Comparison of exchange-correlation functionals: from LDA to GGA and beyond

Martin Fuchs

Fritz-Haber-Institut der MPG, Berlin, Germany

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Density-functional theory

DFT is an exact theory of the ground state of an interacting many-particle system:

$E_0 = \min\limits_{n\to N} E_v[n] \quad \Leftrightarrow \quad E_0 = \min\limits_{\Psi\to N} \langle\Psi|\hat{H}_v|\Psi\rangle$ by Hohenberg-Kohn theorem: $v(\mathbf{r}) \longrightarrow v[n(\mathbf{r})]$

Total energy density functional (electrons: $w(\mathbf{r},\mathbf{r}') = 1/|\mathbf{r}-\mathbf{r}'|$)

$$E_v[n] = \boxed{\min_{\Psi\to n}\langle\Psi|\hat{T}+\hat{W}|\Psi\rangle} + \int n(\mathbf{r})v(\mathbf{r})d\tau = \boxed{F[n]} \quad + \int n(\mathbf{r})v(\mathbf{r})\,d\tau$$

Non-interacting case: $w(\mathbf{r},\mathbf{r}') \longrightarrow 0$

$\boxed{F[n]} \longrightarrow \min\limits_{\Psi\to n}\langle\Psi|\hat{T}|\Psi\rangle = \langle\Phi[n]|\hat{T}|\Phi[n]\rangle = T_s[n] \qquad \Phi[n]$ is a Slater determinant

Interacting case rewritten:

$$E_v[n] = \boxed{T_s[n] + E_{xc}[n] + \frac{1}{2}\int n(\mathbf{r})w(\mathbf{r},\mathbf{r}')n(\mathbf{r}')d\tau d\tau'} + \int n(\mathbf{r})v(\mathbf{r})\,d\tau$$

XC energy functional: kinetic correlation energy & exchange and Coulomb correlation energy

$$E_{xc}[n] =: \underline{\langle\Psi[n]|\hat{T}|\Psi[n]\rangle - T_s[n]} + \underline{\langle\Psi[n]|\hat{W}|\Psi[n]\rangle - \tfrac{1}{2}\int n(\mathbf{r})w(\mathbf{r},\mathbf{r}')n(\mathbf{r}')d\tau d\tau'}$$

Kohn-Sham scheme

Minimization of $E_v[n]$ with $n(\mathbf{r}) \longrightarrow N$ determines groundstate:

$$\frac{\delta E_v[n]}{\delta n(\mathbf{r})} = \mu \quad \longrightarrow \quad \frac{\delta F[n]}{\delta n(\mathbf{r})} + v(\mathbf{r}) = \frac{\delta T_s[n]}{\delta n(\mathbf{r})} + v^{KS}([n];\mathbf{r}) = \mu$$

...effective non-interacting system ⟶ Kohn-Sham independent-particle equations:

$$\left[-\frac{\nabla^2}{2} + v^{KS}(\mathbf{r})\right] \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r}) \quad \text{with} \quad v^{KS}(\mathbf{r}) = \int w(\mathbf{r},\mathbf{r}')n(\mathbf{r}')d\tau' + \boxed{\frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})}} + v(\mathbf{r})\,,$$

density $n(\mathbf{r}) = \sum_i f_i |\phi_i(\mathbf{r})|^2$,

occupancies $\epsilon_i < \mu : f_i = 1, \quad \epsilon_i = \mu : 0 \le f_i \le 1, \quad \epsilon_i > \mu : f_i = 0$ (aufbau principle).

- non-interacting kinetic energy treated exactly $\quad T_s[n] = \int \sum_i f_i |\nabla \phi_i(\mathbf{r})|^2 d\tau$
- "classical" electrostatics (e-n & e-e) treated exactly
- "only" need to approximate $E_{xc}[n]$ and $\boxed{v_{xc}([n];\mathbf{r}) = \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})}}$ **determines accuracy in practice!**
- applied is spin density functional theory: $n_{\uparrow,\downarrow}$ treated as separate variables

beware: $v^{KS}(\mathbf{r})$ is a local operator. Direct approximation of whole $F[n]$ possible too: DFT with generalized Kohn-Sham schemes[1] and nonlocal effective potentials, e.g. Hartree-Fock eqs.

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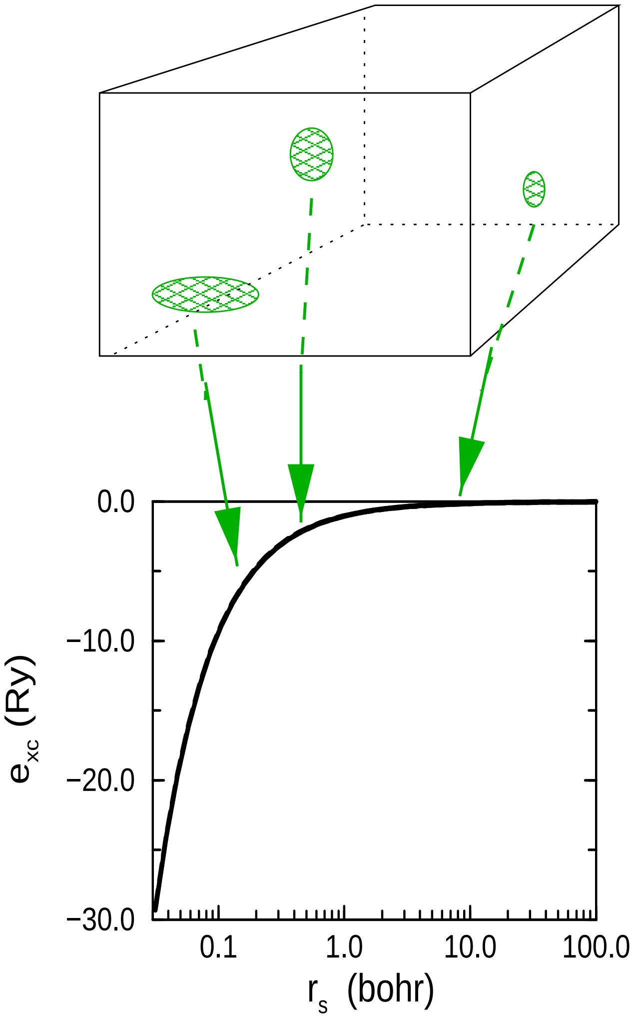
[1] *Seidl, Görling, Vogl, Majewski, Levy, Phys Rev B 53, 3764 (1996).*

