Orbital Functionals in Density Functional Theory:

The Connection with Many-Body Theory

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ESSENCE OF DENSITY-FUNTIONAL THEORY

- **Every observable quantity of a quantum system can be calculated from the density of the system ALONE**

- **The density of particles interacting with each other can be calculated as the density of an auxiliary system of non-interacting particles**

HOHENBERG-KOHN THEOREM

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

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

ρ given $\quad v = v[\rho] \quad (T + W_{ee} + V[\rho])\Psi_i = E_i \Psi_I$

$\Psi_i = \Psi_i[\rho], \; E_i = E_i[\rho]$

- <u>Variational principle</u>

  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

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

  F[ρ] is <u>UNIVERSAL</u>.

  In practice, F[ρ] needs to be approximated

Kohn-Sham Theorem (1965)

The ground state density of the interacting system of interest can be calculated as ground state density of non-interacting particles moving in an effective potential $v_s(r)$:

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + v_s[\rho](r)\right)\phi_i(r) = \varepsilon_i \phi_i(r)$$

$$\rho(r) = \sum_{\text{N lowest } \varepsilon_j} |\phi_j(r)|^2$$

$$v_s[\rho](r) = v_0(r) + \int \frac{\rho(r')}{|r-r'|} d^3r' + v_{xc}[\rho](r)$$

Coulomb potential of nuclei

Hartree potential

exchange-correlation potential

$$v_{xc}(r) = \frac{\delta E_{xc}[\rho]}{\delta \rho(r)}$$ universal

Generalized Gradient Approximation (GGA)

Detailed study of molecules (atomization energies)

B. G. Johnson, P. M. W. Gill, J. A. Pople, *J. Chem. Phys.* 97, 7847 (1992)

32 molecules (all neutral diatomic with first-row atoms only + H_2)

Atomization energies (kcal/mol) from:

	$E_x^B + E_c^{VWN}$	$E_x^B + E_c^{LYP}$	HF
mean deviation from experiment	0.1	1.0	-85.8
mean absolute deviation	4.4	5.6	85.8

for comparison:	MP2
	-22.4
	22.4

DEFICIENCIES OF LDA/GGA

- **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**

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

- **band gaps too small:**

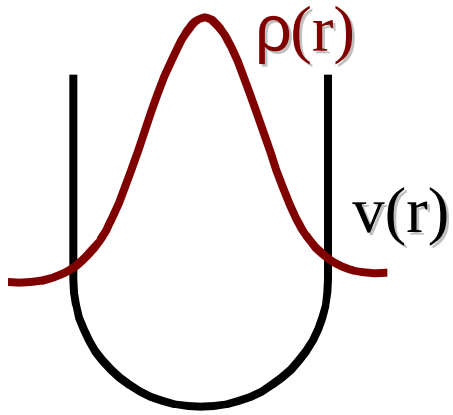
$$E_{gap}^{LDA} \approx 0.5\, E_{gap}^{exp}$$

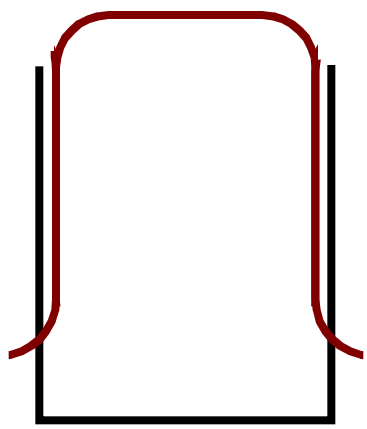
- **Cohesive energies of bulk metals not satisfactory**

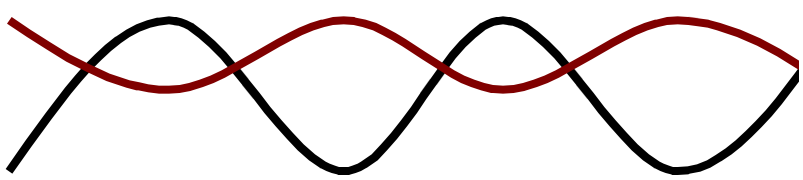
in LDA overestimated
in GGA underestimated

