_{\Psi} \left\{ \langle \Psi | \hat{H}_V | \Psi \rangle \right\} = \min_n \left\{ \min_{\Psi \rightarrow n} \left\{ \langle \Psi | \hat{H}_V | \Psi \rangle \right\} \right\} \\ &= \min_n \left\{ \min_{\Psi \rightarrow n} \left\{ \langle \Psi | \hat{T} + \hat{V}_{\text{int}} + \hat{V} | \Psi \rangle \right\} \right\} \\ &= \min_n \left\{ \min_{\Psi \rightarrow n} \left\{ \langle \Psi | \hat{T} + \hat{V}_{\text{int}} | \Psi \rangle + \int n(\mathbf{r}) V(\mathbf{r}) d\mathbf{r} \right\} \right\} \\ &= \min_n \left\{ F[n] + \int n(\mathbf{r}) V(\mathbf{r}) d\mathbf{r} \right\} = \min_n \left\{ E_V[n] \right\} \end{aligned}$$

where $F[n] = \min_{\Psi \rightarrow n} \left\{ \langle \Psi | \hat{T} + \hat{V}_{\text{int}} | \Psi \rangle \right\}$ is a universal functional of the density ...

Not known explicitly !

The Kohn & Sham approach

The exchange-correlation energy

$F[n]$: large part of the total energy, hard to approximate

Kohn & Sham (Phys. Rev. **140**, A1133 (1965)) :
mapping of the interacting system on a non-interacting system

$$F[n] = \min_{\Psi \rightarrow n} \left\{ \langle \Psi | \hat{T} + \hat{V}_{\text{int}} | \Psi \rangle \right\}$$

If one considers a non-interacting electronic system :

$$T_s[n] = \min_{\Psi \rightarrow n} \left\{ \langle \Psi | \hat{T} | \Psi \rangle \right\} \quad \text{Kinetic energy functional of the density}$$

Exchange-correlation functional of the density :

$$E_{xc}[n] = F[n] - T_s[n] - \frac{1}{2} \int \frac{n(\mathbf{r}_1)n(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2$$

Not known explicitly !
But let's suppose
we know it

The Kohn-Sham potential

So, we have to minimize: (under constraint of total electron number)

$$E_V[n] = T_s[n] + \int V(\mathbf{r})n(\mathbf{r})d\mathbf{r} + \frac{1}{2} \int \frac{n(\mathbf{r}_1)n(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 + E_{xc}[n]$$

Introduction of Lagrange multipliers

$$0 = \delta \left(E_V[n] - \lambda \left\{ \int n(\mathbf{r})d\mathbf{r} - N \right\} \right) = \int \left(\frac{\delta T_s[n]}{\delta n} + V(\mathbf{r}) + \int \frac{n(\mathbf{r}_1)}{|\mathbf{r}_1 - \mathbf{r}|} d\mathbf{r}_1 + \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})} - \lambda \right) \delta n(\mathbf{r})d\mathbf{r}$$

If one considers the minimization for non-interacting electrons in a potential $V_{KS}(\mathbf{r})$, with the same density $n(\mathbf{r})$, one gets

$$0 = \int \left(\frac{\delta T_s[n]}{\delta n} + V_{KS}(\mathbf{r}) - \lambda \right) \delta n(\mathbf{r})d\mathbf{r}$$

Identification :

$$V_{KS}(\mathbf{r}) = V(\mathbf{r}) + \int \frac{n(\mathbf{r}_1)}{|\mathbf{r}_1 - \mathbf{r}|} d\mathbf{r}_1 + \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})}$$

The Kohn-Sham potential

The Kohn-Sham orbitals and eigenvalues

Non-interacting electrons in the Kohn-Sham potential :

$$\left(-\frac{1}{2} \nabla^2 + V_{\text{KS}}(\mathbf{r}) \right) \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r})$$

Density $n(\mathbf{r}) = \sum_i \psi_i^*(\mathbf{r}) \psi_i(\mathbf{r})$

$$V_{\text{KS}}(\mathbf{r}) = V_{\text{ext}}(\mathbf{r}) + \boxed{\int \frac{n(\mathbf{r}_1)}{|\mathbf{r}_1 - \mathbf{r}|} d\mathbf{r}_1} + \boxed{\frac{\delta E_{\text{xc}}[n]}{\delta n(\mathbf{r})}}$$

Hartree potential Exchange-correlation potential

To be solved self-consistently !

Note : by construction, at self-consistency, and supposing the exchange-correlation functional to be exact, the density will be the exact density, the total energy will be the exact one, but Kohn-Sham wavefunctions and eigenenergies correspond to a fictitious set of independent electrons, so they do not correspond to any exact quantity.

