Constrained Density Functional Theory: Formalism, Algorithms and Applications

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Dedicated to P. Dederichs

Prof. Peter Dederichs
(1938-2026)
passed away 1st Aug 2026

"With his passing, Forschungszentrum Jülich has lost an outstanding scientist who played a decisive role in shaping theoretical solid-state physics at Jülich over many decades"

https://www.fz-juelich.de/en/pgi/news/news/2026/obituary

More than 40 years ago ...

The founding paper of cDFT :

VOLUME 53, NUMBER 26 PHYSICAL REVIEW LETTERS 24 DECEMBER 1984

Ground States of Constrained Systems: Application to Cerium Impurities

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(Received 9 October 1984)

We present an extension of the density-functional theory to the lowest states compatible with arbitrary constraints. A broad class of interesting excitation problems connected with charge and magnetization fluctuations can be treated by such a method. We demonstrate the usefulness in *ab initio* calculations for Ce impurities.

... extension of density-functional theory to
lowest states compatible with arbitrary constraints ...

... charge and magnetization fluctuations ...

Dederichs et al, Phys Rev. Lett., 53, 2512 (1984)

Typical use of cDFT

- Placing local (atomic) magnetization (or charge) on a par with atomic positions or cell parameters as basic variables
- Finding parameters of many-body model Hamiltonians

  of real materials, e.g.

Hubbard model (here one band)

$$\hat{H} = -\sum_{\langle ij\rangle,\sigma} t_{ij}\, \hat{c}^{\dagger}_{i\sigma}\hat{c}_{j\sigma} + U \sum_{i} \hat{n}_{i\uparrow}\hat{n}_{i\downarrow}$$

Heisenberg model (here isotropic exchange, DM interaction, single-ion anisotropy)

$$\hat{H} = -\sum_{\langle ij\rangle} J_{ij}(\hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_j) - \sum_{\langle ij\rangle} \mathbf{D}_{ij} \cdot (\hat{\mathbf{S}}_i \times \hat{\mathbf{S}}_j) - \sum_{i} A_i (\hat{S}_i^z)^2$$

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For full references and complements, see accompanying lecture notes, as well as additional slides

Density Functional Theory, without spin

Electronic N-body problem

To be considered after Born-Oppenheimer approximation.

- decoupling of the nuclei and electron dynamics
- nuclei positions can be considered as fixed
- effective Born-Oppenheimer potential energy hypersurface

Born-Oppenheimer energy $$E_n^{\mathrm{BO}}\left(\{\mathbf{R}_I\}\right) = E_{II}\left(\{\mathbf{R}_I\}\right) + E_n^{\mathrm{el}}\left(\{\mathbf{R}_I\}\right)$$

Potential created by the nuclei, felt by the N electrons $$v_{\mathrm{ext}}(\mathbf{r}) = -\sum_I \frac{Z_I}{|\mathbf{r}-\mathbf{R}_I|}$$

$$\left[\sum_i \left(-\frac{1}{2}\nabla_i^2 + v_{\mathrm{ext}}(\mathbf{r}_i)\right) + \sum_{i<j}\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|}\right]\Psi_n(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N) = E_n^{\mathrm{el}}\,\Psi_n(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N)$$

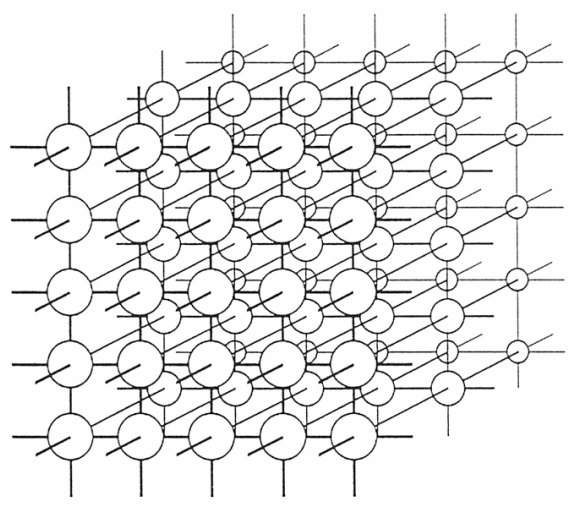
Schrödinger equation, very difficult to solve for more than 2 electrons

Complexity of N-body systems

Classical objects : fields $p(\mathbf{r},t), V(\mathbf{r},t), T(\mathbf{r},t), \mathbf{E}(\mathbf{r},t), \ldots$

or trajectories $\mathbf{R}_1(t), \mathbf{R}_2(t), \mathbf{R}_3(t), \ldots \mathbf{R}_N(t)$

Quantum objects : wavefunctions for interacting particles $\Psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \ldots, \mathbf{r}_N, t)$



Classical positions and velocities of 8 planets : 2x3x8=48 real numbers.

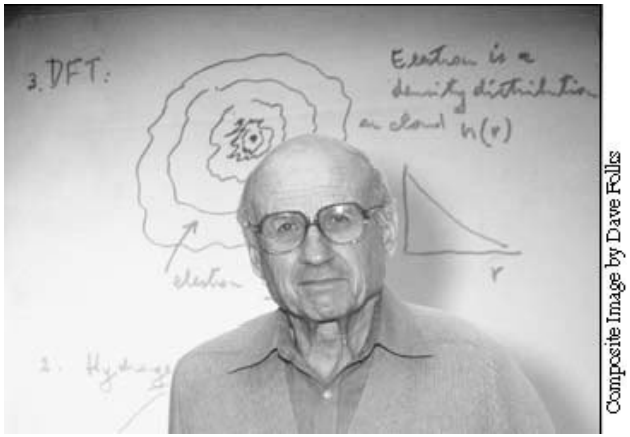
Suppose an oxygen atom : 8 electrons.
Quantum description at a particular time, on a discretized 10x10x10 real space mesh contained in a cube...
24-dimensional object : 10^{24} real numbers

Density-functional theory (DFT)

Quantum objects : wavefunctions
for interacting particles $\Psi(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3,...,\mathbf{r}_N,t)$

Hohenberg & Kohn (1964), Kohn & Sham (1965) :
Legendre transform between the density and potential
gives an effective potential for non-interacting particles

DFT : set of wavefunctions
for non-interacting particles $\psi_1(\mathbf{r},t),\psi_2(\mathbf{r},t),...\psi_N(\mathbf{r},t)$



For the oxygen atom, back to
8x10x10x10 real numbers,
but with an approximate treatment ...

W. Kohn, chemistry Nobel prize 1998

First Hohenberg-Kohn theorem (I)

The ground state density $\rho(\mathbf{r})$ (usually written $n(\mathbf{r})$ in DFT) of a many-electron system determines uniquely the external potential $v_{\text{ext}}(\mathbf{r})$ (modulo one global constant & fixed N electrons)

Context : set of many-body Hamiltonians that have the same kinetic energy but differ by their external potential $v_{\text{ext}}(\mathbf{r})$, a general one-body local potential

$$\hat{H}_{v_{\text{ext}}} = \hat{T} + \hat{V}_{ee} + \sum_i \hat{v}_{\text{ext}}(\mathbf{r}_i)$$

$$\rho(\mathbf{r}) = N \int \Psi^*(\mathbf{r}, \mathbf{r}_2, \mathbf{r}_3, \ldots \mathbf{r}_N) \Psi(\mathbf{r}, \mathbf{r}_2, \mathbf{r}_3, \ldots \mathbf{r}_N) \mathrm{d}\mathbf{r}_2 \mathrm{d}\mathbf{r}_3 \ldots \mathrm{d}\mathbf{r}_N$$

Advantages of working with the electronic density :

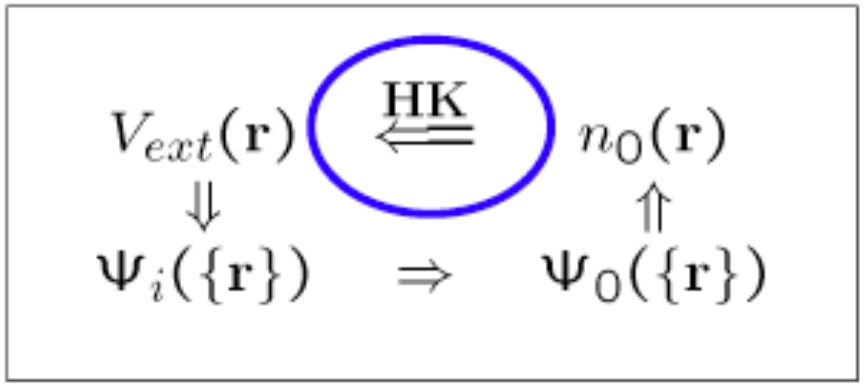
- dimensionality of the problem is reduced from 3N to 3
- visualisation is easy
- the electronic density is an experimental observable

First Hohenberg-Kohn theorem (II)

Proof by reductio ad absurdum (see additional slides) :

If two different (not simply by a global constant) potentials are considered, their ground states will have different densities.

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)

This approach will be crucial for cDFT – see later !

Use the extremal principle of QM (for fixed number of electrons N).

$$E^{\mathrm{GS}}_{v_{\mathrm{ext}}} = \min_{\Psi}\left\{\langle\Psi|\hat{H}_{v_{\mathrm{ext}}}|\Psi\rangle\right\} = \min_{\rho}\left\{\min_{\Psi\to\rho}\left\{\langle\Psi|\hat{H}_{v_{\mathrm{ext}}}|\Psi\rangle\right\}\right\}$$

$$= \min_{\rho}\left\{\min_{\Psi\to\rho}\left\{\langle\Psi|\hat{T}+\hat{V}_{ee}+\hat{v}_{\mathrm{ext}}|\Psi\rangle\right\}\right\}$$

$$= \min_{\rho}\left\{\min_{\Psi\to\rho}\left\{\langle\Psi|\hat{T}+\hat{V}_{ee}|\Psi\rangle+\int\rho(\mathbf{r})v_{\mathrm{ext}}(\mathbf{r})d\mathbf{r}\right\}\right\}$$

$$= \min_{\rho}\left\{F[\rho]+\int\rho(\mathbf{r})v_{\mathrm{ext}}(\mathbf{r})d\mathbf{r}\right\} = \min_{\rho}\left\{E_{v_{\mathrm{ext}}}[\rho]\right\}$$

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

Not known explicitely !

The exchange-correlation energy

$F[\rho] = \min_{\Psi\to\rho}\left\{\langle\Psi|\hat{T}+\hat{V}_{ee}|\Psi\rangle\right\}$ large part of energy, hard to approximate

Kohn & Sham : mapping interacting on non-interacting system

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

Consider a non-interacting electronic system :

$T_s[\rho] = \min_{\Psi\to\rho}\left\{\langle\Psi|\hat{T}|\Psi\rangle\right\}$ Kinetic energy functional of the density

Also introduce Hartree energy

=classical electrostatic energy

$$E_H[\rho] = \frac{1}{2}\int \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1-\mathbf{r}_2|}\mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2$$

Exchange-correlation functional of the density :

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

Not known explicitely !
But much smaller !
Let's suppose it is known …

The Kohn-Sham potential

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

$$E_{v_{\rm ext}}[\rho] = T_{\rm s}[\rho] + \int v_{\rm ext}(\mathbf{r})\rho(\mathbf{r})\,\mathrm{d}\mathbf{r} + \frac{1}{2}\int \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}\,\mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2 + E_{\rm xc}[\rho]$$

Introduction of Lagrange multipliers

$$0 = \delta\left(E_{v_{\rm ext}}[\rho] - \lambda\left\{\int \rho(\mathbf{r})\,\mathrm{d}\mathbf{r} - \mathbf{N}\right\}\right) = \int\left(\frac{\delta T_{\rm s}[\rho]}{\delta\rho(\mathbf{r})} + v_{\rm ext}(\mathbf{r}) + \int\frac{\rho(\mathbf{r}_1)}{|\mathbf{r}_1 - \mathbf{r}|}\,\mathrm{d}\mathbf{r}_1 + \frac{\delta E_{\rm xc}[\rho]}{\delta\rho(\mathbf{r})} - \lambda\right)\delta\rho(\mathbf{r})\mathrm{d}\mathbf{r}$$

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

$$0 = \int\left(\frac{\delta T_s[\rho]}{\delta\rho} + v_{\rm KS}(\mathbf{r}) - \lambda\right)\delta\rho(\mathbf{r})\mathrm{d}\mathbf{r}$$

Identification :

$$v_{\rm KS}(\mathbf{r}) = v_{\rm ext}(\mathbf{r}) + \int\frac{\rho(\mathbf{r}_1)}{|\mathbf{r}_1 - \mathbf{r}|}\,\mathrm{d}\mathbf{r}_1 + \frac{\delta E_{\rm xc}[\rho]}{\delta\rho(\mathbf{r})}$$

Kohn-Sham potential

The Kohn-Sham orbitals and eigenvalues

Non-interacting electrons in the Kohn-Sham potential :

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

Density $\rho(\mathbf{r}) = \sum_i \psi_i^*(\mathbf{r})\psi_i(\mathbf{r})$ Sum over occupied states only

$$v_{\rm KS}(\mathbf{r}) = v_{\rm ext}(\mathbf{r}) + \int \frac{\rho(\mathbf{r}_1)}{|\mathbf{r}_1 - \mathbf{r}|} d\mathbf{r}_1 + \frac{\delta E_{\rm xc}[\rho]}{\delta\rho(\mathbf{r})}$$

Hartree potential Exchange-correlation potential

To be solved self-consistently !

