Degeneracies, orbital currents, and non-collinear magnetism: What can we learn from current-density functionals and orbital functionals

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OUTLINE

- Basics of ground-state DFT
- Optimized effective potential method (OPM, OEP)
- Construction of orbital functionals for E_{xc} using TDDFT
- CDFT-OEP
- Non-collinear OEP

THANKS

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Basic theorems of ground-state density functional theory

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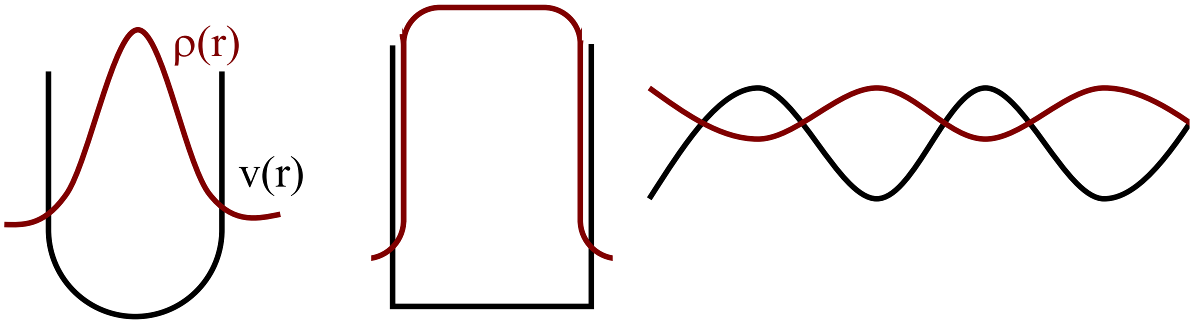
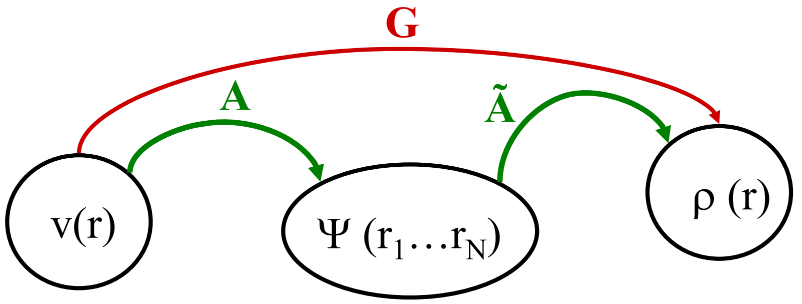
compare ground-state densities $\rho(r)$ resulting from different external potentials $v(r)$.



QUESTION: **Are the ground-state densities coming from different potentials always different?**



single-particle
potentials having
nondegenerate
ground state

ground-state
wavefunctions

ground-state
densities

Hohenberg-Kohn-Theorem (1964)

$$\boxed{G: v(r) \rightarrow \rho\,(r) \quad \text{is invertible}}$$

Proof

Step 1: Invertibility of map A

Solve many-body Schrödinger equation for the external potential:

$$\hat{V} = \frac{\left(E - \hat{T} - \hat{W}_{ee}\right)\Psi}{\Psi}$$

$$\sum_{j=1}^{N} v\left(r_j\right) = -\frac{\hat{T}\Psi}{\Psi} - W_{ee}\left(\vec{r}_1 \ldots \vec{r}_N\right) + \text{constant}$$

This is manifestly the inverse map: A given Ψ uniquely yields the external potential.

Step 2: Invertibility of map Ã (HK proof by reductio ad absurdum)

Consequence

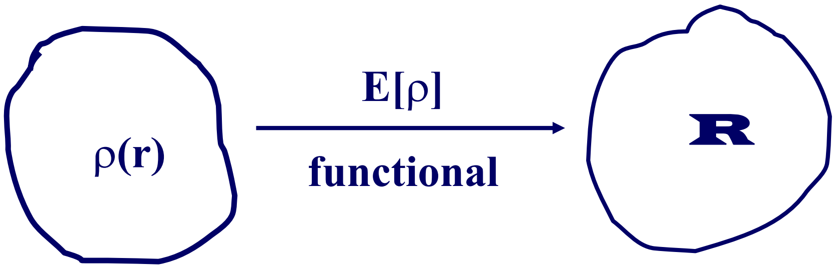
Every quantum mechanical observable is completely determined by the ground state density.

Proof: $\rho \xrightarrow{G^{-1}} v[\rho] \xrightarrow{\text{solve MBSE}} \Phi_i[\rho]$

Observables $\hat{B} : B_i[\rho] = \left\langle \Phi_i[\rho] \middle| \hat{B} \middle| \Phi_i[\rho] \right\rangle$

e.g. excitation spectrum: $E_i[\rho]$

What is a FUNCTIONAL?



$\rho(\mathbf{r})$

$E[\rho]$

functional

$\mathbb{R}$

set of functions

set of real numbers

Generalization:

$v_r[\rho] = v[\rho](\vec{r})$ functional depending parametrically on $\vec{r}$

$\psi_{\vec{r}_1 \ldots \vec{r}_N}[\rho] = \psi[\rho](\vec{r}_1 \ldots \vec{r}_N)$ or on $(\vec{r}_1 \ldots \vec{r}_N)$

Explicit construction of the HK map $v_s[\rho]$

(van Leeuwen & Baerends, or Zhao & Parr)

$$\left(-\frac{h^2\nabla^2}{2m} + v_s(r)\right)\varphi_i = \epsilon_i\,\varphi_i \qquad \Big|\ \sum_i \varphi_i^* \cdot$$

$$\sum_{i=1}^{N} \varphi_i^*\left(-\frac{h^2\nabla^2}{2m}\right)\varphi_i + v_s(r)\rho(r) = \sum_{i=1}^{N} \epsilon_i\,|\varphi_i(r)|^2$$

$$\Rightarrow\ v_s(r) = \frac{1}{\rho(r)}\cdot\sum_{i=1}^{N}\left(\epsilon_i\,|\varphi_i(r)|^2 - \varphi_i^*\left(-\frac{\hbar^2\nabla^2}{2m}\right)\varphi_i\right)$$

Iterative procedure

$\rho_0(r)$ given (e.g. from experiment)

Start with an initial guess for $v_s(r)$ (e.g. GGA potential)

solve $\left(-\frac{\hbar^2\nabla^2}{2m} + v_s(r)\right)\varphi_i = \epsilon_i\,\varphi_i$

$$v_s^{new}(r) = \frac{1}{\rho_0(r)}\cdot\sum_{i=1}^{N}\left(\epsilon_i\,|\varphi_i(r)|^2 - \varphi_i^*\left(-\frac{\hbar^2\nabla^2}{2m}\right)\varphi_i\right)$$

solve SE with v_s^{new} and iterate, keeping $\rho_0(r)$ fixed

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QUESTION:

How to calculate ground state density $\rho_o(\vec{r})$ of a given system (characterized by external potential $V_o = \sum v_o(\vec{r})$) without recourse to the Schrödinger Equation?

Theorem:

There exists a density functional $E_{HK}[\rho]$ with properties

i) $E_{HK}[\rho] > E_o$ for $\rho \neq \rho_o$

ii) $E_{HK}[\rho_o] = E_o$

where E_o = exact ground state energy of the system

Thus, Euler equation $$\frac{\delta}{\delta\rho(\vec{r})} E_{HK}[\rho] = 0$$

yields exact ground state density ρ_o.

proof:

formal construction of $E_{HK}[\rho]$:

for arbitrary ground state density $\rho(\vec{r}) \xrightarrow{\tilde{A}^{-1}} \Psi[\rho]$

define: $$\boxed{E_{HK}[\rho] \equiv \left\langle \Psi[\rho] \middle| \hat{T} + \hat{W} + \hat{V}_o \middle| \Psi[\rho] \right\rangle}$$

$$\begin{aligned} &> \mathbf{E_o} \quad \textbf{for} \quad \rho \neq \rho_o \\ &= \mathbf{E_o} \quad \textbf{for} \quad \rho = \rho_o \end{aligned}$$

q.e.d.

$$E_{HK}[\rho] = \int d^3r\, \rho(r)\, v_o(r) + \underbrace{\left\langle \Psi[\rho] \middle| \hat{T} + \hat{W} \middle| \Psi[\rho] \right\rangle}_{F[\rho] \text{ is } \boxed{\text{universal}}}$$

HOHENBERG-KOHN THEOREM

1. $v(r) \xleftrightarrow{1—1} \rho(r)$

   one-to-one correspondence between external potentials v(r) and ground-state densities ρ(r)

2. Variational principle

   Given a particular system characterized by the external potential $\mathbf{v_0(r)}$. Then the solution of the Euler-Lagrange equation

   $$\frac{\delta}{\delta\rho(r)} E_{HK}[\rho] = 0$$

   yields the exact ground-state energy $\mathbf{E_0}$ and ground-state density $\boldsymbol{\rho_0(r)}$ of this system

3. $E_{HK}[\rho] = F[\rho] + \int \rho(r)\, \mathbf{v_0(r)}\, d^3r$

   F[ρ] is UNIVERSAL. **In practice, F[ρ] needs to be approximated**

Expansion of F[ρ] in powers of e^2

$$F[\rho] = F^{(0)}[\rho] + e^2 F^{(1)}[\rho] + e^4 F^{(2)}[\rho] + \cdots$$

where: $F^{(0)}[\rho] = T_s[\rho]$ (kinetic energy of <u>non</u>-interacting particles)