Minimum principle for the energy

Using the variational principle for non-interacting electrons, one can show that the solution of the Kohn-Sham self-consistent system of equations is equivalent to the minimisation of

$$E_{\text{KS}} [\{\psi_i\}] = \sum_i \langle \psi_i | -\frac{1}{2} \nabla^2 | \psi_i \rangle + \int V_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \int \frac{n(\mathbf{r}_1) n(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 + E_{\text{xc}}[n]$$

under constraints of orthonormalization $\langle \psi_i | \psi_j \rangle = \delta_{ij}$
for the occupied orbitals.

Density Functional Theory : approximations

An exact result for the exchange-correlation energy

(without demonstration)

The exchange-correlation energy, functional of the density is the integral over the whole space of the density times the local exchange-correlation energy per particle

$$E_{xc}[n] = \int n(\mathbf{r}_1) \varepsilon_{xc}(\mathbf{r}_1; n) d\mathbf{r}_1$$

while the local exchange-correlation energy per particle is the electrostatic interaction energy of a particle with its DFT exchange-correlation hole.

$$\varepsilon_{xc}(\mathbf{r}_1; n) = \int \frac{1}{2} \frac{\overline{n^{xc}(\mathbf{r}_2 | \mathbf{r}_1; n)}}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_2$$

$$\text{Sum rule : } \int \overline{n^{xc}(\mathbf{r}_2 | \mathbf{r}_1; n)} d\mathbf{r}_2 = -1$$

The local density approximation (I)

Hypothesis :

- the local XC energy per particle only depend on the local density
- and is equal to the local XC energy per particle of an homogeneous electron gas of same density (in a neutralizing background - « jellium »)

$$\epsilon_{xc}^{LDA}(\mathbf{r}_1; n) = \epsilon_{xc}^{hom}(n(\mathbf{r}_1))$$

Gives excellent numerical results ! Why ?

- 1) Sum rule is fulfilled
- 2) Characteristic screening length indeed depend on local density

The local density approximation (II)

Actual function : exchange part (x) + correlation part (c)

$$\varepsilon_x^{\text{hom}}(n) = Cn^{1/3} \quad \text{with} \quad C = -\frac{3}{4\pi} \left(3\pi^2\right)^{1/3}$$

for the correlation part, one resorts to accurate numerical simulations beyond DFT (e.g. Quantum Monte Carlo)

Corresponding exchange-correlation potential $V_{\text{xc}}(\mathbf{r}) = \frac{\delta E_{\text{xc}}[n]}{\delta n(\mathbf{r})}$

$$V_{\text{xc}}^{\text{approx}}(\mathbf{r}) = \mu_{\text{xc}}(n(\mathbf{r})) \quad \mu_{\text{xc}}(n) = \frac{d(n\varepsilon_{\text{xc}}^{\text{approx}}(n))}{dn}$$

$$\mu_x(n) = C \frac{4}{3} n^{1/3} = \frac{4}{3} \varepsilon_x^{\text{hom}}(n)$$

The local density approximation (III)

To summarize :

$$E^{LDA}[n] = T_s[n] + \int V_{ext}(\mathbf{r})n(\mathbf{r})d\mathbf{r} + \frac{1}{2} \int \frac{n(\mathbf{r}_1)n(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 + E_{xc}^{LDA}[n]$$

or

$$E^{LDA}[\{\psi_i\}] = \sum_i \langle \psi_i | -\frac{1}{2} \nabla^2 | \psi_i \rangle + \int V_{ext}(\mathbf{r})n(\mathbf{r})d\mathbf{r} + \frac{1}{2} \int \frac{n(\mathbf{r}_1)n(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 \\ + \int n(\mathbf{r}_1) \epsilon_{xc}^{LDA}(n(\mathbf{r}_1)) d\mathbf{r}_1$$

and

$$V_{KS}^{LDA}(\mathbf{r}) = V_{ext}(\mathbf{r}) + \int \frac{n(\mathbf{r}_1)}{|\mathbf{r}_1 - \mathbf{r}|} d\mathbf{r}_1 + \mu_{xc}^{hom}(n(\mathbf{r}))$$

Beyond the local density approximation

Generalized gradient approximations (GGA)