Note : by construction, at self-consistency, and supposing 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.

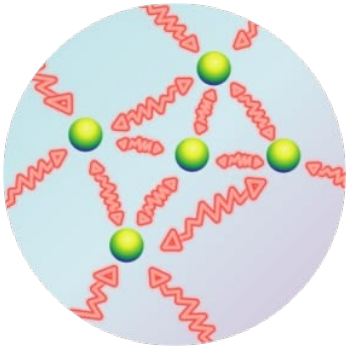
Minimum principle for energy

Using the variational principle for non-interacting electrons, solving Kohn-Sham self-consistent system of equations is equivalent to minimize

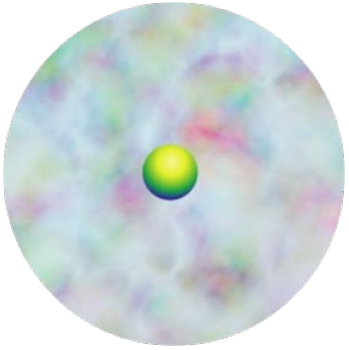
$$E_{\mathrm{DFT}}\left[\{\psi_i\}\right]=\sum_i\langle\psi_i|-\frac{1}{2}\nabla^2|\psi_i\rangle+\int v_{\mathrm{ext}}(\mathbf{r})\rho(\mathbf{r})\mathrm{d}\mathbf{r}+\frac{1}{2}\int\frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1-\mathbf{r}_2|}\mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2+E_{\mathrm{xc}}[\rho]$$

under constraints of orthonormalization $\langle\psi_i|\psi_j\rangle=\delta_{ij}$

for the occupied states.



Wavefunctions



DFT-KS : monoelectronic states

The XC energy

To be approximated !

Exact result : the XC energy can be expressed as

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

Local density approximation (LDA) :

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

$$\varepsilon_{\rm xc}^{\rm LDA}(\mathbf{r};\rho) = \varepsilon_{\rm xc}^{\rm hom}(\rho(\mathbf{r}))$$

$$E_{\rm xc}^{\rm LDA}[n] = \int n(\mathbf{r}_1)\varepsilon_{\rm xc}^{\rm LDA}(n(\mathbf{r}_1))\,\mathrm{d}\mathbf{r}_1$$

Generalized gradient approximations (GGA)

$$E_{\rm xc}^{\rm GGA}[n] = \int n(\mathbf{r}_1)\varepsilon_{\rm xc}^{\rm GGA}(n(\mathbf{r}_1),|\nabla n(\mathbf{r}_1)|)\,\mathrm{d}\mathbf{r}_1$$

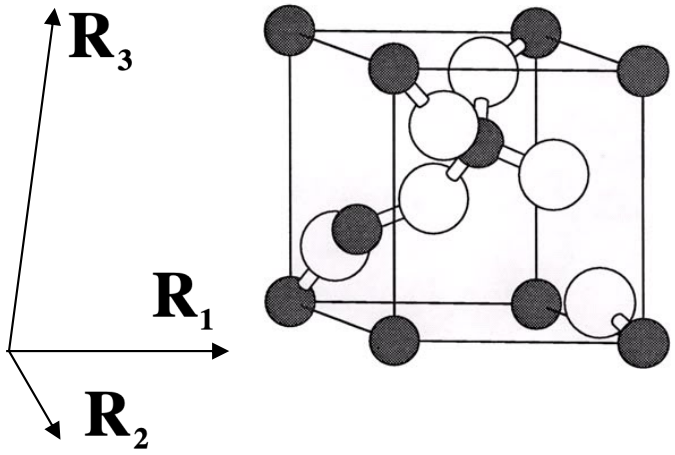
GGA can be e.g « PBE »

Perdew, Burke and Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996)

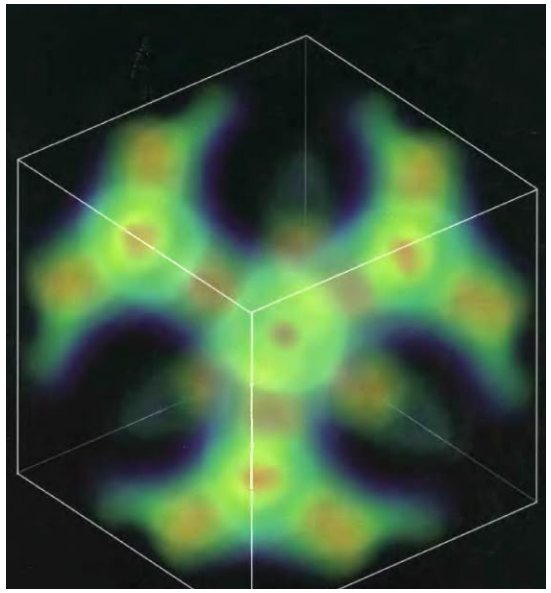
Beyond GGA : hybrids, mGGA,
+ van der Waals XC functionals

Logic of DFT (here for crystalline solids)

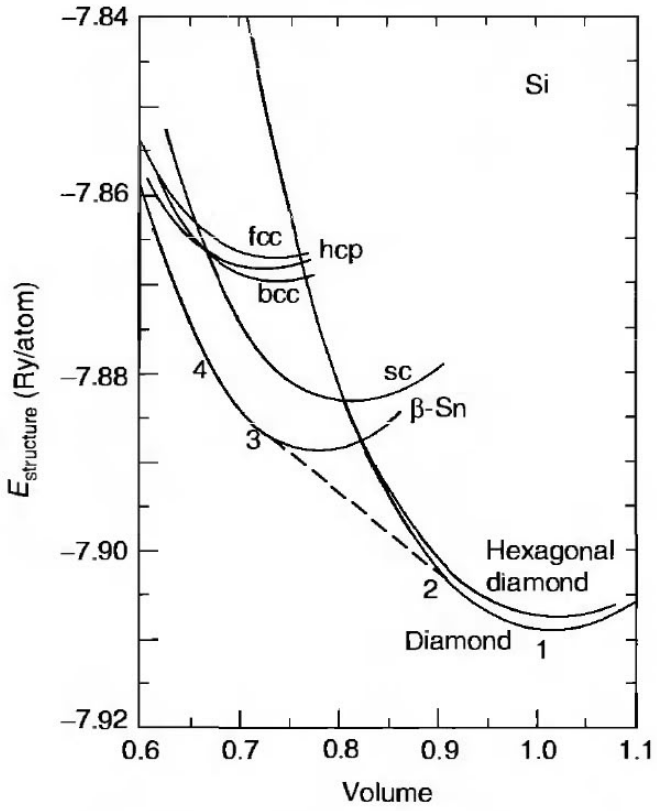
Input : Primitive vectors $\mathbf{R}_j$ + atomic species and positions



Output : Total energy
+ electronic density



Then (outside SCF loop)
equilibrium atomic positions and lattice parameters
from optimization of E



Properties from DFT…

Computation of ...

interatomic distances, angles, total energies

electronic charge densities ...

A basis for the computation of ..

chemical reactions

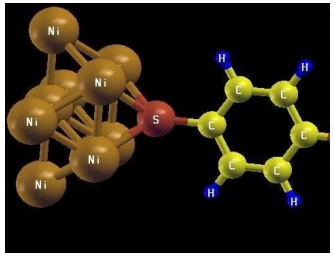
vibrational properties

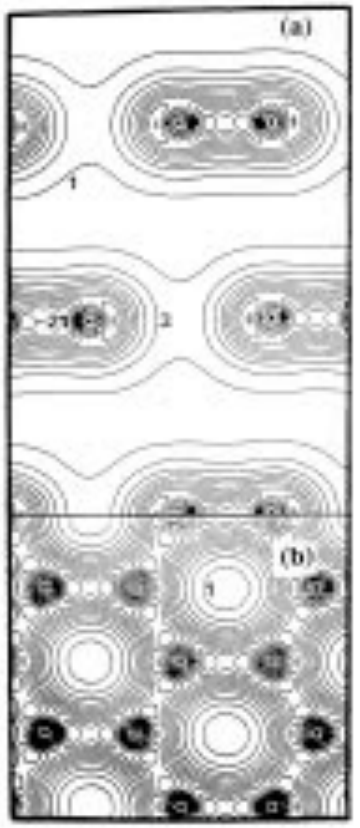
thermodynamic properties

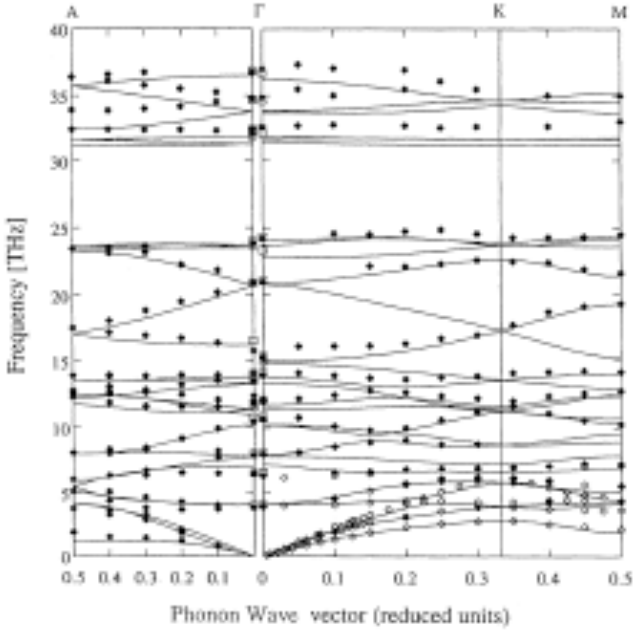
surface properties

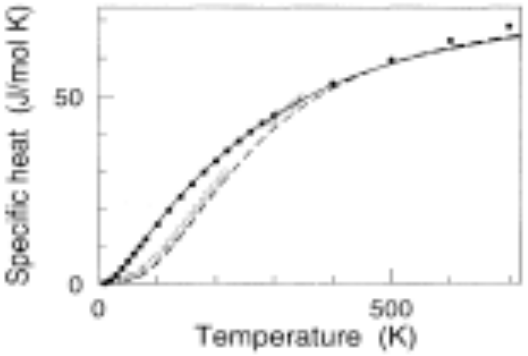
mechanical responses

...









DFT used for > hundred thousands

publications in the last 40 years

Constrained DFT, the basics

From Many-body WF or DFT to models ?