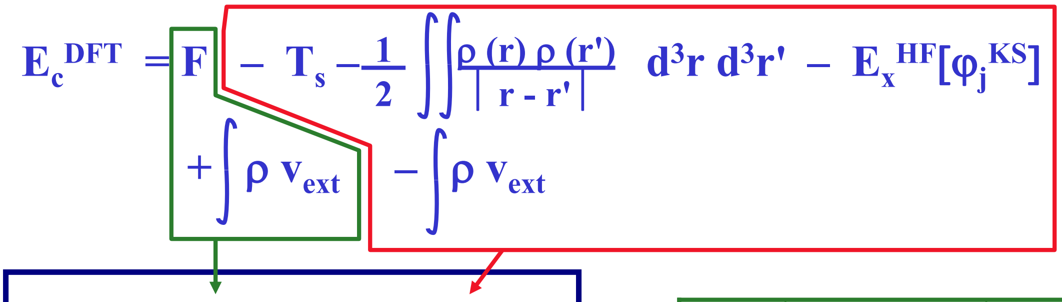
$$e^2 F^{(1)}[\rho] = \frac{e^2}{2}\iint \frac{\rho(r)\rho(r')}{|r-r'|}\, dr^3 d^3r' + E_x[\rho] \quad \text{(Hartree + exchange energies)}$$

$$\sum_{i=2}^{\infty} \left(e^2\right)^i F^{(i)}[\rho] = E_c[\rho] \qquad \text{(correlation energy)}$$

$$\Rightarrow \quad \mathbf{F[\rho] = T_s[\rho] + \frac{e^2}{2}\iint \frac{\rho(r)\,\rho(r')}{|r-r'|}\, d^3r\, d^3r' + E_x[\rho] + E_c[\rho]}$$

DF correlation energy versus traditional QC correlation energy

$$\boxed{E_c^{QC} := E_{tot} - E_{tot}^{HF}[\varphi_j^{HF}]}$$



$$E_c^{DFT} = F - T_s - \frac{1}{2}\iint \frac{\rho(r)\,\rho(r')}{|r-r'|}\, d^3r\, d^3r' - E_x^{HF}[\varphi_j^{KS}] + \int \rho\, v_{ext} - \int \rho\, v_{ext}$$

$$\boxed{E_c^{DFT} := E_{tot} - E_{tot}^{HF}[\varphi_j^{KS}]}$$

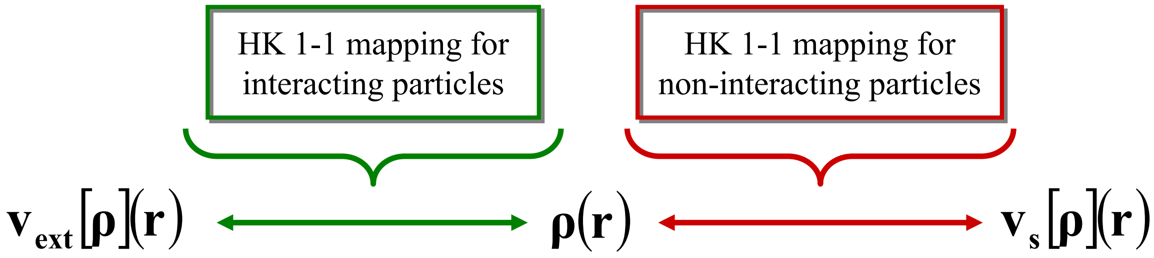
$$E_{tot}^{HF}[\varphi_j^{HF}] \le E_{tot}^{HF}[\varphi_j^{KS}]$$

$$\Rightarrow E_c^{DFT} \le E_c^{QC}$$

	E_c^{DFT}	E_c^{QC}
H^-	-0.04195	-0.039821
He	-0.042107	-0.042044
Be^{2+}	-0.044274	-0.044267

in Hartree units

details see: E.K.U.G., M.Petersilka, T.Grabo, in: Chemical Applications of Density Functional Theory, B.B. Laird, R.B. Ross, T. Ziegler, eds., ACS Symposium Series <u>629</u>, 42 (1996).



HK 1-1 mapping for interacting particles

HK 1-1 mapping for non-interacting particles

$$v_{ext}[\rho](\mathbf{r}) \longleftrightarrow \rho(\mathbf{r}) \longleftrightarrow v_s[\rho](\mathbf{r})$$

Kohn-Sham Theorem

Let $\rho_o(r)$ be the ground-state density of interacting electrons moving in the external potential $v_o(r)$. Then there exists a local potential $v_{s,o}(r)$ such that non-interacting particles exposed to $v_{s,o}(r)$ have the ground-state density $\rho_o(r)$, i.e.

$$\left(-\frac{\nabla^2}{2} + v_{s,o}(\mathbf{r})\right)\varphi_j(\mathbf{r}) = \epsilon_j\, \varphi_j(\mathbf{r}) \ , \qquad \rho_o(\mathbf{r}) = \sum_{\substack{j\,(\text{with}\\ \text{lowest } \epsilon_j)}}^{N} \left|\varphi_j(\mathbf{r})\right|^2$$

proof: $v_{s,o}(\mathbf{r}) = v_s[\rho_o](\mathbf{r})$

Uniqueness follows from HK 1-1 mapping

Existence follows from V-representability theorem

By construction, the HK mapping is well-defined for all those functions $\rho(r)$ that are ground-state densities of some potential (so called V-representable functions $\rho(r)$).

QUESTION: Are all “reasonable” functions $\rho(r)$ V-representable?

V-representability theorem (Chayes, Chayes, Ruskai, J Stat. Phys. 38, 497 (1985))

On a lattice (finite or infinite), any normalizable positive function $\rho(r)$, that is compatible with the Pauli principle, is (both interacting and non-interacting) ensemble-V-representable.

In other words: For any given $\rho(r)$ (normalizable, positive, compatible with Pauli principle) there exists a potential, $v_{ext}[\rho](r)$, yielding $\rho(r)$ as interacting ground-state density, and there exists another potential, $v_s[\rho](r)$, yielding $\rho(r)$ as non-interacting ground-state density.

In the worst case, the potential has degenerate ground states such that the given $\rho(r)$ is representable as a linear combination of the degenerate ground-state densities (ensemble-V-representable).

Define $v_{xc}[\rho](\mathbf{r})$ by the equation

$$v_s[\rho](\mathbf{r}) =: v_{ext}[\rho](\mathbf{r}) + \underbrace{\int \frac{\rho(r')}{|r-r'|}\, d^3r'}_{v_H[\rho](\mathbf{r})} + v_{xc}[\rho](\mathbf{r})$$

$v_s[\rho]$ and $v_{ext}[\rho]$ are well defined through HK.

KS equations

$$\boxed{\left(-\frac{\nabla^2}{2} + \underbrace{v_{ext}[\rho_o](\mathbf{r})}_{\substack{v_o(\mathbf{r})\\ \text{fixed}}} + v_H[\rho_o](\mathbf{r}) + v_{xc}[\rho_o](\mathbf{r})\right)\varphi_j(\mathbf{r}) = \epsilon_j\, \varphi_j(\mathbf{r})}$$

to be solved selfconsistently with $\rho_o(\mathbf{r}) = \sum |\varphi_j(\mathbf{r})|^2$

Note: The KS equations do **not** follow from the variational principle. They follow from the HK 1-1 mapping and the V-representability theorem.

Variational principle gives an additional property of v_{xc}:

$$\boxed{v_{xc}[\rho_o](\mathbf{r}) = \left.\frac{\delta E_{xc}[\rho]}{\delta\rho(\mathbf{r})}\right|_{\rho_o}}$$

where $E_{xc}[\rho] := F[\rho] - \frac{1}{2}\int \frac{\rho(r)\rho(r')}{|r - r'|}\, d^3r\, d^3r' - T_s[\rho]$

Consequence:

Approximations can be constructed either for $E_{xc}[\rho]$ or directly for $v_{xc}[\rho](\mathbf{r})$.