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

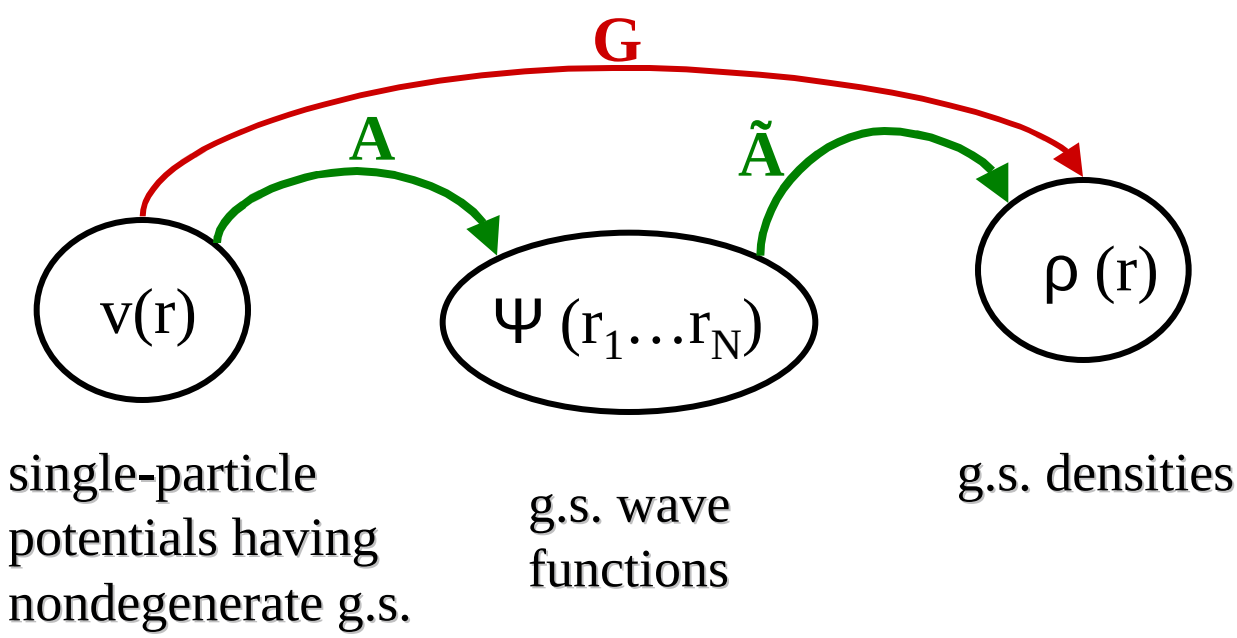
compare ground-state densities $\rho(r)$ resulting from different external potentials $v(r)$.







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



Hohenberg-Kohn-Theorem (1964)

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

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

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

observables $\hat{B}: \; B_i[\rho] = \langle \Phi_i[\rho] | \hat{B} | \Phi_i[\rho] \rangle$

Explicit construction of the HK map for non-interacting particles

(van Leeuwen & Baerends, or Zhao & Parr)

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

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

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

<u>Iterative procedure</u>

$\rho_0(r)$ given

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

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

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

given (fixed)

solve SE with v_s^{new} and iterate

This is an explicit procedure of calculating the <u>functional</u> $v_s[\rho]$

Hence

given $\rho(\mathbf{r})$, we can explicity calculate

$$v_s[\rho]\,,\ \ \varphi_j[\rho](\mathbf{r})\,,\ \ \in_j[\rho]$$

and, e.g.

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

Consequence: Any explicit orbital functional is an implicit density functional

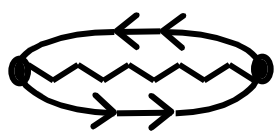
Traditional approximations for $E_{xc}[\rho]$

$$E_{xc}^{LDA}[\rho] = \int d^3r\, e_{xc}^{hom}(\rho(r))$$

$$E_{xc}^{GGA}[\rho] = \int d^3r\, e_{xc}(\rho(r), \quad \rho, \ldots)$$

Systematic approach with MBPT

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



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

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

$$G_{s\sigma}(r,r') = \sum_k \frac{\phi_{k\sigma}(r)\phi_{k\sigma}(r')}{\omega - \varepsilon_{k\sigma}}$$

The <u>exact</u> $E_{xc}[\rho]$ is an orbital functional

Expansion of $F[\rho]$ in powers of e^2

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

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

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

(Hartree + exchange energies)

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

$\Rightarrow$

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

DF correlation energy versus traditional QC correlation energy

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

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

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

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

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

	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, ACS proceedings (1996)

TOWARDS THE EXACT FUNCTIONAL

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

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

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

HK variational principle Thomas-Fermi-type equations

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

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

HK variational principle KS equations

3rd generation of DFT: Use $T_s^{exact}[\rho]$, and an orbital functional $E_{xc}[\phi_1, \phi_2, \ldots]$

e.g.