Model Hamiltonians consider « atomic » or « orbital » operators

(magnetization of an embedded atom, atomic charge, site occupation …)

$$\hat{H} = -\sum_{\langle ij\rangle,\sigma} t_{ij}\,\hat{c}^{\dagger}_{i\sigma}\hat{c}_{j\sigma} + U\sum_{i}\hat{n}_{i\uparrow}\hat{n}_{i\downarrow}$$

$$\hat{H} = -\sum_{\langle ij\rangle} J_{ij}(\hat{\mathbf{S}}_i\cdot\hat{\mathbf{S}}_j) - \sum_{\langle ij\rangle}\mathbf{D}_{ij}\cdot(\hat{\mathbf{S}}_i\times\hat{\mathbf{S}}_j) - \sum_{i} A_i(\hat{S}^z_i)^2$$

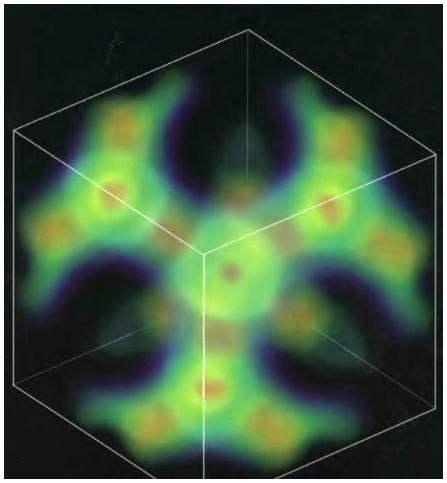
MBWF or DFT : Atomic charge ? Atomic magnetization ?

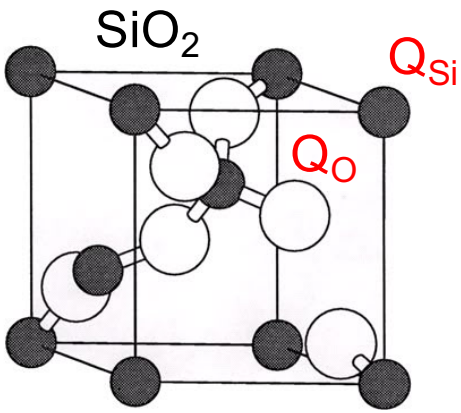
$$\rho(\mathbf{r}) = N\int \Psi^*(\mathbf{r},\mathbf{r}_2,\mathbf{r}_3,\ldots\mathbf{r}_N)\Psi(\mathbf{r},\mathbf{r}_2,\mathbf{r}_3,\ldots\mathbf{r}_N)\,d\mathbf{r}_2 d\mathbf{r}_3\ldots d\mathbf{r}_N = \langle\Psi|\delta(\hat{\mathbf{r}}-\mathbf{r})|\Psi\rangle$$

Charge density = (One-body) operator expectation value

A function of 3D space, not value for an atom !

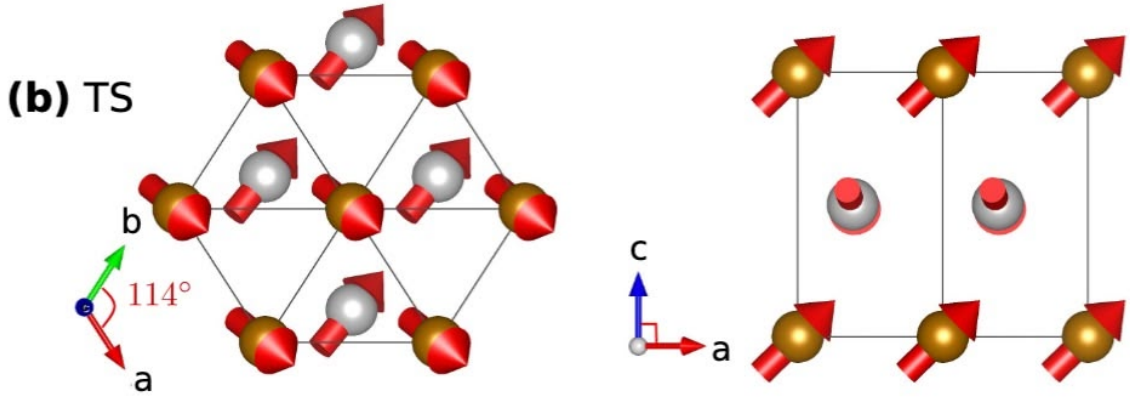
Definition of « atomic » quantities ?

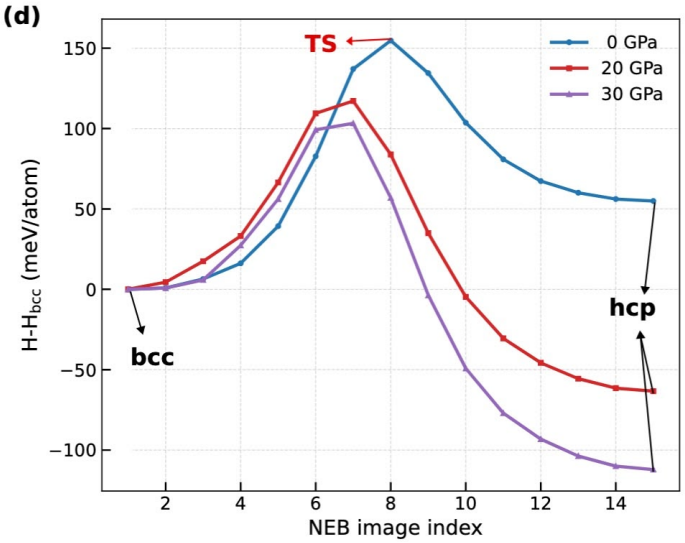




Can an atomic charge concept be present in DFT?
Output ?
Even better : input ?

Same problem : Atomic magnetization ?





"Atomic charge" : define V around atom, then $C_V[\rho] = \int_V \rho(\mathbf{r})\, d\mathbf{r}$

Some arbitrariness …

Dederichs et al, Phys Rev. Lett., 53, 2512 (1984)

Definition of generic « constraints » in cDFT

From Dederichs et al : atomic charge on atom τ

$$C_\tau = \langle \Psi | \hat{O}_{C\tau} | \Psi \rangle \qquad \text{with} \qquad \hat{O}_{C\tau} = \int_{V_\tau} \delta(\hat{\mathbf{r}} - \mathbf{r}) d\mathbf{r}$$

Different formulations of constraints :

- Use of smooth “weight function”
- Partitioning of space

$$C_I[\rho] = \int w_I(\mathbf{r})\, \rho(\mathbf{r})\, d\mathbf{r}$$

$$\sum_I w_I(\mathbf{r}) = 1 \qquad \text{e.g. “promolecules”} \qquad w_A(\mathbf{r}) = \frac{\rho_A^{(0)}(\mathbf{r})}{\sum_I \rho_I^{(0)}(\mathbf{r})}$$

Some arbitrariness … !

Constraints: magnetization, multipoles, charge

Magnetization (see later)

$$C_A[\rho_{\alpha\beta}] = \int w_A(\mathbf{r}) \left(\rho^{\uparrow}(\mathbf{r}) - \rho^{\downarrow}(\mathbf{r})\right) d\mathbf{r}$$

(collinear case)

$$\mathbf{C}_A[\rho_{\alpha\beta}] = \int w_A(\mathbf{r})\, \mathbf{m}(\mathbf{r})\, d\mathbf{r}$$

(non-collinear case)

Constraining to some multipole value or orbital content

$$C_A[\rho] = \int w_A(\mathbf{r}) r^l Y_{lm}(\hat{\mathbf{r}})\, \rho(\mathbf{r})\, d\mathbf{r}$$

$$C_d[\rho] = \int w(\mathbf{r}) \rho_d(\mathbf{r})\, d\mathbf{r}$$

For I running from 1 to maximum number of constraints $N_{\max}$:

Target values $N_I = \langle \Psi | \hat{O}_I | \Psi \rangle$ for the expectation value of a set of operators

Formal constrained DFT (I)

Constrained-search formulation of DFT (Levy1979)

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

started from $$E^{\mathrm{GS}}_{v_{\mathrm{ext}}} = \min_{\Psi}\left\{\langle\Psi|\hat{H}_{v_{\mathrm{ext}}}|\Psi\rangle\right\}$$

DFT gave $$E^{\mathrm{GS}}_{v_{\mathrm{ext}}} = \min_{\rho}\left\{E_{v_{\mathrm{ext}}}[\rho]\right\}$$ with

$$E_{v_{\mathrm{ext}}}[\rho] = F[\rho] + \int \rho(\mathbf{r}) v_{\mathrm{ext}}(\mathbf{r})\, d\mathbf{r} \quad \text{and} \quad F[\rho] = \min_{\Psi\to\rho}\left\{\langle\Psi|\hat{T}+\hat{V}_{ee}|\Psi\rangle\right\}$$

In cDFT, introduce constraints … $$N_I = \langle\Psi|\hat{O}_I|\Psi\rangle$$

What is the lowest-energy state respecting constraints ?

$$E^{\{N_I\}}_{v_{\mathrm{ext}}} = \min_{\substack{\Psi \\ \langle\Psi|\hat{O}_I|\Psi\rangle = N_I}}\left\{\langle\Psi|\hat{H}_{v_{\mathrm{ext}}}|\Psi\rangle\right\}$$

Formal constrained DFT (II)

Mimicking constrained-search approach + Kohn-Sham :

$$E_{v_{\rm ext}}^{\{N_I\}} = \min_{\substack{\Psi \\ \langle\Psi|\hat{O}_I|\Psi\rangle = N_I}} \left\{ \langle\Psi|\hat{H}_{v_{\rm ext}}|\Psi\rangle \right\} = \min_{\rho} \left\{ \min_{\substack{\Psi\to\rho \\ \langle\Psi|\hat{O}_I|\Psi\rangle = N_I}} \left\{ \langle\Psi|\hat{H}_{v_{\rm ext}}|\Psi\rangle \right\} \right\}$$

Introduce $$F^{\{N_I\}}[\rho] = \min_{\substack{\Psi\to\rho \\ \langle\Psi|\hat{O}_I|\Psi\rangle = N_I}} \left\{ \langle\Psi|\hat{T}+\hat{V}_{ee}|\Psi\rangle \right\} \qquad T_{\rm s}^{\{N_I\}}[\rho] = \min_{\substack{\Psi\to\rho \\ \langle\Psi|\hat{O}_I|\Psi\rangle = N_I}} \left\{ \langle\Psi|\hat{T}|\Psi\rangle \right\}$$

Then $$E_{v_{\rm ext}}^{\{N_I\}} = \min_{\rho} \left\{ E_{v_{\rm ext}}^{\{N_I\}}[\rho] \right\} \qquad E_{v_{\rm ext}}^{\{N_I\}}[\rho] = F^{\{N_I\}}[\rho] + \int \rho(\mathbf{r}) v_{\rm ext}(\mathbf{r}) d\mathbf{r}$$

and $$E_{\rm xc}^{\{N_I\}}[\rho] = F^{\{N_I\}}[\rho] - T_{\rm s}^{\{N_I\}}[\rho] - \frac{1}{2}\int \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \mathrm{d}\mathbf{r}_1 \mathrm{d}\mathbf{r}_2$$

In principle exact, but XC functional depends on constraints !

In practice …

Keep the usual XC functionals !