TOWARDS THE EXACT FUNCTIONAL

$$F[\rho] = T_s[\rho] + \frac{1}{2}\int d^3r \int d^3r' \frac{\rho(r)\rho(r')}{|r-r'|} + E_x[\rho] + E_c[\rho]$$

1st generation of DFT: Use approximate functionals (LDA/GGA) for T_s, E_x and E_c e.g.

$$T_s[\rho] = \int d^3r \left(a\rho(r)^{5/3} + b\frac{(\nabla\rho)^2}{\rho} + \cdots \right)$$

⇒ Thomas-Fermi-type equation has to be solved

2nd generation of DFT: Use exact functional $T_s^{exact}[\rho]$ and LDA/GGA for E_x and E_c

$$T_s^{exact}[\rho] = \sum_{j_{occ}} \int d^3r \varphi_j^*[\rho](r)\left(-\frac{\nabla^2}{2}\right)\varphi_j[\rho](r)$$

⇒ KS equations have to be solved

3rd generation of DFT: Use $T_s^{exact}[\rho]$, and an orbital functional $E_{xc}[\varphi_1, \varphi_2, \ldots]$ e.g.

$$E_x^{exact}[\rho] = -\sum_{\sigma=\uparrow\downarrow}\sum_{j,k}^{N\sigma}\int \frac{\varphi_{k\sigma}^*[\rho](r')\varphi_{k\sigma}(r)\varphi_{j\sigma}^*(r)\varphi_{j\sigma}(r')}{|r-r'|} d^3r d^3r'$$

⇒ KS equations have to be solved self-consistently with OPM integral equation

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Limitations of 2nd generation (LDA/GGA for E_{xc})

- **Not free from spurious self-interactions KS potential decays more rapidly than r^{-1}**

  Consequences:
  - **no Rydberg series**
  - **negative atomic ions not bound**
  - **ionization potentials (if calculated from highest occupied orbital energy) too small**

- **Dispersion forces cannot be described**

  $$W_{int}(R) \longrightarrow e^{-R} \quad \text{(rather than } R^{-6}\text{)}$$

- **band gaps too small:**

  $$E_{gap}^{LDA} \approx 0.5\, E_{gap}^{exp}$$

- **Cohesive energies of bulk metals not satisfactory**

  in LDA overestimated
  in GGA underestimated

- **Wrong ground state for strongly correlated solids, e.g. FeO, La_2CuO_4 predicted as metals**

Orbital Functionals in DFT:
Historical Overview

OEP idea (within EXX): Sharp, Horton, Phys. Rev. 90, 317 (1953)

First OEP calculation: Talman, Shadwick, Phys. Rev. A 14, 36 (1976)

KS potential ≡ OEP: J. Perdew (1983 NATO ASI in Alcabideche)

Derivation given here:
V. Shaginyan, PRA 47, 1507 (1993)
A. Görling, M. Levy, PRA 50, 196 (1994)
R. Van Leeuwen (PhD thesis 1994)

First OEP calculation with orbital functional for correlation energy:
T. Grabo, E.K.U.G., Chem. Phys. Lett. 240, 141 (1995)

Approximate semi-analytical ("KLI") solution of OEP equations:
Krieger, Li, Iafrate, Phys. Lett. A 148, 470 (1990)

Apply HK theorem to non-interacting particles

ρ given $\Rightarrow$ $v_s = v_s[\rho]$ $\Rightarrow$ $\left(-\frac{\nabla^2}{2} + v_s[\rho](r)\right)\varphi_i(r) = \epsilon_i\,\varphi_i(r)$

$\varphi_i = \varphi_i[\rho]$
$\epsilon_i = \epsilon_i[\rho]$

consequence:

Any orbital functional, $E_{xc}[\varphi_1, \varphi_2 \ldots]$, is an (implicit) density functional provided that the orbitals come from a local (i.e., multiplicative) potential.

"optimized effective potential" ≡ KS xc potential

$$v_{xc}^{OEP}(r) = \frac{\delta}{\delta\rho(r)} E_{xc}[\varphi_1 \ldots \varphi_N]$$

$$v_{xc}^{OEP}(r) = \sum_j \int d^3r' \int d^3r'' \frac{\delta E_{xc}}{\delta\varphi_j(r')} \frac{\delta\varphi_j(r')}{\delta v_s(r'')} \underbrace{\frac{\delta v_s(r'')}{\delta\rho(r)}}_{\chi_{KS}^{-1}(r'',r)} + \text{c.c.}$$

act with χ_{KS} on equation:

$$\Rightarrow \quad \boxed{\int \chi_{KS}(r,r') v_{xc}^{OPM}(r') d^3r' = \sum_j \int d^3r' \underbrace{\frac{\delta E_{xc}}{\delta\varphi_j(r')} \frac{\delta\varphi_j(r')}{\delta v_s(r)}}_{\text{known functional of } \{\varphi_j\}} + \text{c.c.}}$$

OPM integral equation

OEP integral equation

$$\sum_{i=1}^{N_\sigma} \int d^3r' \left(V_{xc,\sigma}(r') - u_{xc,i\sigma}(r') \right) K_{i\sigma}(r,r') \varphi_{i\sigma}(r) \varphi_{i\sigma}^*(r') + c.c. = 0$$

where $K_{i\sigma}(r,r') = \sum_{\substack{k=1 \\ k \neq i}}^{\infty} \frac{\varphi_{k\sigma}^*(r)\varphi_{k\sigma}(r')}{\epsilon_{k\sigma} - \epsilon_{i\sigma}}$

and $\quad u_{xc,i\sigma}(r) := \frac{1}{\varphi_{i\sigma}^*(r)} \cdot \frac{\delta E_{xc}[\varphi_{1\sigma}\ldots]}{\delta\varphi_{i\sigma}(r)}$

to be solved simultaneously with KS equation:

$$\left(-\frac{\nabla^2}{2} + v_o(r) + \int \frac{\rho(r')}{|r - r'|} + V_{xc,\sigma}(r) \right) \varphi_{j\sigma}(r) = \epsilon_{j\sigma} \varphi_{j\sigma}(r)$$

Orbital functionals available

- **order-by-order KS-MBPT**
- **Resummation of infinitely many terms of the MBP-series (e.g. RPA)**
- **Functionals from TDDFT**
- **Self-Interaction-Corrected LDA or GGA (SIC)**
- **Meta-GGA**
- **Interaction-Strength-Interpolation (ISI)**
- **Hybrid functionals (e.g. B3LYP)**
- **Colle-Salvetti**

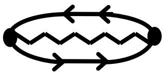
Systematic approach to construct E_{xc} using KS-MBPT

$H_{KS} \longrightarrow$ **unperturbed system**

$$H = H_{KS} + \lambda H_1 ,$$

where $H_1 = W_{ee} - \int d^3r\, \rho(r)(v_H(r) + v_{xc}(r))$

$$E_x^{exact}[\rho] =$$



$$= -\frac{1}{2}\sum_{\sigma=\uparrow\downarrow}\sum_{j,k}^{N_\sigma}\int \frac{\varphi^*_{k\sigma}(r')\varphi_{k\sigma}(r)\varphi^*_{j\sigma}(r)\varphi_{j\sigma}(r')}{|r-r'|}\, d^3r d^3r'$$

$E_c[\rho]$ = sum of all higher-order diagrams in terms of the Green's function

$$G_{s\sigma}(r,r') = \sum_k \frac{\varphi_{k\sigma}(r)\varphi^*_{k\sigma}(r')}{\omega - \varepsilon_{k\sigma}} \Rightarrow$$

The exact $E_{xc}[\rho]$ is an orbital functional

Ionization energies for atoms and ions

Ionization energies (in a.u.) from highest occupied KS energy

Atom/Ion	KLI		BLYP	PW91	exact
	EXX	EXX+CS			
He	0.918	0.945	0.585	0.583	0.904
Be^{2+}	5.667	5.699	4.876	4.870	5.656
Be	0.309	0.329	0.201	0.207	0.343
C^{2+}	1.693	1.723	1.480	1.486	1.759
Ne	0.849	0.884	0.491	0.494	0.795
N^+	1.796	1.834	1.338	1.342	1.741

Atomic ionization potentials from highest occupied Kohn-Sham orbital energy

	OPM	LDA	BLYP	PW91	experiment
He	0.945	0.570	0.585	0.583	0.903
Li	0.200	0.116	0.111	0.119	0.198
Be	0.329	0.206	0.201	0.207	0.343
B	0.328	0.151	0.143	0.149	0.305
C	0.448	0.228	0.218	0.226	0.414
N	0.579	0.309	0.297	0.308	0.534
O	0.559	0.272	0.266	0.267	0.500
F	0.714	0.384	0.376	0.379	0.640
Ne	0.884	0.498	0.491	0.494	0.792
Na	0.189	0.113	0.106	0.113	0.189
Mg	0.273	0.175	0.168	0.174	0.281
Al	0.222	0.111	0.102	0.112	0.220
Si	0.306	0.170	0.160	0.171	0.300
P	0.399	0.231	0.219	0.233	0.385
S	0.404	0.228	0.219	0.222	0.381
Cl	0.506	0.305	0.295	0.301	0.477
Ar	0.619	0.382	0.373	0.380	0.579
$\overline{\Delta}$	0.030	0.176	0.183	0.177	

Total absolute ground-state energies for first-row atoms from various self-consistent calculations. All numbers in hartree. (OPM values from T. Grabo, E.K.U.G., Chem. Phys. Lett. 240, 141 (1995))

	OPM	BLYP	PW91	QCI	EXACT
He	2.9033	2.9071	2.9000	2.9049	2.9037
Li	7.4829	7.4827	7.4742	7.4743	7.4781
Be	14.6651	14.6615	14.6479	14.6657	14.6674
B	24.6564	24.6458	24.6299	24.6515	24.6539
C	37.8490	37.8430	37.8265	37.8421	37.8450
N	54.5905	54.5932	54.5787	54.5854	54.5893
O	75.0717	75.0786	75.0543	75.0613	75.067
F	99.7302	99.7581	99.7316	99.7268	99.734
Ne	128.9202	128.9730	128.9466	128.9277	128.939
$\overline{\Delta}$	0.0047	0.0108	0.0114	0.0045	

Comparison: $\overline{\Delta}(\text{LDA}) = 0.383 \qquad \overline{\Delta}(\text{HF}) = 0.177$

- $\overline{\Delta}$: Mean absolute deviation from the exact nonrelativistic values.
- QCI: Complete basis set quadratic configuration-interaction/atomic pair natural orbital model: J.A. Montgomery, J.W. Ochterski, G.A. Petersson, J. Chem. Phys. 101, 5900 (1994).
- EXACT: E.R. Davison, S.A. Hagstrom, S.J. Chakravorty, V.M. Umar, C. Froese Fischer, Phys. Rev. A 44, 7071 (1991).