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

HK variational principle KS equations plus OPM integral equation

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

Apply HK theorem to <u>non</u>-interacting particles

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

$$\phi_i = \phi_i[\rho], \quad \epsilon_i = \epsilon_i[\rho]$$

<u>consequence:</u>

Any orbital functional, $E_{xc}[\phi_1, \phi_2 \ldots]$, is an (implicit) density functional provided that the orbitals come from a local (i.e., multiplicative) potential.

<u>"optimized effective potential" ≡ KS xc potential</u>

$$v_{xc}^{OPM}(r) = \frac{\delta}{\delta\rho(r)} E_{xc}[\phi_1 \ldots \phi_N]$$

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

act with χ_{KS} on equation:

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

OPM integral equation

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
$\bar{\Delta}$	0.0047	0.0108	0.0114	0.0045	

Comparison: $\bar{\Delta}(\text{LDA}) = 0.383$

$\bar{\Delta}(\text{HF}) = 0.177$

- $\bar{\Delta}$: 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}:

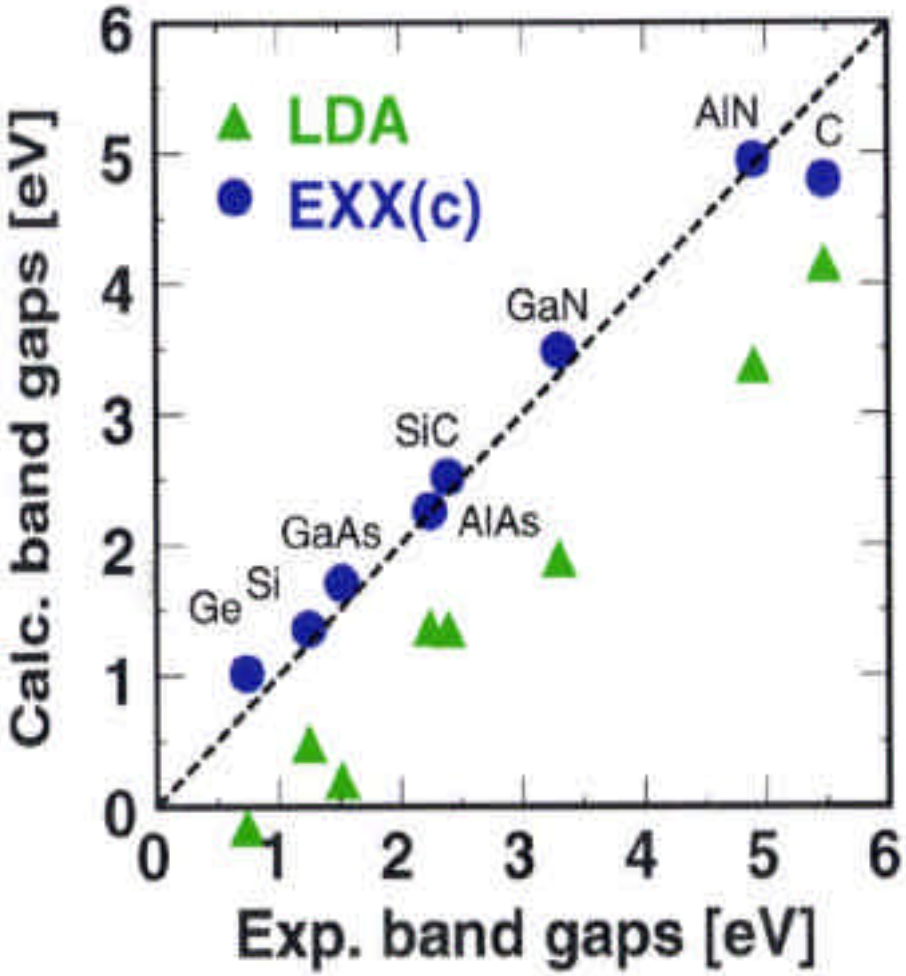
$E_x[\varphi_1 \ldots \varphi_N]$ = exact Fock term
$E_c[\varphi_1 \ldots \varphi_N]$ = Colle-Salvetti functional

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)).