[Anyhow, exact XC functional is not known, even for the ground state …]

So, we have to minimize:

$$E_{\rm DFT}\left[\{\psi_i\}\right]=\sum_i\langle\psi_i|-\frac{1}{2}\nabla^2|\psi_i\rangle+\int v_{\rm ext}(\mathbf{r})\rho(\mathbf{r})\,\mathrm{d}\mathbf{r}+\frac{1}{2}\int\frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1-\mathbf{r}_2|}\mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2+E_{\rm xc}\left[\rho\right]$$

under constraints of orthonormalization $\langle\psi_i|\psi_j\rangle=\delta_{ij}$

for the occupied states

AND under constraints $N_I=\langle\Psi|\hat{O}_I|\Psi\rangle$

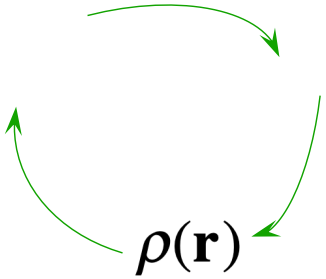
For a one-body operator : $N_I=\sum_i\langle\psi_i|\hat{O}_I|\psi_i\rangle$

Algorithms

Basic equations in DFT

Solve self-consistently Kohn-Sham equations

$$\left\{\begin{array}{l} \left(-\frac{1}{2}\nabla^2 + v_{\rm KS}(\mathbf{r})\right)\psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r}) \\ \rho(\mathbf{r}) = \sum_i \psi_i^*(\mathbf{r})\psi_i(\mathbf{r}) \quad \text{for occupied states} \\ v_{\rm KS}(\mathbf{r}) = v_{\rm ext}(\mathbf{r}) + \int \frac{\rho(\mathbf{r}_1)}{|\mathbf{r}_1 - \mathbf{r}|}\mathrm{d}\mathbf{r}_1 + \frac{\delta E_{\rm xc}[\rho]}{\delta\rho(\mathbf{r})} \end{array}\right.$$



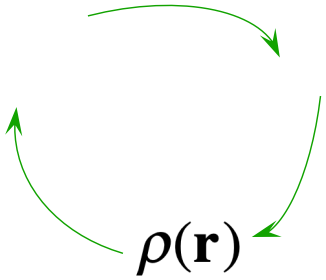
or minimize

$$E_{\rm DFT}\left[\{\psi_i\}\right] = \sum_i \langle\psi_i| -\frac{1}{2}\nabla^2 |\psi_i\rangle + \int v_{\rm ext}(\mathbf{r})\rho(\mathbf{r})\mathrm{d}\mathbf{r} + \frac{1}{2}\int \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}\mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2 + E_{\rm xc}[\rho]$$

with orthonormalization $\langle\psi_i|\psi_j\rangle = \delta_{ij}$ for occupied states

Algorithms for usual DFT

Many algorithms : e.g. potential-based SCF iterative approach



Natural iterative methodology (KS : in => out) :

$$v^{\text{in}}(\mathbf{r}) \rightarrow \psi_i(\mathbf{r}) \rightarrow \rho(\mathbf{r}) \rightarrow v^{\text{out}}(\mathbf{r})$$

Cycles will be numbered with n index/subscript

Monitor the difference $v^{\text{out}}(\mathbf{r}) - v^{\text{in}}(\mathbf{r})$

$$R^{\text{v}}[v_n^{\text{in}}] \triangleq v_n^{\text{out}} - v_n^{\text{in}}$$

(generic name : a "residual", here at step n)

Choose next « trial » input potential :

previous one + linear combination of previous residuals

such as to minimize norm of expected residual (Pulay-RMM)

$$v_{n+1}^{\text{in}} = v_n^{\text{in}} + P_n^{\text{v}} \sum_{j=1}^{n} \lambda_j R^{\text{v}}[v_j^{\text{in}}]$$

with $\{\lambda_j\}$ computed to minimize new residual

cDFT : how to impose the constraints ?

Introduce Lagrange multipliers $\{\lambda_I\}$,
and an “augmented” energy functional :

$$E_{v_{\text{ext}}}^{\{N_I\}+}\left[\rho,\{\lambda_I\}\right]=E_{v_{\text{ext}}}\left[\rho\right]+\sum_I \lambda_I\left(C_I\left[\rho\right]-N_I\right)$$

Dederich et al, Phys Rev. Lett., 53, 2512 (1984)

then $$E_{v_{\text{ext}}}^{\{N_I\}+}\left[\{\lambda_I\}\right]=\min_{\rho}\left\{E_{v_{\text{ext}}}^{\{N_I\}+}\left[\rho,\{\lambda_I\}\right]\right\}$$

The selected density acquires a dependence on $\{\lambda_I\}$

=> select Lagrange parameters to satisfy constraints …

Works in theory, but real departure from usual DFT algos !
In particular : inner SCF + outer determination of $\{\lambda_I\}$.

cDFT from penalty function

Energy functional with "penalty" term

$$E_{v_{\text{ext}}}^{\{N_I\}\text{pen}}\left[\rho,\{\kappa_I\}\right]=E_{v_{\text{ext}}}\left[\rho\right]+\sum_I\frac{\kappa_I}{2}\left(C_I\left[\rho\right]-N_I\right)^2$$

Ma & Dudarev, Phys Rev. B, 91, 054429 (2015)

then $E_{v_{\text{ext}}}^{\{N_I\}}=\lim_{\{\kappa_I\}\to\infty}E_{v_{\text{ext}}}^{\{N_I\}\text{pen}}\left[\{\kappa_I\}\right]=\lim_{\{\kappa_I\}\to\infty}\min_{\rho}\left\{E_{v_{\text{ext}}}^{\{N_I\}\text{pen}}\left[\rho,\left[\{\kappa_I\}\right]\right]\right\}$

Constrained energy is obtained by taking a limit !

If one works at finite $\{\kappa_I\}$ usual DFT algos are OK, but

- The limit has to be taken
- Numerically, optimization problem becomes "ill-conditioned" for large values of $\{\kappa_I\}$

cDFT from Lagrange multipliers again

Consider a potential-based SCF algorithm + cDFT

Lagrange multipliers can be determined exactly
from residual of the trial potential !
=> Formulation of new functional, in terms of the trial potential

In the case of one constraint labelled "A", trial potential "u" ,

$$E^{\mathrm{cDFT}}_{v_{\mathrm{ext}},N_A}[u] = E^{\mathrm{v}}_{v_{\mathrm{ext}}}[u] - R^{\mathrm{v}}_A[u]\left(W_{AA}\right)^{-1}\left(\rho^{\mathrm{v}}_A[u] - N_A\right)$$

Lagrange multiplier (for W_{AA} see lecture notes)

Then, generalization to multiple constraints ...
"Usual" DFT algorithms can be used (e.g. Pulay-RMM)

XG et al, J. Chemical Theory & Computation, 18, 6099 (2022)

Computation of Hubbard U from cDFT

The Hubbard U

$$\hat{H} = -\sum_{\langle ij\rangle,\sigma} t_{ij}\,\hat{c}^{\dagger}_{i\sigma}\hat{c}_{j\sigma} + U\sum_{i}\hat{n}_{i\uparrow}\hat{n}_{i\downarrow}$$

cDFT approach proposed by :

Cococcioni & de Gironcoli, Phys Rev. B, 71, 035105 (2005)

Compare DFT and non-self-consistent KS energy changes as a function of constrained charge q_I on orbital+site I

Warning : change to be done on one site –
not to be done on neighboring or other repeated ones => need supercell

$$E_{\mathrm{DFT}}\left[\{\psi_i\}\right] = \sum_i \langle\psi_i|-\frac{1}{2}\nabla^2|\psi_i\rangle + \int v_{\mathrm{ext}}(\mathbf{r})\rho(\mathbf{r})\,\mathrm{d}\mathbf{r} + \frac{1}{2}\int\frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1-\mathbf{r}_2|}\mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2 + E_{\mathrm{xc}}\left[\rho\right]$$

$$E_{\mathrm{KS}}\left[\{\psi_i\}\right] = \sum_i \langle\psi_i|-\frac{1}{2}\nabla^2|\psi_i\rangle + \int v_{\mathrm{KS}}(\mathbf{r})\rho(\mathbf{r})\,\mathrm{d}\mathbf{r}$$

U from curvatures of constrained functionals

$$E_{\mathrm{DFT}}\left[\{q_I\}\right] = \min_{\{\psi_i\}\to q_I}\left\{E_{\mathrm{DFT}}\left[\{\psi_i\}\right]\right\} = \min_{\{\psi_i\}}\left\{E_{\mathrm{DFT}}\left[\{\psi_i\}\right] + \sum_I \Lambda_I\left(n_I\{\psi_i\} - q_I\right)\right\}$$

$$E_{\mathrm{KS}}\left[\{q_I\}\right] = \min_{\{\psi_i\}\to q_I}\left\{E_{\mathrm{KS}}\left[\{\psi_i\}\right]\right\} = \min_{\{\psi_i\}}\left\{E_{\mathrm{KS}}\left[\{\psi_i\}\right] + \sum_I \Lambda_I^{\mathrm{KS}}\left(n_I\{\psi_i\} - q_I\right)\right\}$$

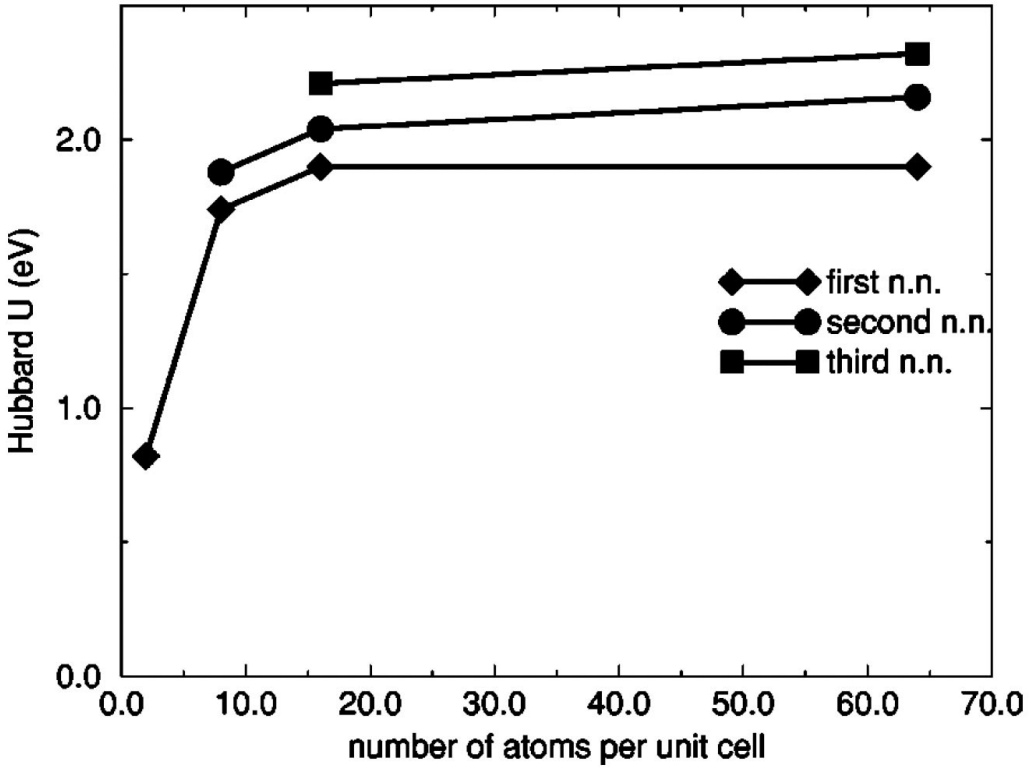
NB: These equations replace Eq.(106) and (108) of lecture notes.