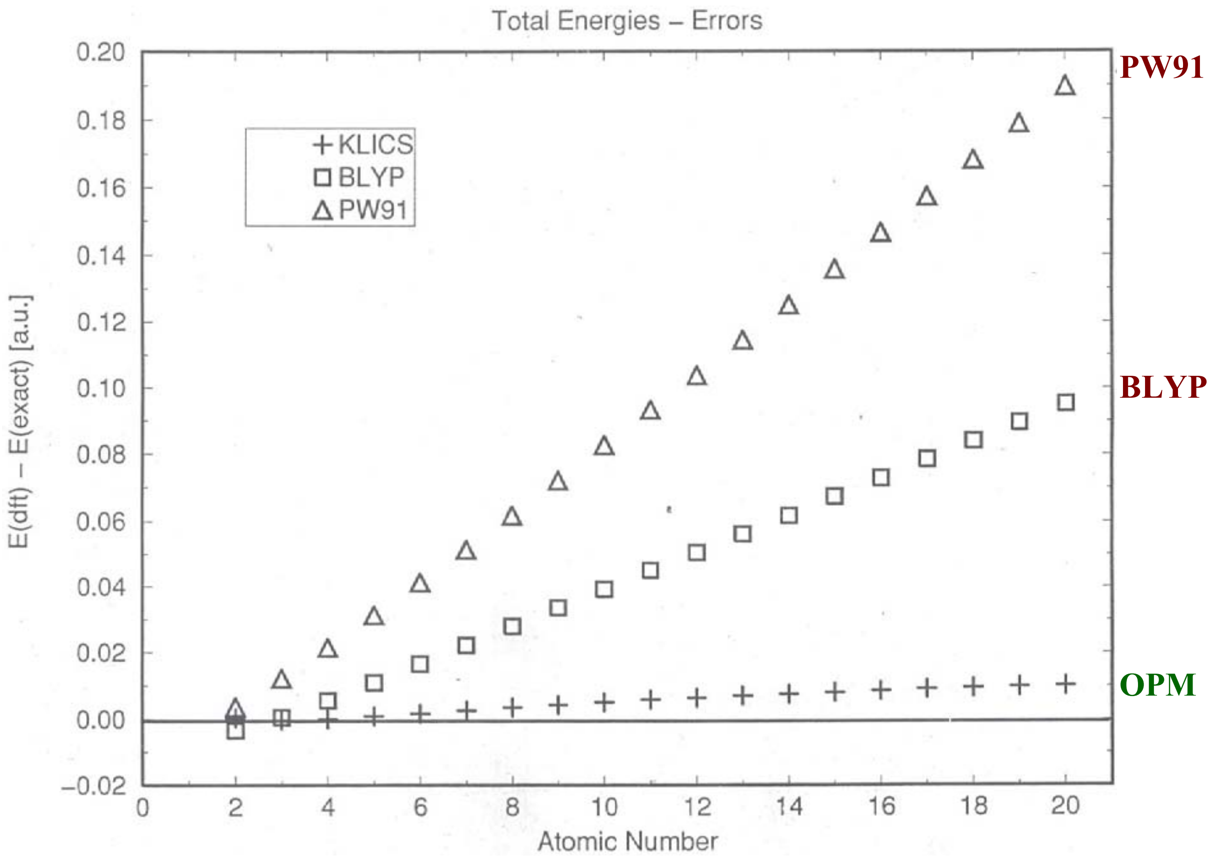
Approximation employed for E_{xc}: **$E_x[\varphi_1 \ldots \varphi_N]$ = exact Fock term (EXX)**
$E_c[\varphi_1 \ldots \varphi_N]$ = Colle-Salvetti functional

Total absolute ground-state energies for second-row atoms from various self-consistent calculations. All numbers in hartree. (OPM values from T. Grabo, E.K.U.G., Chem. Phys. Lett. 240, 141 (1995))

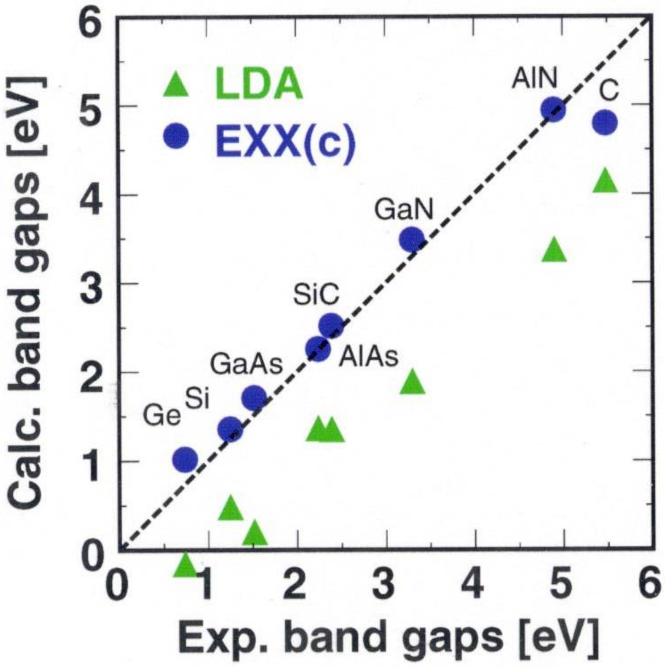
	OPM	BLYP	PW91	EXPT
Na	162.256	162.293	162.265	162.257
Mg	200.062	200.093	200.060	200.059
Al	242.362	242.380	242.350	242.356
Si	289.375	289.388	289.363	289.374
P	341.272	341.278	341.261	341.272
S	398.128	398.128	398.107	398.139
Cl	460.164	460.165	460.147	460.196
Ar	527.553	527.551	527.539	527.604
$\bar{\Delta}$	0.013	0.026	0.023	

- $\bar{\Delta}$: Mean absolute deviation from Lamb-shift corrected experimental values, taken from R.M. Dreizler and E.K.U.G., Density functional theory: an approach to the quantum many-body problem (Springer, Berlin, 1990)).

Helium Isoelectronic Series



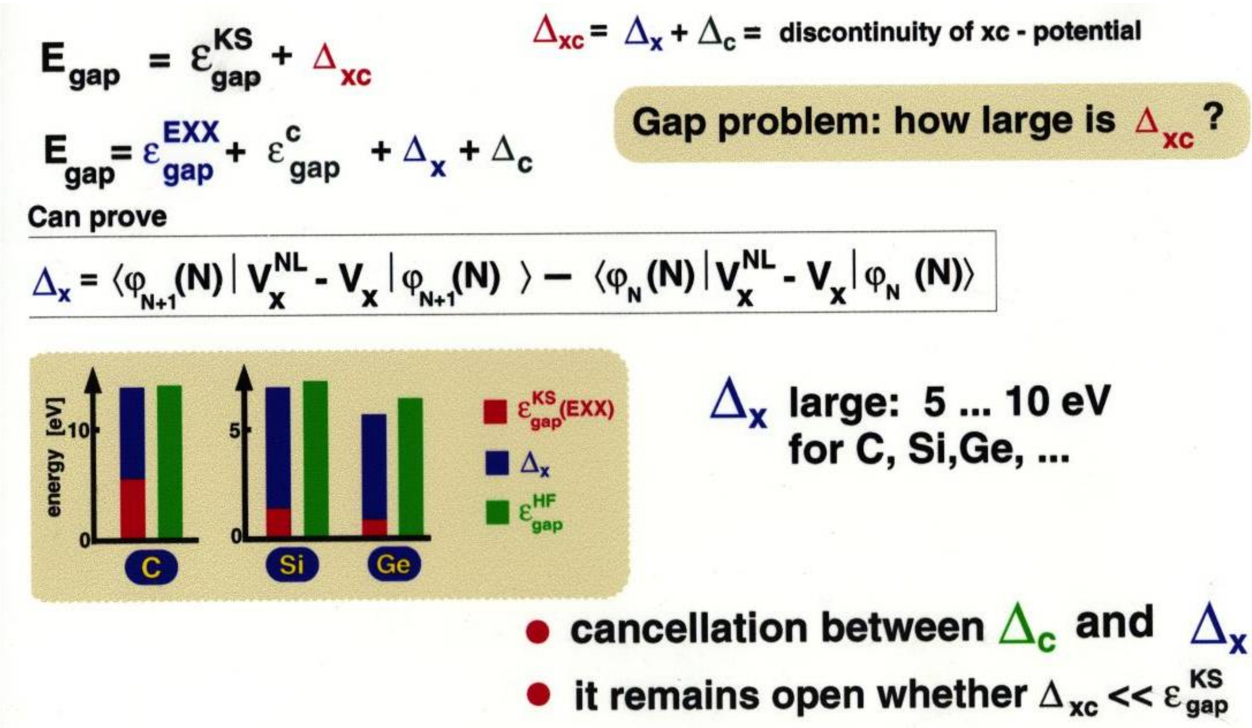
Fundamental Energy gaps



- EXX gives excellent band gaps: larger than LDA by ~1 eV
- Small influence of correlation
- EXX pseudopotential important for Ge: minimum of conduction band in L

from: Städele et al., Phys. Rev. B 59, 10031 (1999)

True gap vs. KS gap; Discontinuity of V_x



$E_{gap} = \varepsilon^{KS}_{gap} + \Delta_{xc}$

$\Delta_{xc} = \Delta_x + \Delta_c =$ discontinuity of xc - potential

Gap problem: how large is Δ_{xc} ?