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**

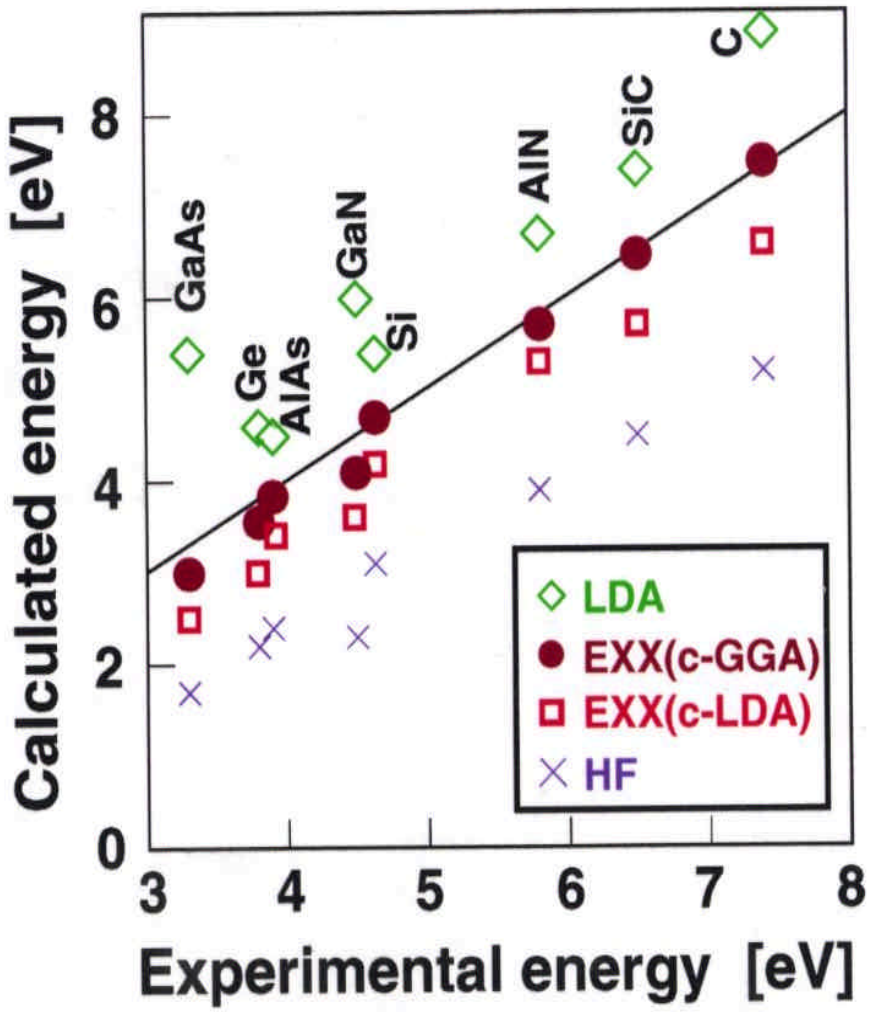
from: M. Städele, M. Morokuma, J.A. Majewski, P. Vogl, and A. Görling, Phys. Rev. B 59, 10031 (1999)

TABLE IX. Comparison of energy gaps between occupied and empty states with experiment. All energies in eV.