Cococcioni & de Gironcoli argue that U is curvature with respect to occupation of orbital+site, due to interaction part of energy, around DFT+KS solution

$$U = \frac{\partial^2\left(E_{\mathrm{DFT}}\left[\{q_I\}\right] - E_{\mathrm{KS}}\left[\{q_I\}\right]\right)}{\partial q_I^2} = \frac{\partial^2 E_{\mathrm{DFT}}\left[\{q_I\}\right]}{\partial q_I^2} - \frac{\partial^2 E_{\mathrm{KS}}\left[\{q_I\}\right]}{\partial q_I^2}$$

In practice: computed in a supercell of increasing size, by applying a small local perturbation, then inverting a susceptibility matrix of increasing size

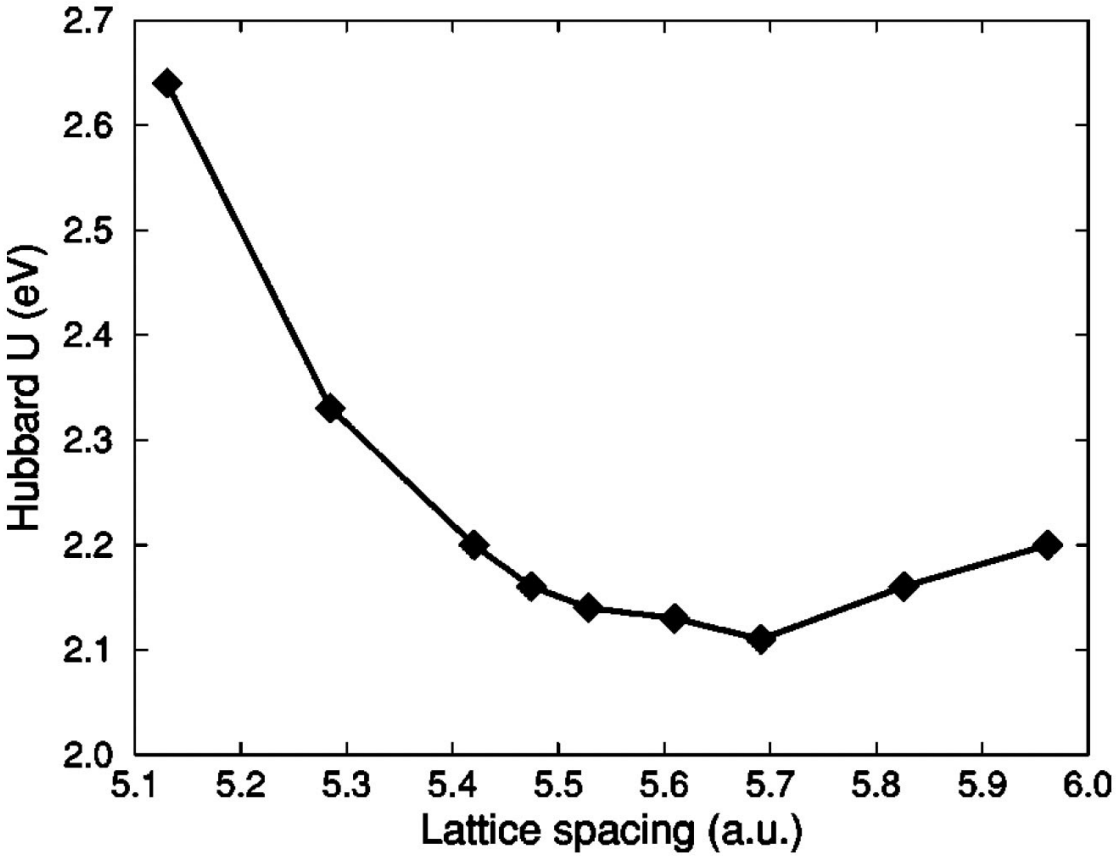
Hubbard U in metallic iron



Calculated Hubbard U in metallic iron for different supercells. Lines connect results from cell-extrapolation procedure and different symbols correspond to inclusion of screening contributions up to the indicated shell of (nearest-)neighbors of the perturbed atom.

Cococcioni & de Gironcoli, Phys Rev. B, 71, 035105 (2005)

Hubbard U in metallic iron



Hubbard U is not constant in real materials !

Lattice spacing dependence of the calculated Hubbard U parameter for iron.

Cococcioni & de Gironcoli, Phys Rev. B, 71, 035105 (2005)

(Constrained) Density Functional Theory with spin

Representation of spin

Spinorial WF (1-electron) 2-component vector = “spinor”

$$\Psi(\mathbf{r}) = \begin{pmatrix} \psi_{\uparrow}(\mathbf{r}) \\ \psi_{\downarrow}(\mathbf{r}) \end{pmatrix}$$

Norm $$N^2 = \langle \Psi | \Psi \rangle = \int \begin{pmatrix} \psi_{\uparrow}(\mathbf{r}) & \psi_{\downarrow}(\mathbf{r}) \end{pmatrix}^* \begin{pmatrix} \psi_{\uparrow}(\mathbf{r}) \\ \psi_{\downarrow}(\mathbf{r}) \end{pmatrix} d\mathbf{r} = \int |\psi_{\uparrow}(\mathbf{r})|^2 + |\psi_{\downarrow}(\mathbf{r})|^2 \, d\mathbf{r}$$

Scalar product $$\langle \Phi | \Psi \rangle = \int \begin{pmatrix} \varphi_{\uparrow}(\mathbf{r}) & \varphi_{\downarrow}(\mathbf{r}) \end{pmatrix}^* \begin{pmatrix} \psi_{\uparrow}(\mathbf{r}) \\ \psi_{\downarrow}(\mathbf{r}) \end{pmatrix} d\mathbf{r}$$

$$= \int \varphi_{\uparrow}^*(\mathbf{r})\psi_{\uparrow}(\mathbf{r}) + \varphi_{\downarrow}^*(\mathbf{r})\psi_{\downarrow}(\mathbf{r}) \, d\mathbf{r}$$

Pure spin-up or -down wavefunctions

Most often : pure spin up wavefunctions, or pure spin down wavefunctions

Explicitly $\Psi(\mathbf{r}) = \begin{pmatrix} \psi_{\uparrow}(\mathbf{r}) \\ 0 \end{pmatrix}$ or $\Psi(\mathbf{r}) = \begin{pmatrix} 0 \\ \psi_{\downarrow}(\mathbf{r}) \end{pmatrix}$

Such pure spin-up or spin-down wavefunctions
are orthogonal to each others.
Correspond to different quantum states.

Simply using spin-up or spin-down wavefunctions
often referred to “scalar wavefunctions”, at variance
with “spinorial wavefunctions” or “spinors”

Pauli matrices : spin along x, y, z + …

Pauli matrices : $\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$ $\sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$ $\sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$

Warning. Potential notation conflict : σ is for $\downarrow$ or $\uparrow$ in Hubbard Hamiltonian

Spin-magnetization vector (expectation value):

$$m_x(\mathbf{r}) = \left(\psi_\downarrow^*(\mathbf{r})\psi_\uparrow(\mathbf{r}) + \psi_\uparrow^*(\mathbf{r})\psi_\downarrow(\mathbf{r})\right)\frac{\hbar}{2} = \Psi^+(\mathbf{r})\sigma_x\Psi(\mathbf{r})\frac{\hbar}{2}$$

$$m_y(\mathbf{r}) = \left(i\psi_\downarrow^*(\mathbf{r})\psi_\uparrow(\mathbf{r}) - i\psi_\uparrow^*(\mathbf{r})\psi_\downarrow(\mathbf{r})\right)\frac{\hbar}{2} = \Psi^+(\mathbf{r})\sigma_y\Psi(\mathbf{r})\frac{\hbar}{2}$$

$$m_z(\mathbf{r}) = \left(\left|\psi_\uparrow(\mathbf{r})\right|^2 - \left|\psi_\downarrow(\mathbf{r})\right|^2\right)\frac{\hbar}{2} = \Psi^+(\mathbf{r})\sigma_z\Psi(\mathbf{r})\frac{\hbar}{2}$$

Spin-density matrix : $\rho_{\alpha\beta}(\mathbf{r}) = \psi_\alpha^*(\mathbf{r})\psi_\beta(\mathbf{r})$

$$\rho(\mathbf{r}) = \rho_{\uparrow\uparrow}(\mathbf{r}) + \rho_{\downarrow\downarrow}(\mathbf{r}) \qquad m_z(\mathbf{r}) = \left(\rho_{\uparrow\uparrow}(\mathbf{r}) - \rho_{\downarrow\downarrow}(\mathbf{r})\right)\frac{\hbar}{2}$$

Notation, often : $\rho_\uparrow(\mathbf{r}) \triangleq \rho_{\uparrow\uparrow}(\mathbf{r})$ $\rho_\downarrow(\mathbf{r}) \triangleq \rho_{\downarrow\downarrow}(\mathbf{r})$

Exchange-correlation functionals

In principle, exact functional is still a functional of density only !

$$E_{\mathrm{xc}}^{\mathrm{DFT}}[\rho] = \int \rho(\mathbf{r}) \varepsilon_{\mathrm{xc}}^{\mathrm{DFT}}(\mathbf{r};\rho)\,\mathrm{d}\mathbf{r}$$

However, information on density **+ spin** gives better approximate functionals.
"Spin-density functional theory" (SDFT).

O. Gunnarsson and B.I. Lunqvist, *Phys. Rev. B* **13**, 4274 (1976)

If spin-orbit coupling is ignored, most materials have either no magnetization (nowhere in space), or their magnetization is aligned with only one direction (chosen as z), everywhere in space.
The latter gives the collinear case :

$$E_{\mathrm{xc}}^{\mathrm{SDFT,coll}}[\rho_\uparrow,\rho_\downarrow] = \int \rho(\mathbf{r}) \varepsilon_{\mathrm{xc}}^{\mathrm{SDFT,coll}}(\mathbf{r};\rho_\uparrow,\rho_\downarrow)\,\mathrm{d}\mathbf{r}$$

If spin-orbit coupling is taken into account, either there is no magnetization (nowhere in space), or magnetization is not constrained to be aligned.
The latter gives the non-collinear case :

$$E_{\mathrm{xc}}^{\mathrm{SDFT,non\text{-}coll}}[\rho,\mathbf{m}] = \int \rho(\mathbf{r}) \varepsilon_{\mathrm{xc}}^{\mathrm{SDFT,non\text{-}coll}}(\mathbf{r};\rho,\mathbf{m})\,\mathrm{d}\mathbf{r}$$

Exchange-correlation potentials

Generalisation of Kohn-Sham equations :

Collinear case : pure spin-up or spin-down wavefunctions $|\psi_i^\alpha\rangle$

$$\left(-\frac{1}{2}\nabla^2 + v_{\mathrm{KS},\alpha}(\mathbf{r})\right)\psi_{i\alpha}(\mathbf{r}) = \varepsilon_{i\alpha}\psi_{i\alpha}(\mathbf{r})$$

i and α label the states
$\alpha = \uparrow$ or $\downarrow$

$$v_{\mathrm{KS},\alpha}(\mathbf{r}) = v_{\mathrm{ext}}(\mathbf{r}) + \int \frac{\rho(\mathbf{r}_1)}{|\mathbf{r}_1 - \mathbf{r}|}\mathrm{d}\mathbf{r}_1 + \frac{\delta E_{\mathrm{xc}}^{\mathrm{SDFT,\,coll}}\left[\rho_\uparrow, \rho_\downarrow\right]}{\delta\rho_\alpha(\mathbf{r})}$$

Spin-dependent XC potential

Non-collinear case : spinorial wavefunctions $|\Psi_i\rangle$

$$\left(-\frac{1}{2}\nabla^2 + v_{\mathrm{KS}}(\mathbf{r}) + \frac{\hbar}{2}\mathbf{B}_{xc}(\mathbf{r}).\boldsymbol{\sigma}\right)\Psi_i(\mathbf{r}) = \varepsilon_i\,\Psi_i(\mathbf{r})$$

i labels the states

$$v_{\mathrm{KS}}(\mathbf{r}) = v_{\mathrm{ext}}(\mathbf{r}) + \int \frac{\rho(\mathbf{r}_1)}{|\mathbf{r}_1 - \mathbf{r}|}\mathrm{d}\mathbf{r}_1 + \frac{\delta E_{\mathrm{xc}}^{\mathrm{SDFT,\,non\text{-}coll}}\left[\rho, \mathbf{m}\right]}{\delta\rho(\mathbf{r})}$$

$$B_{\mathrm{xc},j}(\mathbf{r}) = \frac{\delta E_{\mathrm{xc}}^{\mathrm{SDFT,\,non\text{-}coll}}\left[\rho, \mathbf{m}\right]}{\delta m_j(\mathbf{r})} \qquad j = x,\ y,\ z$$

XC magnetic field

Approximate XC functionals

LDA, GGA, hybrids : can easily be generalized.