$E_{gap} = \varepsilon^{EXX}_{gap} + \varepsilon^{c}_{gap} + \Delta_x + \Delta_c$

Can prove

$$\Delta_x = \langle \varphi_{N+1}(N) | V_x^{NL} - V_x | \varphi_{N+1}(N) \rangle - \langle \varphi_N(N) | V_x^{NL} - V_x | \varphi_N(N) \rangle$$

🟥 ε^{KS}_{gap}(EXX)
🟦 Δ_x
🟩 ε^{HF}_{gap}

Δ_x large: 5 ... 10 eV for C, Si,Ge, ...

- cancellation between Δ_c and Δ_x
- it remains open whether $\Delta_{xc} << \varepsilon^{KS}_{gap}$

Fundamental band gap in semiconductors and insulators

Gap in Hartree-Fock:

$$E_g^{HF} = E^{HF}(N+1) - 2\,E^{HF}(N) + E^{HF}(N-1)$$
$$= \epsilon_{N+1}^{HF}(N) - \epsilon_{N}^{HF}(N)$$

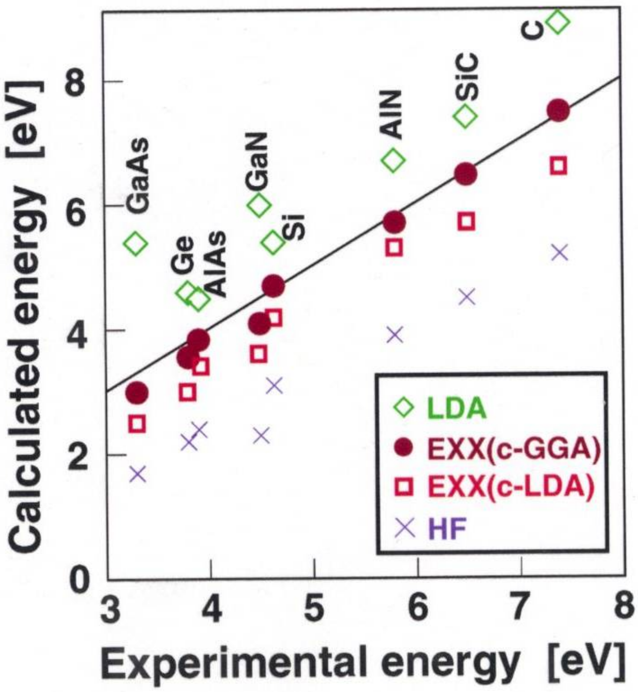
DFT with exact exchange (OPM)

$$E_g^{OEP} = E^{OEP}(N+1) - 2\,E^{OEP}(N) + E^{OEP}(N-1)$$
$$= \epsilon_{N+1}^{KS}(N) - \epsilon_{N}^{KS}(N) + \Delta_x$$

discontinuity of v_x

$$E^{HF} \approx E^{OPM} \quad \Rightarrow \quad E_g^{HF} \approx E_g^{OPM}$$

Cohesive Energies



Exact Exchange + GGA correlation yields cohesive energy close to experimental values.

from: Städele et al., Phys. Rev. B 59, 10031 (1999)

Orbital functionals for the static xc energy derived from TDDFT

First ingredient: Adiabatic Connection Formula

$$H(\lambda) = T + \sum_{i=1}^{N} v_{\lambda}(r_i) + \lambda \frac{e^2}{2} \sum_{\substack{i,k=1 \\ i\neq k}}^{N} \frac{1}{|r_i - r_k|} \qquad 0 \le \lambda \le 1$$

$$H(\lambda=1) = T + \sum_{i=1}^{N} v_{nuc}(r_i) + \frac{e^2}{2} \sum_{\substack{i,k=1 \\ i\neq k}}^{N} \frac{1}{|r_i - r_k|}$$

= Hamiltonian of fully interacting system

Choose $v_{\lambda}(r)$ such that for each λ the ground- state density satisfies $\rho_{\lambda}(r) = \rho_{\lambda=1}(r)$

Hence $v_{\lambda=0}(r) = v_{KS}(r)$

$v_{\lambda=1}(r) = v_{nuc}(r)$

Determine the response function $\chi^{(\lambda)}(r,r';\omega)$ corresponding to $H(\lambda)$, Then

$$\boxed{E_{xc} = -\int_0^1 d\lambda \int_0^\infty \frac{du}{2\pi} \int d^3r \int d^3r' \frac{e^2}{|r-r'|} \left\{ \chi^{(\lambda)}(r,r';iu) + \rho(r)\delta(r-r') \right\}}$$

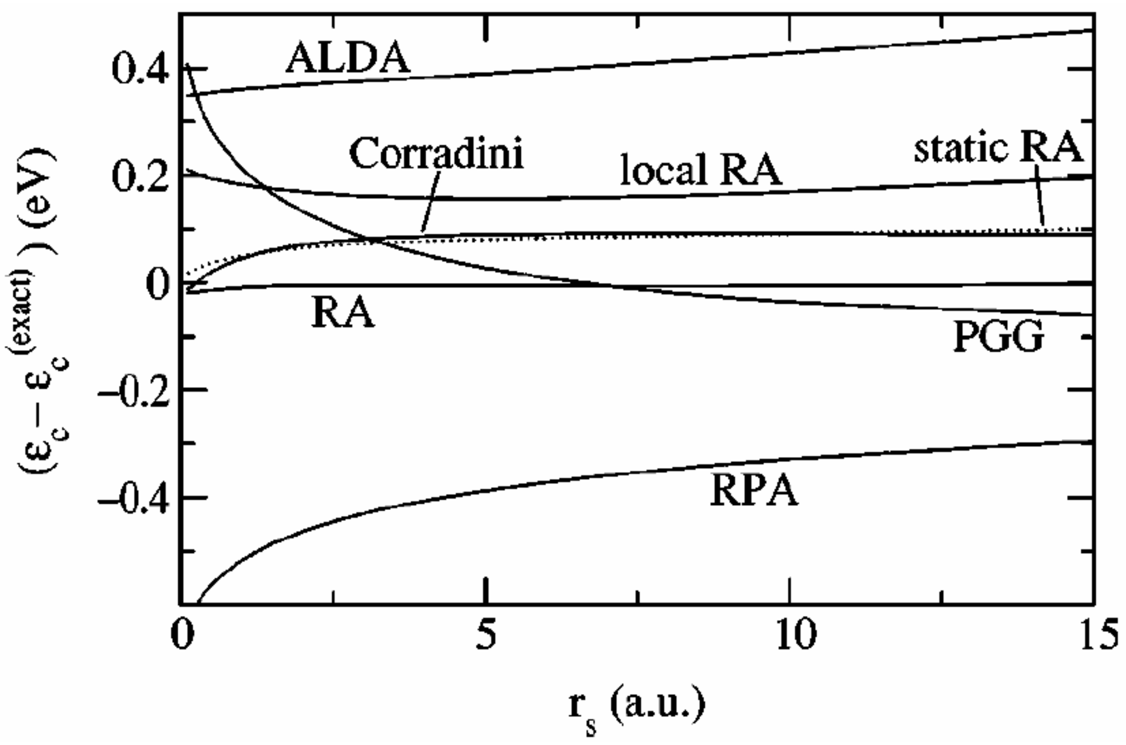
Exact representation of E_{xc}

Second ingredient : TDDFT

$$\boxed{\chi = \chi_s + \chi_s \left[W_{Clb} + f_{xc} \right] \chi}$$

and for $0 \leq \lambda \leq 1$:

$$\boxed{\chi^{(\lambda)} = \chi_s + \chi_s \left[\lambda W_{Clb} + f_{xc}^{(\lambda)} \right] \chi^{(\lambda)}}$$



r_s-dependent deviation of approximate correlation energies from the ‘‘exact’’ correlation energy per electron of the uniform electron gas.

M. Lein, E. K. U. G., J. Perdew, Phys. Rev. B 61, 13431 (2000).

For finite systems, truncate after first iteration:

$$\chi^{(\lambda)} \approx \chi_s + \chi_s [\lambda W_{clb} + f_{xc}^{(\lambda)}]\chi_s$$

plug this approximation into adiabatic connection formula

⇒ Orbital functional for E_c

Resulting Atomic Correlation energies (in a.u.)

atom	LDA	new fctl	exact
He	-0.111	-0.048	-0.042
Be	-0.224	-0.13	-0.096
Ne	-0.739	-0.41	-0.394
Ar	-1.423	-0.67	-0.72

Resulting v.d.W. coefficients C_6

Lein, Dobson, EKUG, J. Comp. Chem. (‘99)

system	Calculated C_6	experiment
He-He	1.639	1.458
He-Ne	3.424	3.029
Ne-Ne	7.284	6.383
Li-Li	1313	1390
Li-Na	1453	1450
Na-Na	1614	1550
H-He	2.995	2.82
H-Ne	5.976	5.71
H-Li	64.96	66.4
H-Na	75.4	71.8

DENSITY-FUNTIONAL THEORY OF MAGNETIC SYSTEMS

Weak magnetic field: **Zeeman coupling of B to the spin magnetization m(r)**

Strong magnetic field: **In addition coupling of vector potential to orbital currents $j_p(r)$**

Include m(r) and $j_p(r)$ as basic variables in the formalism, in addition to the density $\rho(r)$.