	LDA	GW-LDA	EXX	GW-EXX	Experiment
			Si		
E_g	0.51	1.19	1.43	1.54	1.17[a]
E_0'	2.55	3.23	3.28	3.57	3.35[b]
E_1	2.69	3.38	3.35	3.72	3.46[b]
E_1'	4.52	5.26	5.08	5.57	5.38[b]
E_2	3.48	4.18	4.12	4.51	4.32[b]
			Ge		
$E_g(L_c-\Gamma_v)$	0.06	0.62	0.86	0.94	0.74[a]
E_0	−0.07	0.57	0.81	0.94	0.90[c]
$\bar{E}_o'$	2.59	3.17	3.16	3.40	3.16[c]
E_1	1.44	2.03	2.14	2.32	2.22[c]
E_2	3.75	4.31	4.37	4.56	4.45[c]
			GaAs		
E_0	0.49	1.22	1.49	1.65	1.52[d]
E_0'	3.55	4.24	4.16	4.51	4.51[d]
E_1	2.02	2.73	2.80	3.09	3.04[d]
E_2	3.98	4.65	4.72	4.99	5.13[d]
			BeSe		
E_0	4.04	5.46	5.25	5.92	5.55[e]
$\bar{E}_o'$	5.01	6.48	5.78	6.75	7.29[e]
E_1	5.18	6.57	6.00	6.95	6.15[e]
E_1'	6.81	8.31	7.48	8.64	8.47[e]
E_2	5.02	6.43	5.86	6.82	6.56[e]
			BeTe		
$E_g(X_c-\Gamma_v)$	1.60	2.59	2.47	2.88	2.7[f], 2.8[g]
E_0	3.28	4.33	3.91	4.58	4.20[h]
E_1	3.97	4.97	4.61	5.28	4.69[h]
E_2	4.33	5.37	4.99	5.68	5.04 [h]
			MgSe		
E_0	2.47	4.08	3.72	4.71	4.23[i]
			MgTe		
E_0	2.29	3.66	3.33	4.20	3.67[i]

A.Fleszar, PRB 64, 245204 (2001)

Cohesive Energies



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

from: M. Städele, M. Morokuma, J.A. Majewski, P. Vogl, and A. Görling, Phys. Rev. B 59, 10031 (1999)

True gap vs. KS gap; Discontinuity of V_x

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

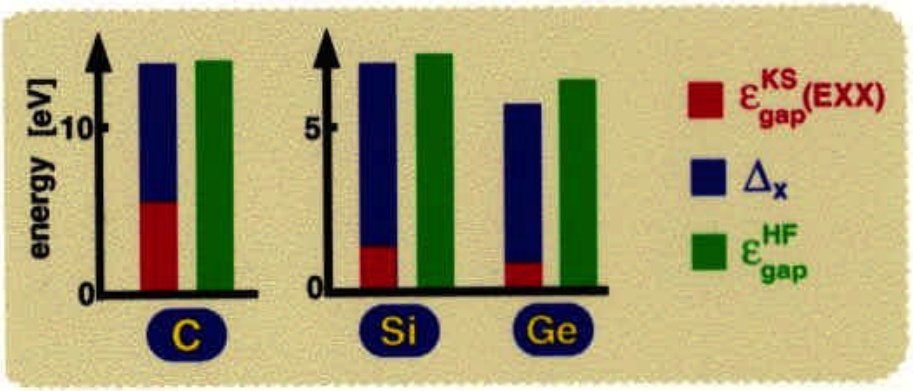
$$E_{gap} = \varepsilon^{EXX}_{gap} + \varepsilon^{c}_{gap} + \Delta_x + \Delta_c$$

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

Gap problem: how large is Δ_{xc} ?

Can prove

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



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

Hartree-Fock

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

$= \quad {}_{N+1}^{HF}(N) - \quad {}_{N}^{HF}(N)$

DFT with exact exchange (OPM)

gap $\Delta_{x\text{-only}}^{OPM} = E^{OPM}(N+1) - 2\,E^{OPM}(N) + E^{OPM}(N-1)$

$= \quad {}_{N+1}^{KS}(N) - \quad {}_{N}^{KS}(N) + D_{x\text{-only}}$

discontinuity of v_x

$\mathbf{E^{HF} \approx E^{OPM} \quad \Rightarrow \quad \Delta^{HF} \approx \Delta_{x\text{-only}}^{OPM}}$

Table 3

Ionization potentials from the highest occupied orbital energy of neutral atoms. $\bar{\Delta}$ denotes the mean absolute deviation from the experimental values, taken from [56]. All values in atomic units. Taken from [31] and modified.