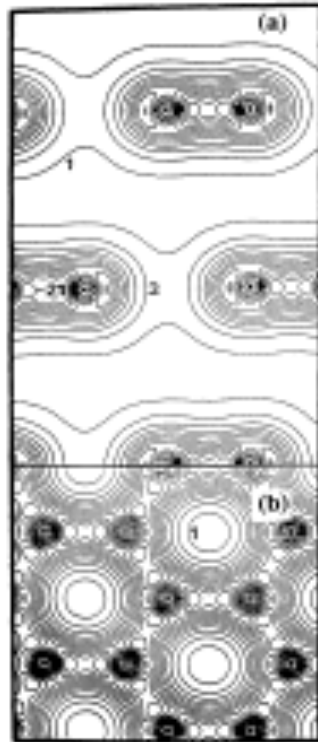
$$E_{xc}^{\text{approx}}[n] = \int n(\mathbf{r}_1) \varepsilon_{xc}^{\text{approx}}(n(\mathbf{r}_1), |\nabla n(\mathbf{r}_1)|, \nabla^2 n(\mathbf{r}_1)) d\mathbf{r}_1$$

No model system like the homogeneous electron gas !
Many different proposals, including one from Perdew, Burke and Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996), often abbreviated « PBE ».

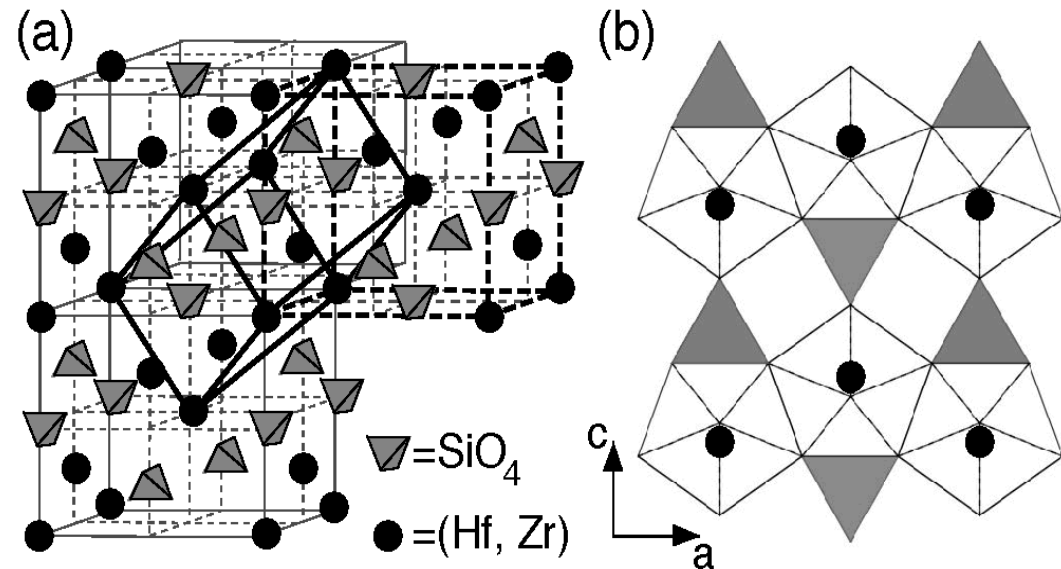
Others : PW86, PW91, LYP ...

Also : « hybrid » functionals (B3LYP),
« exact exchange » functional,
« self-interaction corrected » functionals ...

Example



Charge density of graphite



	HfSiO_4		ZrSiO_4	
	Th.	Expt.	Th.	Expt.
a	6.61	6.57	6.54	6.61
c	5.97	5.96	5.92	6.00
u	0.0672	0.0655	0.0645	0.0646
v	0.1964	0.1948	0.1945	0.1967
Volume	130.42	128.63	126.60	131.08
$d(\text{Si-O})$	1.62	1.61	1.61	1.62
$d(\text{M-O})$	2.14	2.10	2.10	2.13
	2.27	2.24	2.24	2.27
$\angle(\text{O-Si-O})$	97°	97°	97°	97°
	116°	117°	116°	116°

Accuracy, typical usage.

If covalent bonds, metallic bonds, ionic bonds :

2-3% for the geometry (bond lengths, cell parameters)

0.2 eV for the bonding energies (GGA)

problem with the band gap

For weak bonding situations (Hydrogen bonding, van derWaals), worse

Treatment of a few hundred atoms is OK on powerful parallel computers

Up to 50-100 atoms is OK on a PC.