DFT for spin-polarized systems

$$\hat{H}_{v,\vec{B}} = \hat{T} + \hat{W} + \int \hat{\rho}(r) v(r) d^3r - \int \hat{\vec{m}}(r) \cdot \vec{B}(r) d^3r$$

$\vec{m}$ = spin magnetization : $\hat{\vec{m}}(r) = -\mu_o \sum_{\alpha\beta} \hat{\psi}^{+}_{\alpha}(r) \vec{\sigma}_{\alpha\beta} \hat{\psi}_{\beta}(r)$

HK theorem

$$[\rho(r), \vec{m}(r)] \xleftrightarrow{1\text{-}1} [\psi]$$

total energy:

$$E_{v,\vec{B}}[\rho, \vec{m}] = \underset{\substack{\uparrow \\ \text{universal}}}{F}[\rho, \vec{m}] + \int d^3r \left(v(r)\rho(r) - \vec{B}(r) \cdot \vec{m}(r) \right)$$

KS scheme

For simplicity: $\vec{B}(\boldsymbol{r}) = \begin{pmatrix} 0 \\ 0 \\ B(\boldsymbol{r}) \end{pmatrix}$, $\vec{m}(\boldsymbol{r}) = \begin{pmatrix} 0 \\ 0 \\ m(\boldsymbol{r}) \end{pmatrix}$

$$\left(-\frac{\nabla^2}{2m} + \left[v(\mathbf{r}) + v_H(\mathbf{r}) + \mathbf{v_{xc}(r)}\right] \pm \mu_o \left[B(\mathbf{r}) - \mathbf{B_{xc}(r)}\right]\right) \varphi_{\pm}^{j}(\mathbf{r}) = \in_{\pm}^{j} \varphi_{\pm}^{j}(\mathbf{r})$$

$$\mathbf{v_{xc}[\rho,m] = \delta E_{xc}[\rho,m]/\delta\, \rho \qquad B_{xc}[\rho,m] = \delta E_{xc}[\rho,m]/\delta\, m}$$

$$\rho\,(\mathbf{r}) = \rho_+\,(\mathbf{r}) + \rho_-\,(\mathbf{r}) \;,\; \mathbf{m}\,(\mathbf{r}) = \rho_+\,(\mathbf{r}) - \rho_-\,(\mathbf{r}) \;,\; \rho_\pm = \Sigma\left|\varphi^{\,j}_{\pm}\right|^2$$

<u>B ⟶ 0 limit</u>

These equations do <u>not</u> reduce to the original KS equations for B → 0 if, in this limit, the system has a finite m(r).

Traditional DFT: $E_{xc}[\rho]$ $\qquad v_{xc}(r) = \dfrac{\delta E_{xc}[\rho]}{\delta \rho(r)}$

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Collinear SDFT: $E_{xc}[\rho,m]$ $\quad v_{xc}(r)=\frac{\delta E_{xc}[\rho,m]}{\delta\rho(r)}$ $\quad B_{xc}(r)=-\frac{\delta E_{xc}[\rho,m]}{\delta m(r)}$

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Non-Collinear SDFT: $E_{xc}[\rho,\vec{m}]$ $\quad v_{xc}(r)=\frac{\delta E_{xc}[\rho,\vec{m}]}{\delta\rho(r)}$ $\quad \vec{B}_{xc}(r)=-\frac{\delta E_{xc}[\rho,\vec{m}]}{\delta\vec{m}(r)}$

Traditional DFT: $E_{xc}[\rho]$ $\qquad v_{xc}(r)=\dfrac{\delta E_{xc}[\rho]}{\delta\rho(r)}$

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Collinear CSDFT: $E_{xc}[\rho,m,\vec{j}_p]$ $\qquad v_{xc}(r)=\dfrac{\delta E_{xc}[\rho,m,\vec{j}_p]}{\delta\rho(r)} \qquad B_{xc}(r)=-\dfrac{\delta E_{xc}[\rho,m,\vec{j}_p]}{\delta m(r)}$

$$\vec{A}_{xc}(r)=c\,\frac{\delta E_{xc}[\rho,m,\vec{j}_p]}{\delta \vec{j}_p(r)}$$

Traditional DFT: $E_{xc}[\rho]$ $\qquad v_{xc}(r)=\dfrac{\delta E_{xc}[\rho]}{\delta\rho(r)}$

Collinear SDFT: $E_{xc}[\rho,m]$ $\qquad v_{xc}(r)=\dfrac{\delta E_{xc}[\rho,m]}{\delta\rho(r)} \qquad B_{xc}(r)=-\dfrac{\delta E_{xc}[\rho,m]}{\delta m(r)}$

Non-Collinear SDFT: $E_{xc}[\rho,\vec{m}]$ $\qquad v_{xc}(r)=\dfrac{\delta E_{xc}[\rho,\vec{m}]}{\delta\rho(r)} \qquad \vec{B}_{xc}(r)=-\dfrac{\delta E_{xc}[\rho,\vec{m}]}{\delta \vec{m}(r)}$

Collinear CSDFT: $E_{xc}[\rho,m,\vec{j}_p]$ $\qquad v_{xc}(r)=\dfrac{\delta E_{xc}[\rho,m,\vec{j}_p]}{\delta\rho(r)} \qquad B_{xc}(r)=-\dfrac{\delta E_{xc}[\rho,m,\vec{j}_p]}{\delta m(r)}$

$$\vec{A}_{xc}(r)=c\,\frac{\delta E_{xc}[\rho,m,\vec{j}_p]}{\delta \vec{j}_p(r)}$$

Non-Col. CSDFT: $E_{xc}[\rho,\vec{m},\vec{j}_p]$ $\qquad v_{xc}(r)=\dfrac{\delta E_{xc}[\rho,\vec{m},\vec{j}_p]}{\delta\rho(r)} \qquad \vec{B}_{xc}(r)=-\dfrac{\delta E_{xc}[\rho,\vec{m},\vec{j}_p]}{\delta \vec{m}(r)}$

$$\vec{A}_{xc}(r)=c\,\frac{\delta E_{xc}[\rho,\vec{m},\vec{j}_p]}{\delta \vec{j}_p(r)}$$

KS equation for the most general case (non-collinear CSDFT):

$$\boxed{\left[\frac{1}{2}\left(-i\vec{\nabla}+\frac{1}{c}\vec{A}_s(r)\right)^2+v_s(r)+\mu_B\vec{\sigma}\cdot\vec{B}_s(r)\right]\Phi_i(r)=\varepsilon_i\Phi_i(r)}$$

$$v_s(r)=v_0(r)+v_H(r)+v_{xc}(r)+\frac{1}{2c^2}\left[A_0^2(r)-A_s^2(r)\right]$$

$$\vec{B}_s(r)=\vec{B}_0(r)+\vec{B}_{xc}(r) \qquad \vec{A}_s(r)=\vec{A}_0(r)+\vec{A}_{xc}(r)$$

$$\rho(r)=\sum_{i=1}^{N}\Phi_i^\dagger(r)\Phi_i(r) \qquad \vec{m}(r)=-\mu_B\sum_{i=1}^{N}\Phi_i^\dagger(r)\vec{\sigma}\Phi_i(r)$$

$$\vec{j}_p(r)=\frac{1}{2i}\sum_{i=1}^{N}\left[\Phi_i^\dagger(r)\vec{\nabla}\Phi_i(r)-\left(\vec{\nabla}\Phi_i^\dagger(r)\right)\Phi_i(r)\right]$$

Functionals available:

Ordinary LSDA yields GLOBAL collinearity

$$\boxed{\vec{B}_{xc}(r)=\begin{pmatrix}0\\0\\B_{xc}(r)\end{pmatrix} \qquad \vec{m}(r)=\begin{pmatrix}0\\0\\m(r)\end{pmatrix}}$$

$\vec{B}_{xc}$, $\vec{m}$ parallel to $\begin{pmatrix}0\\0\\1\end{pmatrix}$ everywhere in space

$$\int \rho(r)v(r)d^3r - \int \vec{m}(r)\cdot\vec{B}(r)d^3r$$

$$\equiv \sum_{\alpha,\beta=\uparrow\downarrow} \int \rho_{\alpha,\beta}(r)v_{\alpha,\beta}(r)$$

$\{\rho(r),\vec{m}(r)\}$: 4 independent functions

$\rho_{\alpha\beta}$ is Hermitian $\Rightarrow$ 4 independent functions

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Non-collinear LSDA:

(Kübler ’80s)

$\vec{r}$ given point in space:

① Find unitary matrix U(r) such that

$$U^+(r)(\rho_{\alpha\beta})U(r) = \begin{pmatrix} n_\uparrow(r) & 0 \\ 0 & n_\downarrow(r) \end{pmatrix}$$

② Calculate $v_{xc}^\uparrow(r)$ and $v_{xc}^\downarrow(r)$ from $\{n_\uparrow, n_\downarrow\}$
using the normal LSDA expressions

③ $$(v_{xc}^{\alpha\beta}) = U(r)\begin{pmatrix} v_{xc}^\uparrow(r) & 0 \\ 0 & v_{xc}^\downarrow(r) \end{pmatrix}U^+(r)$$

in this approximation $\vec{B}_{xc}(r)$ and $\vec{m}(r)$ may change their direction in space, but locally they are always parallel