	OPM		GGAs		
	KLICS	xcLDA	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
$\bar{\Delta}$	0.030	0.176	0.183	0.177	

Orbital functionals for the static xc energy derived from TDDFT

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

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

Second ingredient : TDDFT

$$\rho_1 = \chi_s v_{s,1} = \chi_s\left(v_1 + \left[W_{clb} + f_{xc}\right]\rho_1\right)$$

$$\rho_1 = \chi v_1$$

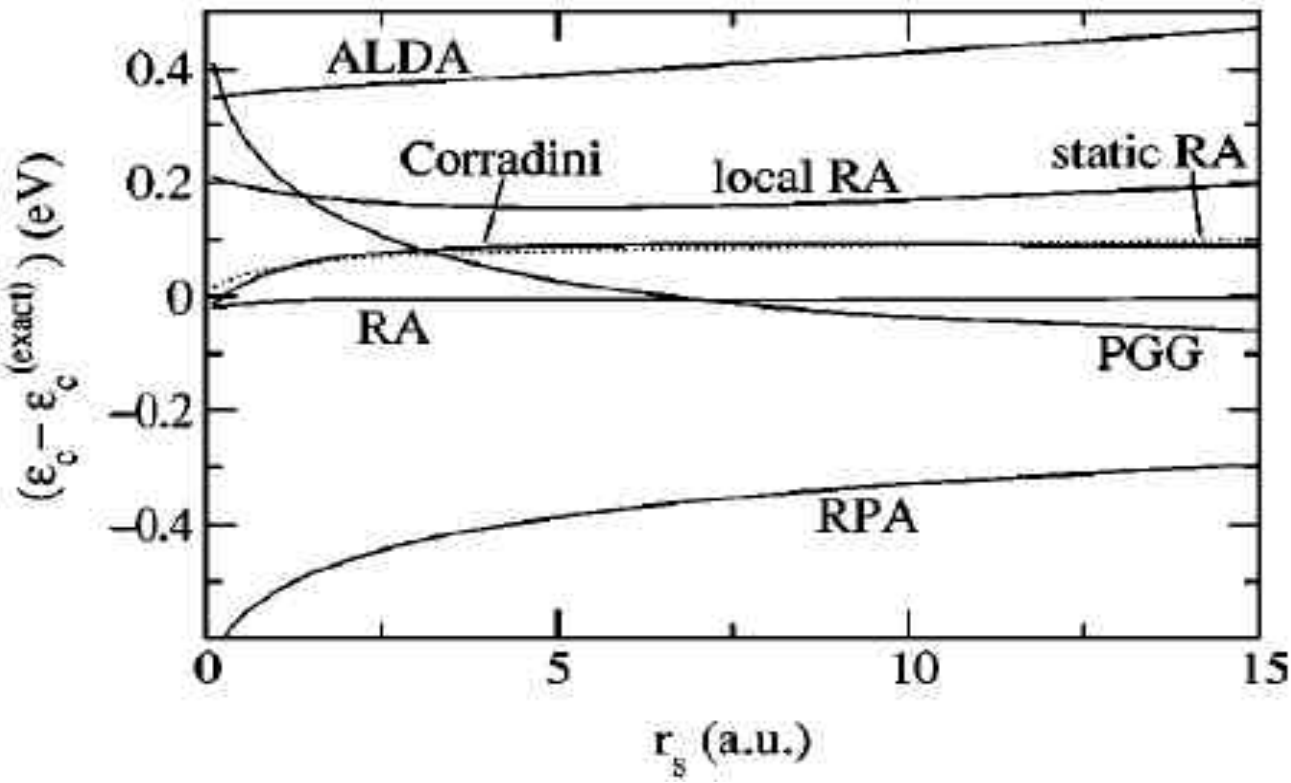
$$\chi v_1 = \chi_s\left(v_1 + \left[W_{clb} + f_{xc}\right]\chi v_1\right)$$

$$\Rightarrow$$

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

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

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



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

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

truncate after first iteration:

$$\chi^{(\lambda)} \approx \chi_s + \chi_s [\lambda \mathbf{W}_{clb} + \mathbf{f}_{xc}^{(\lambda)}]\chi_s$$

plug this approoximation into adiabatic connection formula, integrations over λ and ω can be done analytically

$\Rightarrow$ **Orbital functional for E_c**

Resulting Atomic Correlation energies (in a.u.)