The band gap problem

The DFT bandgap problem (I)

- DFT is a ground state theory
=> no direct interpretation of Kohn-Sham eigenenergies ε_i in

$$\left(-\frac{1}{2} \nabla^2 + V_{ext}(\mathbf{r}) + \int \frac{n(\mathbf{r}_1)}{|\mathbf{r}_1 - \mathbf{r}|} d\mathbf{r}_1 + V_{xc}(\mathbf{r}) \right) \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r})$$

- However $\{ \varepsilon_i \}$ are similar to quasi-particle band structure :
LDA / GGA results for valence bands are accurate ... but

NOT for the band gap $E_g^{KS} = \varepsilon_c - \varepsilon_v$

- The band gap can alternatively be obtained from total energy differences

$$E_g = E(N+1) + E(N-1) - 2 E(N) = \left\{ E(N+1) - E(N) \right\} - \left\{ E(N) - E(N-1) \right\} \quad \text{[correct expression !]}$$

in the limit $N \rightarrow \infty$

(where $E(N)$ is the total energy of the N - electron system)

The DFT bandgap problem (II)

- For LDA & GGA, the XC potential is a continuous functional of the number of electrons

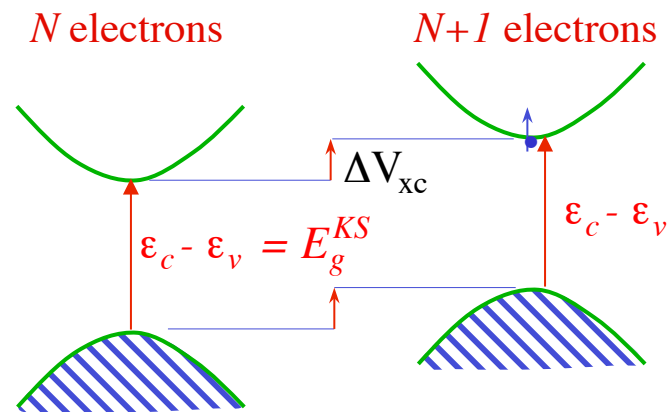
$$\epsilon_i = \frac{\partial E}{\partial f_i} \quad [\text{Janak's theorem}]$$

$$\Rightarrow E_g^{KS} = \epsilon_c - \epsilon_v \underset{N \rightarrow \infty}{=} E_g = E(N+1) + E(N-1) - 2E(N)$$

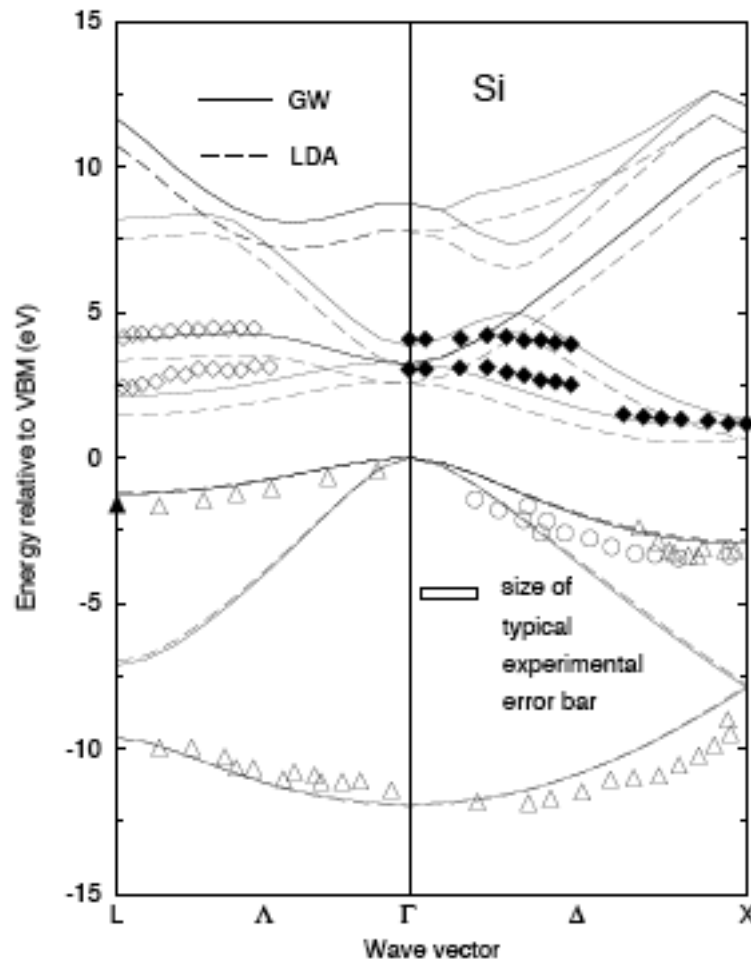
- In general, the XC potential might be discontinuous with the number of particle

e.g. xOEP

$$E_g^{KS} \neq E_g$$



The DFT bandgap problem (III)



Comparison of LDA and GW band Structures with photoemission and Inverse photoemission experiments for Silicon.

From "Quasiparticle calculations in solids",
by Aulbur WG, Jonsson L, Wilkins JW,

in Solid State Physics 54, 1-218 (2000)