Extension of OEP to non-collinear spin DFT

Ordinary Spin-DFT: KS orbitals are spin eigenfunctions

Generalization to include relativistic effects on the level of spin-orbit coupling: KS orbitals are two-component (Pauli) spinors

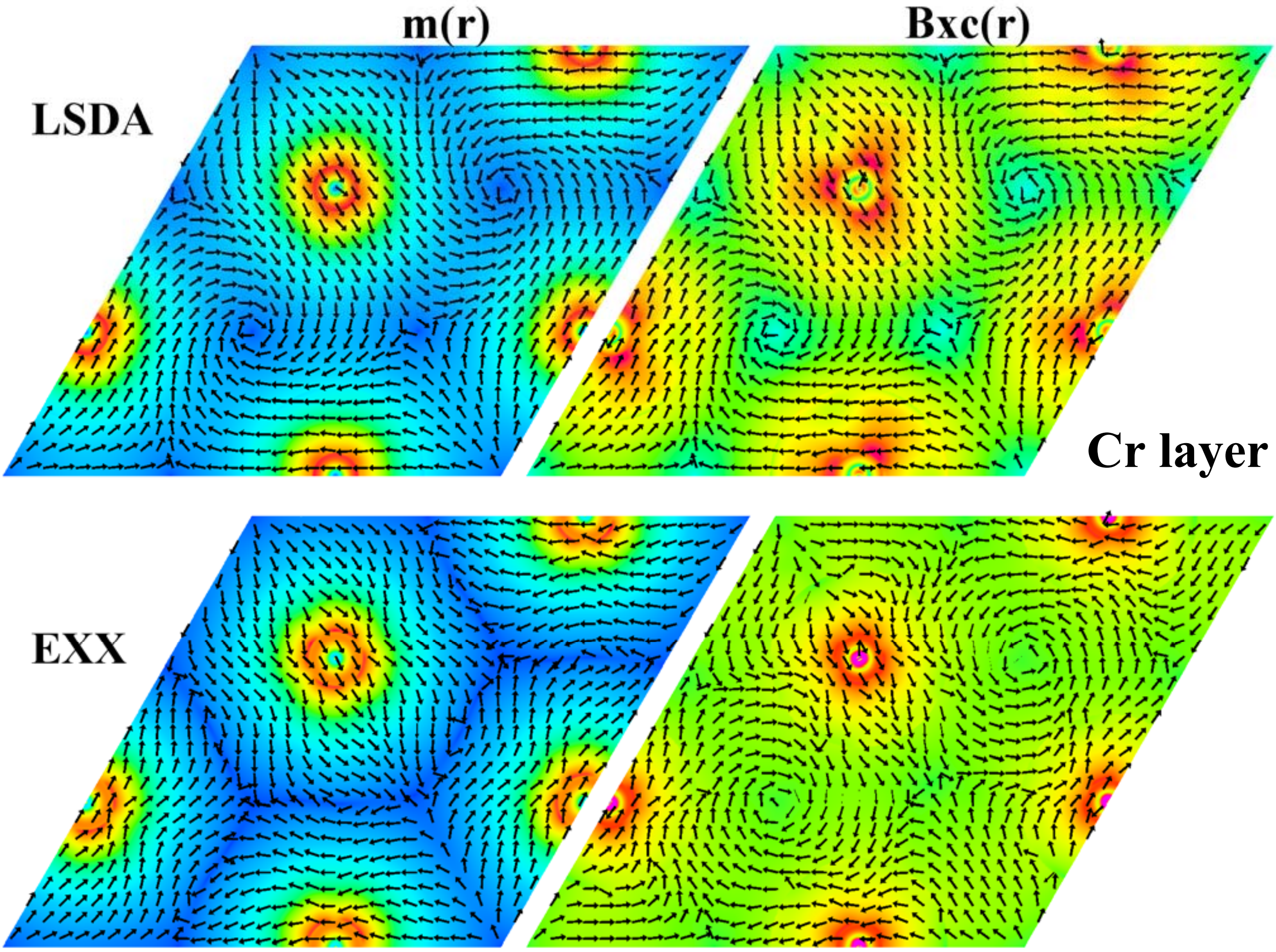
xc magnetic field **B**$_{\mathbf{xc}}$(r) not globally and not locally collinear with **m**(r)

OEP equations are easily formulated:

$$v_{xc}^{OEP} = \sum_j \int\int \frac{\delta E_{xc}}{\delta \varphi_j} \frac{\delta \varphi_j}{\delta v_s} \frac{\delta v_s}{\delta \rho} + \sum_j \int\int \frac{\delta E_{xc}}{\delta \varphi_j} \frac{\delta \varphi_j}{\delta \vec{B}_s} \frac{\delta \vec{B}_s}{\delta \rho}$$

$$\vec{B}_{xc}^{OEP} = \sum_j \int\int \frac{\delta E_{xc}}{\delta \varphi_j} \frac{\delta \varphi_j}{\delta v_s} \frac{\delta v_s}{\delta \vec{m}} + \sum_j \int\int \frac{\delta E_{xc}}{\delta \varphi_j} \frac{\delta \varphi_j}{\delta \vec{B}_s} \frac{\delta \vec{B}_s}{\delta \vec{m}}$$

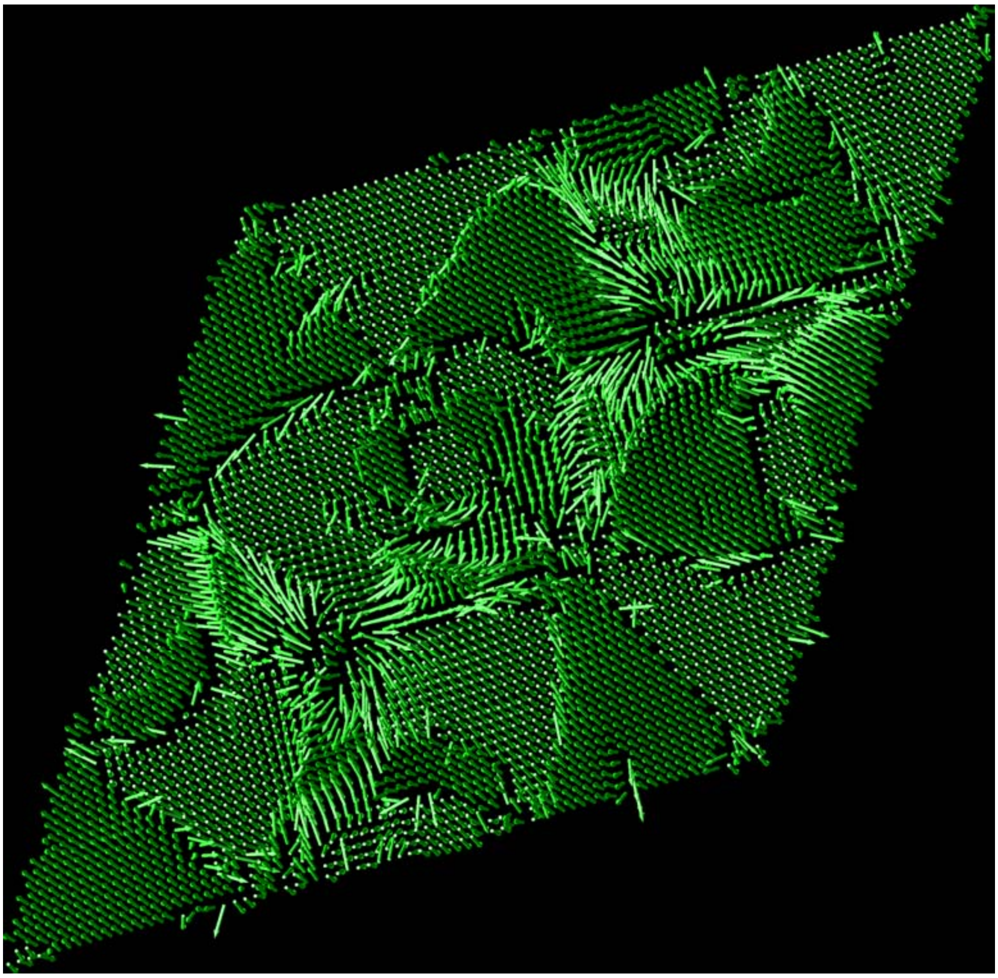
$\Rightarrow$ One has to deal with a 4x4 matrix of response functions