E.g. Local spin-density approximation for the collinear case :

$$E_{\mathrm{xc}}^{\mathrm{LSDA}}\left[\rho_{\uparrow},\rho_{\downarrow}\right]=\int\rho(\mathbf{r})\varepsilon_{\mathrm{xc}}^{\mathrm{LSDA}}(\rho_{\uparrow}(\mathbf{r}),\rho_{\downarrow}(\mathbf{r}))\,\mathrm{d}\mathbf{r}$$

$\varepsilon_{\mathrm{xc}}^{\mathrm{LSDA}}(\rho_{\uparrow}(\mathbf{r}),\rho_{\downarrow}(\mathbf{r}))$ parameterized from homogeneous electron gas

Moreover, exchange energy in collinear case has simple general relationship with unpolarized exchange energy :

G.L. Oliver and J.P. Perdew, *Phys. Rev. A* **20**, 397 (1979)

$$E_{\mathrm{x}}^{\mathrm{SDFT,coll}}\left[\rho_{\uparrow},\rho_{\downarrow}\right]=\frac{1}{2}\left(E_{\mathrm{x}}^{\mathrm{DFT}}\left[2\rho_{\uparrow}\right]+E_{\mathrm{x}}^{\mathrm{DFT}}\left[2\rho_{\downarrow}\right]\right)$$

Indeed, comes from separate contribution of spins to exchange energy:

$$E_{\mathrm{x}}=-\frac{1}{2}\sum_{\alpha}\sum_{i,j}^{\mathrm{occ}}\int d\mathbf{r}\,d\mathbf{r}'\frac{\psi_{j\alpha}^{*}(\mathbf{r}')\psi_{i\alpha}^{*}(\mathbf{r}')\psi_{j\alpha}(\mathbf{r})\psi_{i\alpha}(\mathbf{r})}{|\mathbf{r}-\mathbf{r}|}$$

For non-collinear case, neglect directional dependence of local magnetization => falls back to collinear case.

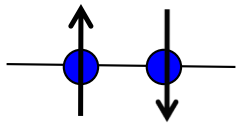
Methodologies : spin+symmetry

In practice … ?

Materials are treated within one of the following methodologies:

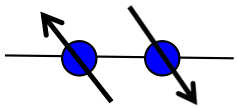
(1) No spin-polarization, scalar wavefunctions

(Many metals/covalent/ionic solids with light nuclei)



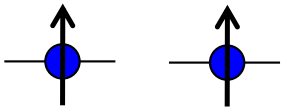
(2) No spin-polarization, spinorial wavefunctions (spin-orbit coupling)

(Many metals/covalent/ionic solids with heavier nuclei ;
the spin-polarization vanishes because of non-broken
time-reversal (TR) symmetry, compensation from TR symmetric states)



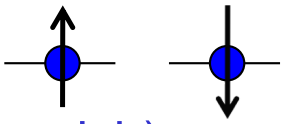
(3) Collinear spin, different spin-up and spin-down wavefunctions

(Ferromagnetic materials with light nuclei, finite systems with net spin,
in particular open shell atoms, and paramagnetic molecules, if light nuclei)



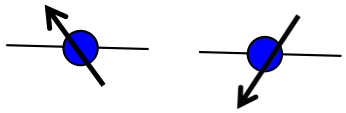
(4) Collinear spin, antiferromagnetic case

(Specific materials, often oxydes – the spin-down density
is space-symmetric to the spin-up density – spin-polarization does not vanish)



(5) Non-collinear spin-polarization

(Heavy nuclei with magnetization, need TR symm. spontaneously broken,
also important for some properties like the magnetocrystalline field,
or spin diffusion)



Constraints: magnetization or only its direction

Atomic magnetization

$$C_A[\rho_{\alpha\beta}] = \int w_A(\mathbf{r}) \left(\rho^{\uparrow}(\mathbf{r}) - \rho^{\downarrow}(\mathbf{r})\right) d\mathbf{r}$$

(collinear case)

$$\mathbf{C}_A[\rho_{\alpha\beta}] = \int w_A(\mathbf{r})\, \mathbf{m}(\mathbf{r})\, d\mathbf{r}$$

(non-collinear case)

Constraining only magnetization direction $\mathbf{n}_A$ (not the length) ?

Impose $\mathbf{C}_A[\rho_{\alpha\beta}] = C_A\, \mathbf{n}_A$ where C_A is left free

or $\mathbf{n}_A \times \mathbf{C}_A[\rho_{\alpha\beta}] = \mathbf{0}.$

Since $\mathbf{n}_A$ normalized, equivalent to impose $\mathbf{m}_A = \mathbf{n}_A \left(\mathbf{n}_A \cdot \mathbf{m}_A\right)$

Anyhow, will need one vector of Lagrange multipliers, for each atom

Applications

cDFT calculations with

Representation of mathematical formalism
with a Plane Wave basis set :
- wavefunctions
- density, potential

Periodic boundary conditions
=> wavefunctions characterized by a wavevector (k-vector)
PseudoPotentials (or Projector Augmented Waves – PAW)
Iterative techniques to solve the equations
(Schrödinger equation ; DFT Self-consistency ; optimisation of atomic positions)

cDFT potential-based SCF algorithm

XG et al, J. Chemical Theory & Computation, 18, 6099 (2022)

ABINIT software project

Ideas (1997) :

1) Softwares for first-principles simulations are more and more complex : needs a worldwide collaboration, of specialized, complementary, groups
2) Linux software development : ‘free software’ model

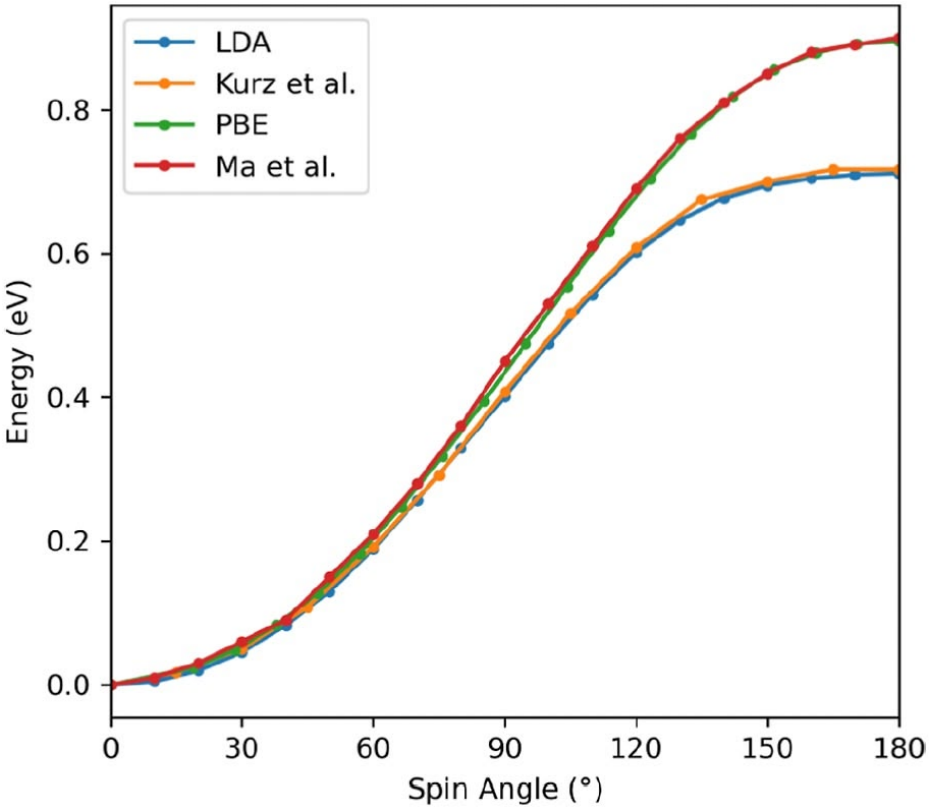
Now (2026) :

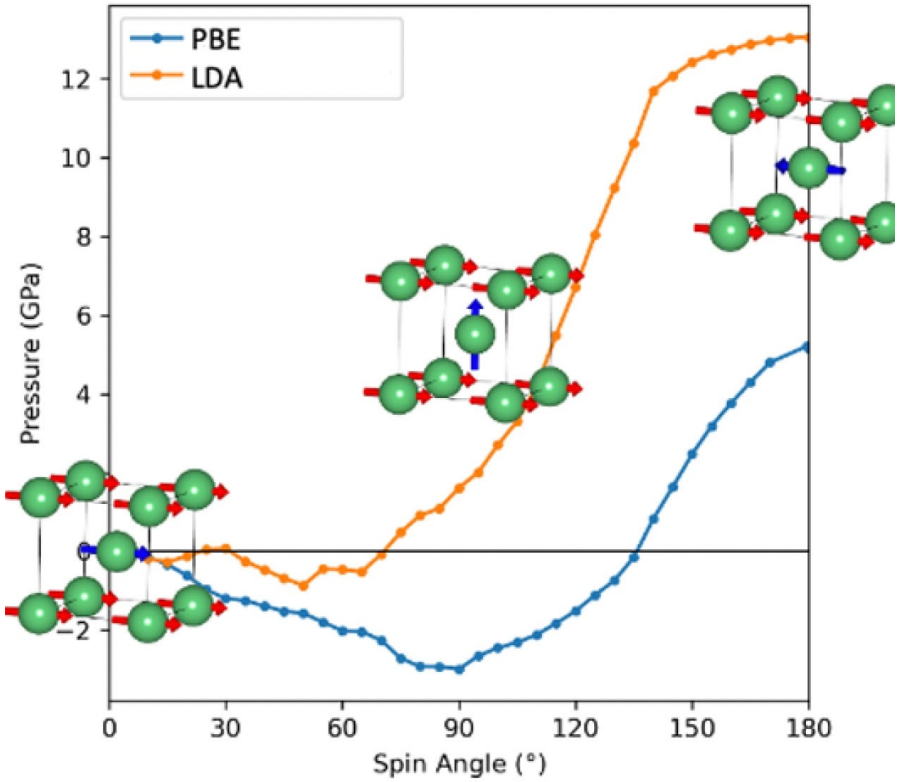
Estimated >2000 users worldwide
>900 kLines of F90 + many python scripts (abipy)
about 60 contributors to ABINITv8/v9/v10

ABINIT v10 used
in this presentation
https://www.abinit.org

Available freely
(GPL, like Linux).