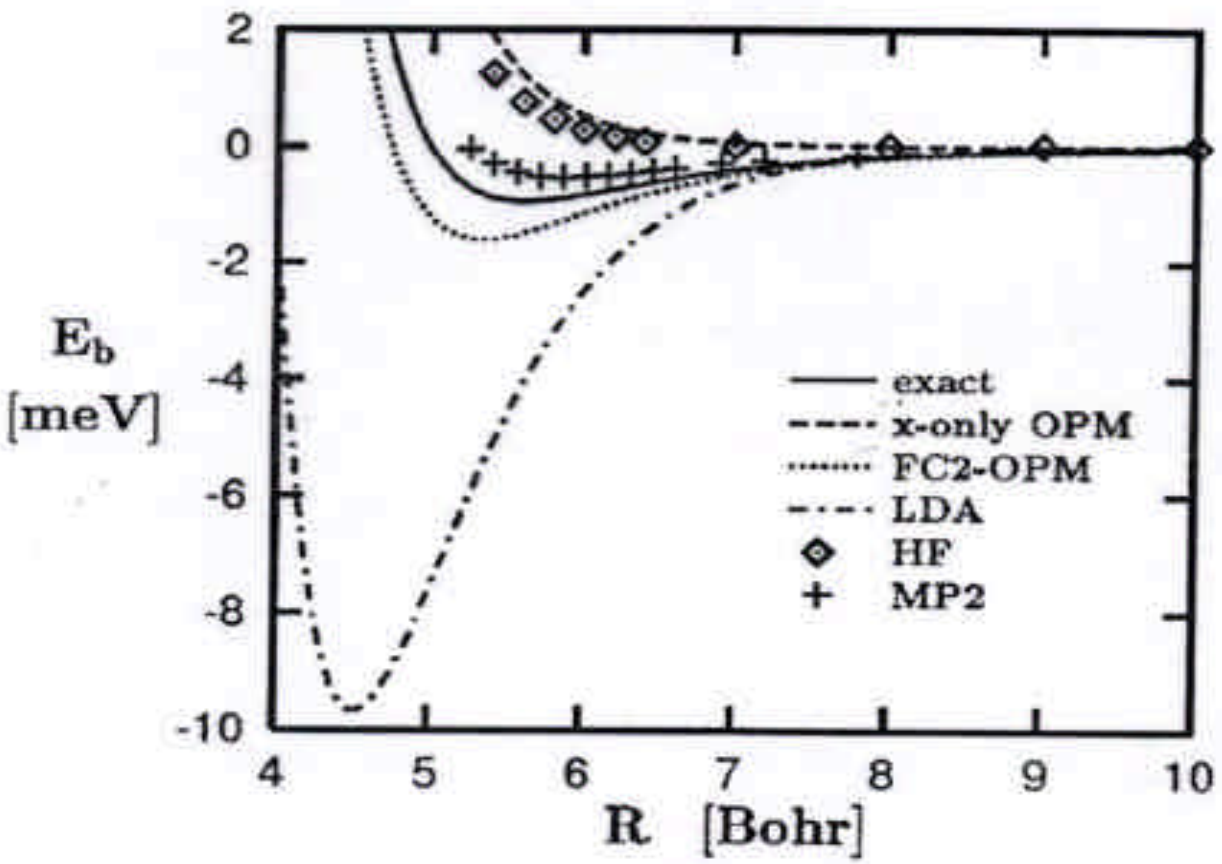
atom	LDA	new fctl	exact
He	-0.111	-0.048	-0.042
Be	-0.224	-0.13	-0.096
Ne	-0.739	-0.41	-0.394
Ar	-1.423	-0.67	-0.72

Resulting v.d.W. coefficients C_6

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

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

Successful calculation of the full PES of He_2: E. Engel, A. Höck, R.M. Dreizler, Phys. Rev. A 61, 032502 (2000))



Energy surface of He_2: x-only and correlated OPM data versus LDA, HF [22], MP2 [23], and exact [21] results.