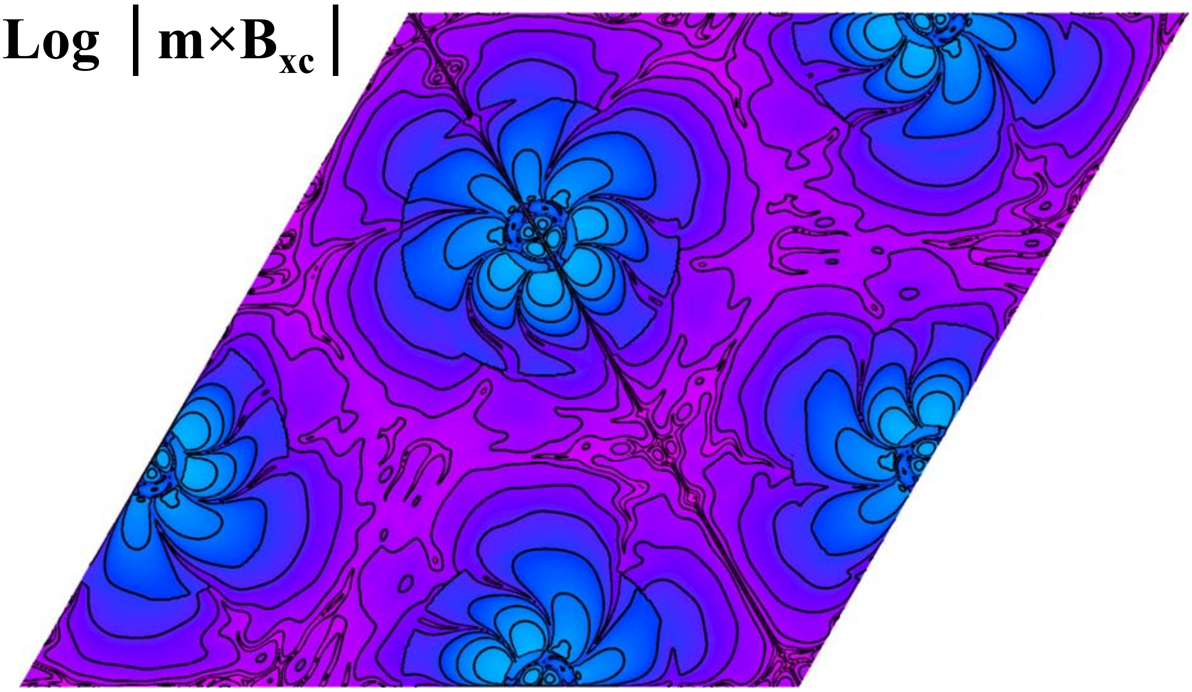
$\mathbf{m}\times\mathbf{B}_{xc}$ **is the spin torque appearing on the r.h.s of the equation of motion of the spin magnetisation. In the LSDA, this term vanishes, leading to an unrealistic spin dynamics.**

⇒ LSDA yields unrealistic spin dynamics.

$\mathbf{m}\times\mathbf{B}_{xc}$



$\mathbf{Log}\ |\mathbf{m}\times\mathbf{B}_{xc}|$



Summary of noncollinear OEP:

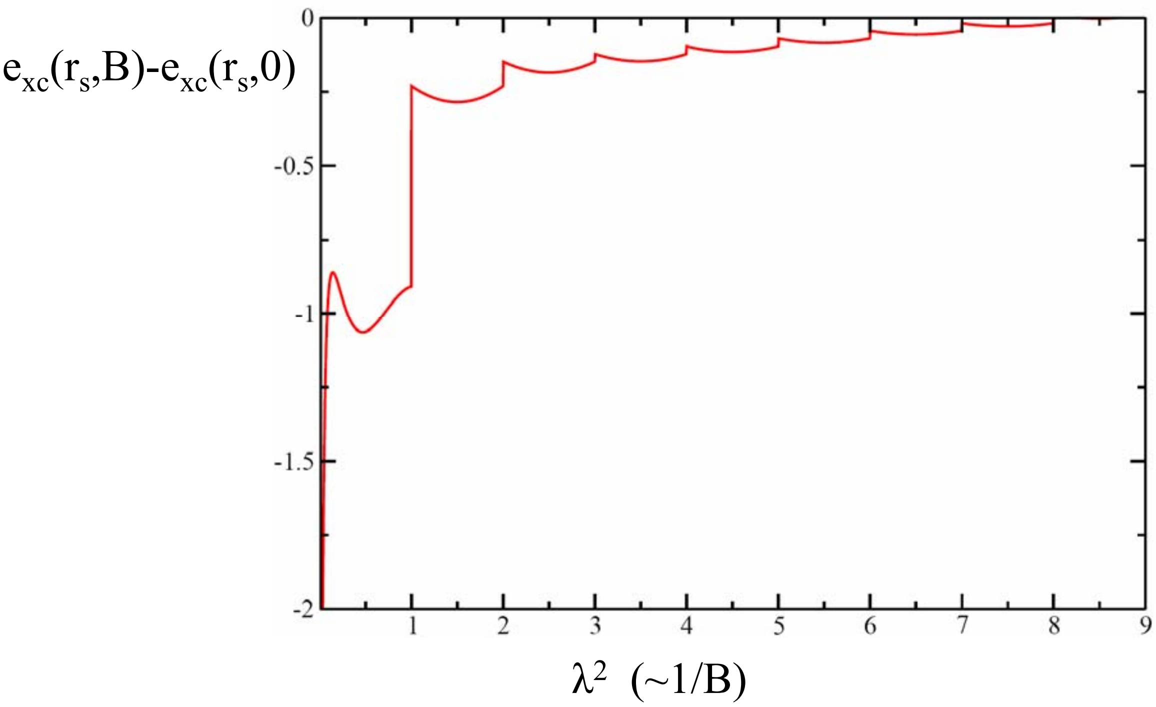
- **m**(r) has stronger spacial variation in EXX than in LSDA
- **m**(r) locally not collinear with $\mathbf{B}_{xc}$
- Improved spin dynamics: Importance for spintronics

Optimized Effective Potential Method for Non-Collinear Magnetism: **S. Sharma, J.K. Dewhurst, C. Ambrosch-Draxl, S. Kurth, N. Helbig, S. Pittalis, S. Shallcross, L. Nordstroem E.K.U.G., Phys. Rev. Lett. 98, 196405 (2007)**

Functionals available in CDFT

CDFT-LDA: B ⟶ vorticity $\nu(r)$, n ⟶ $\rho(r)$

xc energy per particle of uniform gas in constant B field



$A_{xc}(r)$ has divergencies all over the place (Diplom thesis of Klaus Drese (1995))

CDFT-OEP equations are easily formulated:

$$v_{xc}^{OEP} = \sum_j \int\int \frac{\delta E_{xc}}{\delta \varphi_j} \frac{\delta \varphi_j}{\delta v_s} \frac{\delta v_s}{\delta \rho} + \sum_j \int\int \frac{\delta E_{xc}}{\delta \varphi_j} \frac{\delta \varphi_j}{\delta \vec{A}_s} \frac{\delta \vec{A}_s}{\delta \rho}$$

$$\vec{A}_{xc}^{OEP} = \sum_j \int\int \frac{\delta E_{xc}}{\delta \varphi_j} \frac{\delta \varphi_j}{\delta v_s} \frac{\delta v_s}{\delta \vec{m}} + \sum_j \int\int \frac{\delta E_{xc}}{\delta \varphi_j} \frac{\delta \varphi_j}{\delta \vec{A}_s} \frac{\delta \vec{A}_s}{\delta \vec{j}_p}$$

When there is a strong external magnetic field, one has to use CSDFT.

When there is no magnetic field, one can use a given orbital functional, e.g. EXX, within the framework of either

- **DFT-OEP or**
- **SDFT-OEP or**
- **CSDFT-OEP**

In each case, one minimizes the same total-energy functional $E_{HF}[\varphi_1,\varphi_2,\ldots\varphi_N]$. But the minimization is performed over a different orbital sets $\{\varphi_1,\ldots\varphi_N\}$:

DFT-OEP: φs come from a SE with a local potential $v_s(r)$ only.
SDFT-OEP: φs come from a SE with $v_s(r)$ and $B_s(r)$.
CSDFT-OEP: φs come from a SE with $v_s(r)$, $B_s(r)$ and $A_s(r)$.

Obviously, $E_{HF} \le E_{CSDFT\text{-}OEP} \le E_{SDFT\text{-}OEP} \le E_{DFT\text{-}OEP}$
But these total energies are usually extremely close.

In systems without external magnetic field, does CSDFT-OEP give better results than SDFT-OEP for quantities other than the total energy (with EXX functional in both cases)?

Look at:

- Degeneracy of ground states of open-shell atoms
- Orbital magnetic moment of solids

Spurious energy splittings $\Delta = E(M = \pm 1) - E(M = 0)$ (in kcal/mol) between current carrying and zero-current states computed in SDFT and CSDFT.

Atom	Δ^{SDFT}	Δ^{CSDFT}
B	1.66	1.38
C	1.58	1.34
O	2.36	2.29
F	2.32	2.27
Al	1.68	1.58
Si	1.76	1.63
S	3.04	3.01
Cl	3.15	3.10

S. Pittalis, S. Kurth, N. Helbig, E.K.U.G., Phys. Rev. A 74, 062511 (2006)

Orbital magnetic moments in μ_B

Solid	Exp.	LSDA	GGA	EXX-SDFT	EXX-CSDFT
Fe	0.08	0.053	0.051	0.034	0.034
Co	0.14	0.069	0.073	0.013	0.013
Ni	0.05	0.038	0.037	0.029	0.029

S. Sharma, S. Pittalis, S. Kurth, S. Shallcross, J.K. Dewhurst, E.K.U. Gross, Phys. Rev. B (Rapid Comm.) (2007).

Summary

No significant improvement of the spurious energy splittings, and no improvement at all for magnetic moments, by minimizing total energy over the larger class of CSDFT orbitals rather than SDFT orbitals.

To improve magnetic moments and spurious splittings:
⇒⇒ Need orbital functionals for correlation!

Review Article

Orbital functionals in density functional theory: the optimized effective potential method

T. Grabo, T. Kreibich, S. Kurth, E.K.U. Gross, in "Strong Coulomb Correlations in Electronic Structure: Beyond the LDA" edited by V.I. Anisimov
Gordon & Breach (2000), p. 203-311.