BCC Fe : effect of angle between spins

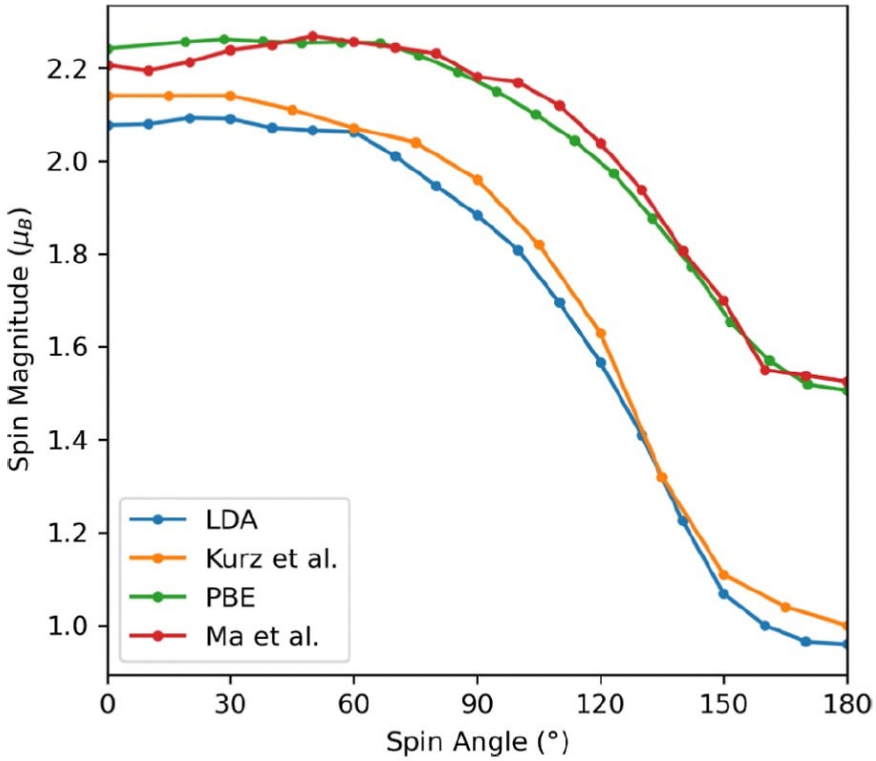


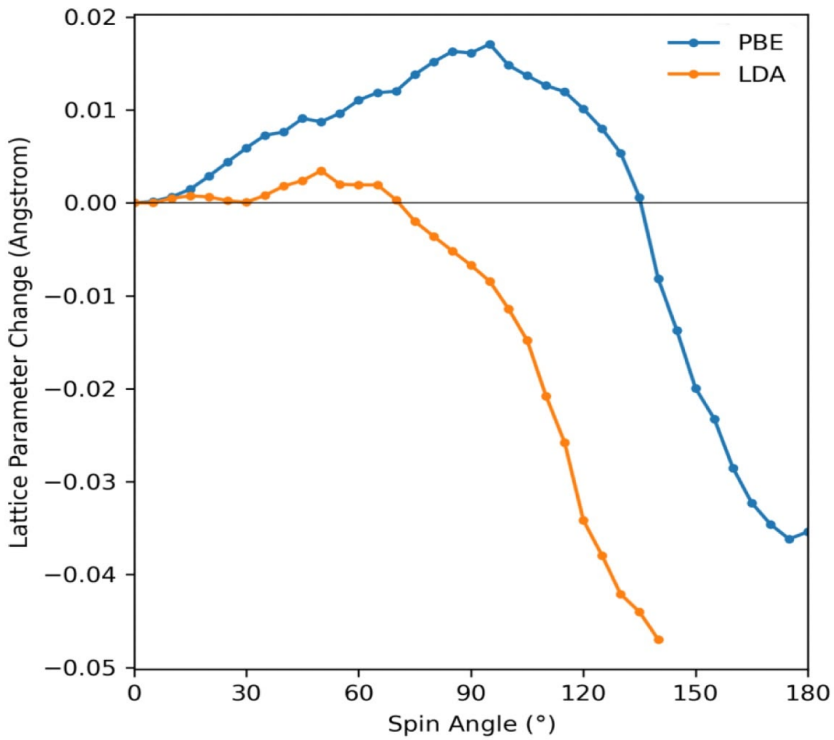


Energy (left), and pressure (right) as a function of the spin angle between the two sublattices in a Fe BCC conventional cell.

XG et al, J. Chemical Theory & Computation, 18, 6099 (2022)

BCC Fe : magnetization and lattice parameter





Spin magnitude (left), and relaxed lattice parameter (right) as a function of the spin angle between the two sublattices in a Fe BCC conventional cell.

XG et al, J. Chemical Theory & Computation, 18, 6099 (2022)

cDFT generalized to time-dependence

M. Royo and M. Stengel, Phys. Rev. X 16, 011049 (2026)

Spin-phonon Hessian becomes frequency-dependent

$$U(\omega) = K + i\omega G - \omega^2 M + \dots$$

K = static (adiabatic) Hessian (IFC, spin susceptibilities, adiabatic coupling)

G = Berry phase, precessional dynamics of spins

M = mass tensor, not only ions, but frequency dependence of electrons

Restriction to spin-spin sector

Generalized equation of motion for the spin amplitudes

$$\sum_l M_{jl}\,\ddot{s}_l - G_{jl}\,\dot{s}_l + K_{jl}\,s_l = 0,$$

j and l label atomic sites

Differs from well-established (Gilbert)-Landau-Lifschitz !

Inertial term $M_{jl}\,\ddot{s}_l$ Arise from inertia of electrons that do not adjust instantaneously

... Very small effect, though - see lecture notes

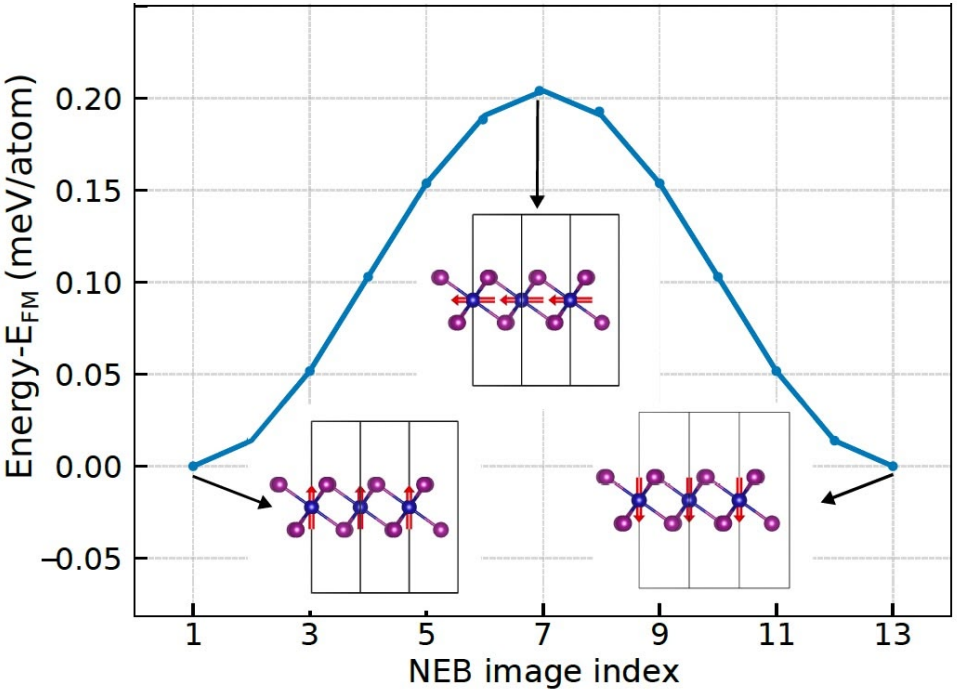
Magnetic transition states : CrI_3

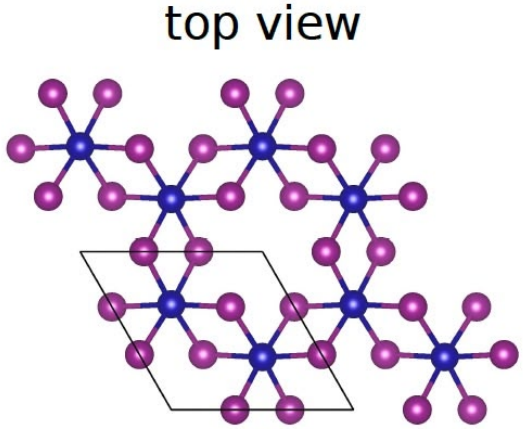
What is the transition state barrier for spin-flips ?

Setup generalized nudged elastic band method to find coupled magnetic and geometric transition states

CrI_3 : 2D ferromagnetic material.

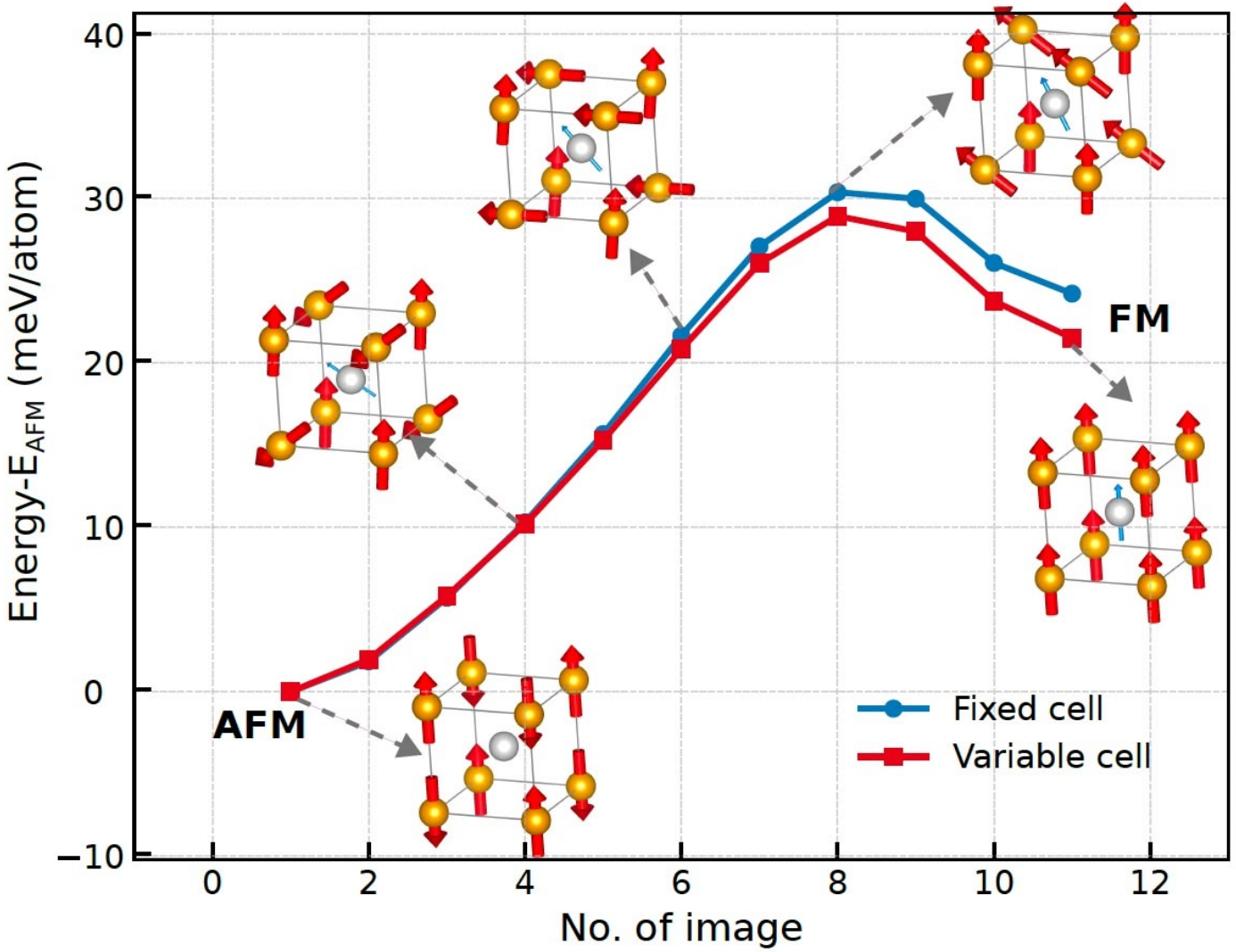
Weak lattice-spin coupling due to spin-orbit





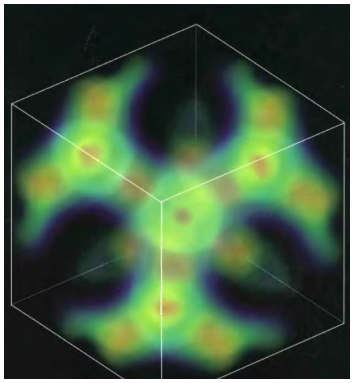
S. Rostami & XG, submitted

Magnetic transition states : FeRh



S. Rostami & XG, submitted

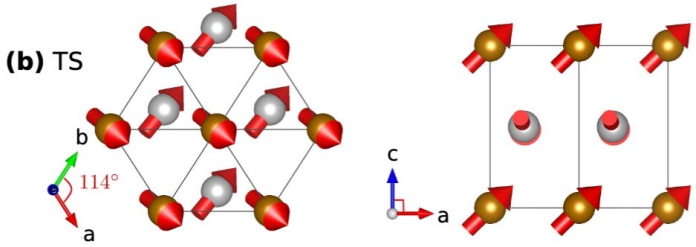
Summary



+ Reviewed DFT: mean-field theory with non-interacting electrons
  including extension to spin-DFT (collinear and non-collinear)

+ Constrained DFT : access to low-energy excited states

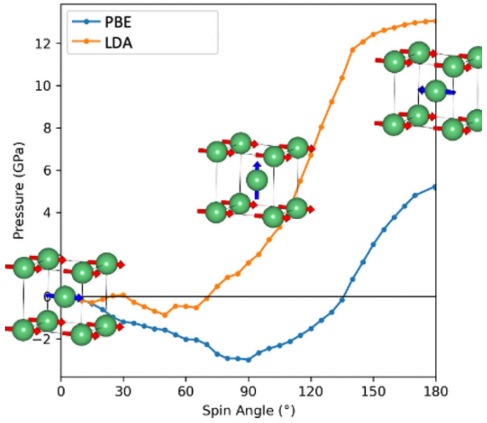
  Formally exact, but in practice, approximated
  Many types of constraints : local charge, atomic magnetization, orbital occupations ...
  Target value of constaints become input variable
  Computation of parameters of models