Self-interaction correction (SIC)

(J. Perdew, 1979)

$$E_{HK} = T_s[\rho] + \int \rho(r) v(r) d^3r + \underbrace{\frac{1}{2}\iint \frac{\rho(r)\rho(r')}{|r-r'|} d^3r d^3r'}_{U[\rho]} + E_{xc}[\rho]$$

$$E_{xc}^{SIC}[\rho_\uparrow, \rho_\downarrow] = E_{xc}^{LSD}[\rho_\uparrow, \rho_\downarrow] - \sum_i \left\{ U[\rho_{i\uparrow}] + E_{xc}^{LSD}[\rho_{i\uparrow}, 0] \right\} - \sum_k \left\{ U[\rho_{k\downarrow}] + E_{xc}^{LSD}[0, \rho_{k\downarrow}] \right\}$$

with $\rho_{i\uparrow}(r) = |\phi_{i\uparrow}(r)|^2$

$\rho_{k\downarrow}(r) = |\phi_{k\downarrow}(r)|^2$

(free) variation of total energy w.r.t. orbitals leads to:

$$\left(-\frac{\nabla^2}{2m} + v_{i,\alpha}(r)\right)\phi_{i,\alpha}(r) = \varepsilon_{i,\alpha}\,\phi_{i,\alpha}(r) \qquad \alpha = \uparrow,\downarrow$$

$$\text{with} \quad v_{i,\alpha}(r) = v_o(r) + \int \frac{\rho(r')}{|r-r'|} d^3r' + v_{xc}^{LSD}(r)$$

$$- \int \frac{\rho_{i,\alpha}(r')}{|r-r'|} d^3r' - v_{xc}^{LSD}[\rho_{i,\alpha}](r)$$

Note: **different single-particle potential $v_{i,\alpha}(r)$ for each orbital**

Consequences:
- **$\{\varphi_{i,\alpha}\}$ not orthonormal**
- **Bloch theorem not valid $\Rightarrow$ allows localization in supercell**

SIC results

Temmerman (1992), Svane (1991)

- MnO, FeO, CoO, NiO, CuO correctly predicted as antiferromagnetic insulators
- VO correctly predicted to be a nonmagnetic metal
- La_2CuO_4 correctly predicted as antiferromagnetic semiconductor

Interaction-Strength-Interpolation

M. Seidl, J. Perdew, S. Kurth,

PRL 84, 5070 (2000)

PRA 62, 012502-1 (2000)

Use $E_{xc}[\rho] = \int_0^1 d\lambda W_\lambda[\rho]$

and construct approximate $W_\lambda[\rho]$ by interpolation between the known limits

$\lambda = 0$: $W_0 = E_x^{exact}$, $W_0' = 2\, E_c^{(2)}$

$\lambda = \infty$: W_∞ , W_∞'

Quality similar to meta-GGA

Atomization energies in units kcal/mol

	Expt	ISI	MGGA	GGA	x-exact + c-MGGA
H_2	109.5	107.3	114.5	104.6	112.7
LiH	57.8	58.8	58.4	53.5	57.8
Li_2	24.4	22.5	22.5	19.9	20.7
LiF	138.9	142.7	128.0	138.6	111.3
Be_2	3.0	5.7	4.5	9.8	-5.2
CH_4	419.3	423.4	421.1	419.8	429.3
NH_3	297.4	300.9	298.8	301.7	288.9
OH	106.4	108.6	107.8	109.8	98.2
H_2O	232.2	235.7	230.1	234.2	215.0
HF	140.8	143.7	138.7	142.0	125.5
B_2	71.0	68.1	68.3	77.1	31.4
CN	178.5	188.1	183.1	197.4	123.3
CO	259.3	265.9	256.0	268.8	218.2
N_2	228.5	234.6	229.2	243.2	175.4
NO	152.9	157.9	158.5	171.9	99.0
O_2	120.5	123.6	131.4	143.7	67.2
O_3	148.2	136.8	161.7	185.3	-1.6
F_2	38.5	34.0	43.2	53.4	-21.8
m.a.e.	-	4.3	4.2	9.7	33.8

MGGA: J.P. Perdew, S. Kurth, A. Zupan, P. Blaha, PRL 82, 2544 (1999)

ISI: M. Seidl, J.P. Perdew, S. Kurth, PRL 84, 5070 (2000)

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.