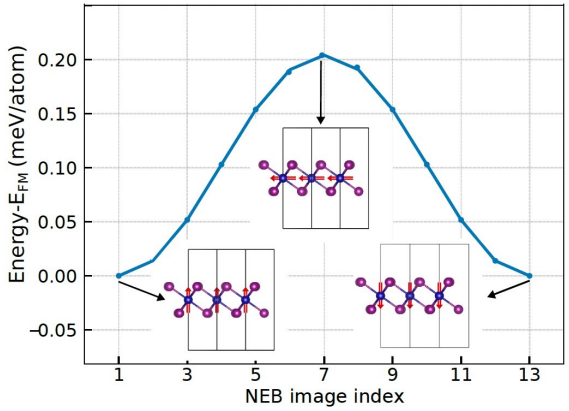


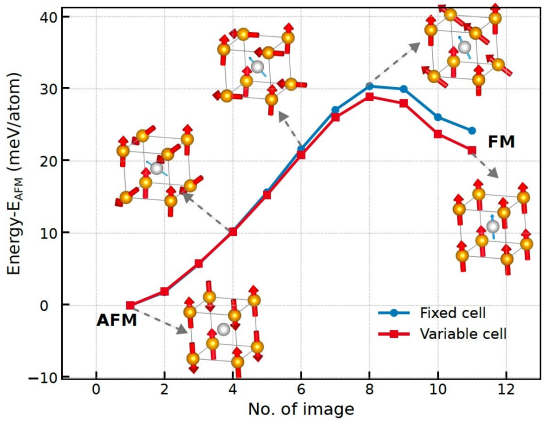
+ Algorithms : Lagrange multipliers,
  penalty function, potential-based SCF

+ Computation of the Hubbard U

+ Applications : spin angle (BCC iron), mass of magnons, magnetic transitions







Additional slides

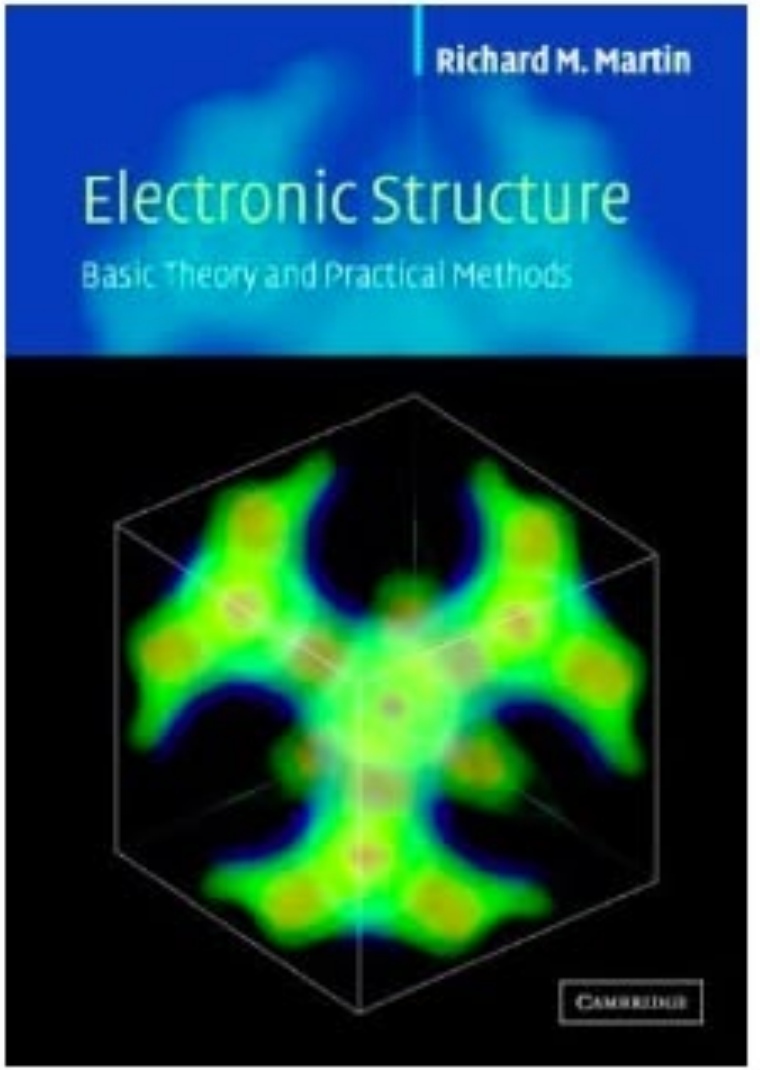
Basic reference on DFT and applications to solids

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

First Hohenberg-Kohn theorem (III)

The proof ...

First, a lemma.
Consider two local potentials $V_1(\mathbf{r})$ and $V_2(\mathbf{r})$.
Their ground-state wavefunctions may or may not be degenerate,
but one wavefunction Ψ cannot be common to both, except if the potentials differ only by a shift, or are identical everywhere
(except at points of zero density - these points forming a set of measure zero).
Indeed, the difference between the corresponding Schrödinger equations would imply

$$\left(\sum_{i=1}^{N}\left[V_1(\mathbf{r}_i)-V_2(\mathbf{r}_i)\right]+\Delta E\right)\Psi(\mathbf{r}_1,\mathbf{r}_2,...,\mathbf{r}_N)=0$$

for each many-dimensional point (=each configuration of electrons).
Fixing the positions corresponding to the indices from 2 to N, one obtains that the difference between $V_1(\mathbf{r})$ and $V_2(\mathbf{r})$ must be a constant in space.

First Hohenberg-Kohn theorem (IV)

So, we define Ψ_1 the (or one of the) ground-state wavefunction(s) of $\hat{H}_{V1}$, with associated charge density $\rho_1(\mathbf{r})$ and Ψ_2 the (or one of the) ground-state wavefunction(s) of H_{V2}, with associated charge density $\rho_2(\mathbf{r})$.

$$E_1 = \langle \Psi_1 | \hat{H}_{V1} | \Psi_1 \rangle \qquad E_2 = \langle \Psi_2 | \hat{H}_{V2} | \Psi_2 \rangle$$

Due to the variational principle, $E_1 = \langle \Psi_1 | \hat{H}_{V1} | \Psi_1 \rangle \; < \; \langle \Psi_2 | \hat{H}_{V1} | \Psi_2 \rangle$

Here, a strict inequality holds, because Ψ_2 cannot be one of the ground-state wavefunctions of $\hat{H}_{V1}$ (see previous slide) . The $\hat{H}_{V1}$ and $\hat{H}_{V2}$ Hamiltonians only differ by their one-electron local potential, so that

$$\begin{aligned}
\langle \Psi_2 | \hat{H}_{V1} | \Psi_2 \rangle &= \langle \Psi_2 | \hat{H}_{V2} | \Psi_2 \rangle + \langle \Psi_2 | \hat{H}_{V1} - \hat{H}_{V2} | \Psi_2 \rangle \\
&= \langle \Psi_2 | \hat{H}_{V2} | \Psi_2 \rangle + \int \left(V_1(\mathbf{r}) - V_2(\mathbf{r}) \right) \rho_2(\mathbf{r}) \, d\mathbf{r} \\
&= E_2 + \int \left(V_1(\mathbf{r}) - V_2(\mathbf{r}) \right) \rho_2(\mathbf{r}) \, d\mathbf{r}
\end{aligned}$$

So that $\boxed{E_1 < E_2 + \int \left(V_1(\mathbf{r}) - V_2(\mathbf{r}) \right) \rho_2(\mathbf{r}) \, d\mathbf{r}}$

First Hohenberg-Kohn theorem (V)

$$E_1 < E_2 + \int \left(V_1(\mathbf{r}) - V_2(\mathbf{r})\right) \rho_2(\mathbf{r}) \mathrm{d}\mathbf{r}$$

By the same line of thought, interchanging 1 and 2, we get

$$E_2 < E_1 + \int \left(V_2(\mathbf{r}) - V_1(\mathbf{r})\right) \rho_1(\mathbf{r}) \mathrm{d}\mathbf{r}$$

Summing the two inequalities give $0 < \int \left(V_2(\mathbf{r}) - V_1(\mathbf{r})\right) \left(\rho_1(\mathbf{r}) - \rho_2(\mathbf{r})\right) \mathrm{d}\mathbf{r}$

Postulating $\rho_1(\mathbf{r})$ equal to $\rho_2(\mathbf{r})$ everywhere leads to 0 < 0 , which is obviously wrong. So, we have proven that the knowledge of the ground-state density defines the one-body local potential up to a constant.
The one-body local potential is thus a functional of the ground-state density, as well as all the quantities that may be known formally once the potential is known up to a constant (like the set of ground-state wavefunctions).

If one fixes the shift in the potential through a simple condition (like "the external potential goes to zero at infinite distance"), the electronic energy is also a functional of the density.
Indeed, the hamiltonian is uniquely defined by the specification of the external potential, and the electronic energy is its expectation value.

Exact XC functional unknown ?!

Need a good approximation ...
Actually, exact results are known !

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

$$E_{\mathrm{xc}}[\rho] = \int \rho(\mathbf{r}) \varepsilon_{\mathrm{xc}}(\mathbf{r};\rho)\, \mathrm{d}\mathbf{r}$$

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

$$\varepsilon_{\mathrm{xc}}(\mathbf{r};\rho) = \int \frac{1}{2} \frac{\overline{\rho^{\mathrm{xc}}}(\mathbf{r}'|\mathbf{r};\rho)}{|\mathbf{r}-\mathbf{r}'|} \mathrm{d}\mathbf{r}'$$

Sum rule : $\int \overline{\rho^{\mathrm{xc}}}(\mathbf{r}'|\mathbf{r};\rho)\, \mathrm{d}\mathbf{r}' = -1$

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 »)

$$\varepsilon_{xc}^{LDA}(\mathbf{r};\rho) = \varepsilon_{xc}^{hom}(\rho(\mathbf{r}))$$

Gives excellent numerical results ! Why ?

1) Sum rule is fulfilled

2) Characteristic screening length indeed depend on local density

Local density approximation (II)

Actual function : exchange part + correlation part

$$\varepsilon_{\mathrm{x}}^{\mathrm{hom}}(\rho) = C\rho^{1/3} \qquad \text{with} \qquad C = -\frac{3}{4\pi}\left(3\pi^2\right)^{1/3}$$

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

Corresponding exchange-correlation potential $v_{\mathrm{xc}}(\mathbf{r}) = \dfrac{\delta E_{\mathrm{xc}}[n]}{\delta\rho(\mathbf{r})}$

$$v_{\mathrm{xc}}^{\mathrm{LDA}}(\mathbf{r}) = \mu_{\mathrm{xc}}\left(\rho(\mathbf{r})\right) \qquad \mu_{\mathrm{xc}}(\rho) = \frac{\mathrm{d}\left(\rho\varepsilon_{\mathrm{xc}}^{\mathrm{hom}}(\rho)\right)}{\mathrm{d}\rho}$$

$$\mu_{\mathrm{x}}(\rho) = C\frac{4}{3}\rho^{1/3} = \frac{4}{3}\varepsilon_{\mathrm{x}}^{\mathrm{hom}}(\rho)$$

Beyond local density approximation

Generalized gradient approximations (GGA)

$$E_{\mathrm{xc}}^{\mathrm{GGA}}[\rho] = \int \rho(\mathbf{r}) \varepsilon_{\mathrm{xc}}^{\mathrm{GGA}}(\rho(\mathbf{r}), |\nabla \rho(\mathbf{r})|) \, \mathrm{d}\mathbf{r}$$

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, HSE06),
« exact exchange » functional,
« self-interaction corrected » functionals ...