Local-density approximation

$$E_{xc}^{LDA}[n] = \int n(\mathbf{r}) e_{xc}^{hom}(n(\mathbf{r})) d\tau$$



- local dependence on density or Wigner-Seitz radius
  $r_s = (\frac{4\pi}{3} n)^{-1/3}$
- XC energy per electron is that of the homogeneous electron gas,
  $e_{xc}[n] = e_{xc}^{hom}(n)|_{n=n(\mathbf{r})}$
  ✓ exchange part $e_x^{hom}(n)$ known analytically
  ✓ correlation part $e_c^{\mathrm{hom}}(n)$ known
    $*$ analytically for $r_s \rightarrow 0$ and $r_s \rightarrow \infty$
    $*$ numerically "exact" for $2 < r_s < 100$ from QMC data[1]
  . . . as parametrization interpolating over all r_s
    "PW91", "Perdew-Zunger", "VWN"[2]

- "workhorse" in DFT applications to solids
- real systems are far from jellium-like homogeneity
  . . . why does LDA work at all?
  . . . where does it fail?
  . . . how to improve beyond it?

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[1] *Ceperley, Alder, Phys Rev Lett 45, 566 (1980).*

[2] *Perdew, Wang, Phys Rev B 45, 13244 (1992); Perdew, Zunger (1980); Vosko, Wilk, Nussair (1980).*

Performance of the LDA

- **structural, elastic, and vibrational properties** often good enough
  - ✓ crystal bulk lattice constants accurate to within 3%, usually underestimated
  - ✓ bulk moduli somewhat too large, $> 10\%$ error not uncommon for d-metals
  - ✓ phonons somewhat too stiff

- **binding energies** are too negative (overbinding), up to several eV
  - ✗ cohesive energies of solids, but formation enthalpies often o.k.
  - ✗ molecular atomization energies, mean error (148 molecules G2 set) ≈ -3 eV

- **activation energies in chemical reactions** unreliable
  - ✗ too small/absent, e.g. for H_2 on various surfaces (Al, Cu, Si, ...)

- **relative stability of crystal bulk phases** can be uncertain
  - ✗ SiO_2 high pressure phase more stable than zero pressure phase
  - ✗ underestimated transition pressure e.g. for diamond $\leftrightarrow$ β-tin phase transitions in Si & Ge
  - ✗ magnetic phases

- **electronic structure** can be usefully interpreted (density of states, band structures), except for band gaps (<u>a more fundamental issue than LDA!</u>)

View on XC through the XC hole

Definition of the XC energy by a coupling constant integration of the e-e interaction[1]:

$$E([n];\lambda) = \langle \Psi_\lambda[n] | \hat{T} + \hat{V}_\lambda + \lambda \hat{W} | \Psi_\lambda[n] \rangle = \min_{\Psi_\lambda \to n} \ldots$$

- by Hohenberg-Kohn theorem: $n(\mathbf{r}) \leftrightarrow v_\lambda([n];\mathbf{r})$ for any $0 \leq \lambda \leq 1$
- $\lambda = 0$ $\longrightarrow$ non-interacting case/ Kohn-Sham potential, $v_{\lambda=0}([n];\mathbf{r}) = v^{KS}([n];\mathbf{r})$
- $\lambda = 1$ $\longrightarrow$ external potential, $v_{\lambda=1}([n];\mathbf{r}) = v(\mathbf{r})$

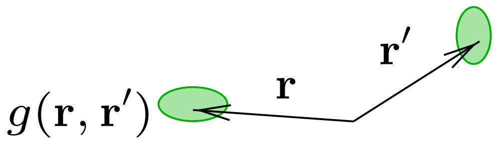
groundstate energy: $E([n];1) = E([n];0) + \int_0^1 \frac{d\,E([n];\lambda)}{d\lambda}\, d\lambda$

➥ $E_{xc}[n] = \int_0^1 \boxed{\langle \Psi_\lambda[n] | \lambda \hat{W} | \Psi_\lambda[n] \rangle} d\lambda - \frac{1}{2} \int n(\mathbf{r}) w(\mathbf{r},\mathbf{r}') n(\mathbf{r}') d\tau d\tau'$

$$\boxed{\phantom{\langle \Psi_\lambda[n] | \lambda \hat{W} |}} = \frac{1}{2} \int w(\mathbf{r},\mathbf{r}') n(\mathbf{r}) n(\mathbf{r}') \boxed{\frac{\langle \Psi_\lambda[n] | \sum_{p,q} \hat{\Psi}_p^\dagger(\mathbf{r}) \hat{\Psi}_q^\dagger(\mathbf{r}') \hat{\Psi}_q(\mathbf{r}') \hat{\Psi}_p(\mathbf{r}) | \Psi_\lambda[n] \rangle}{n(\mathbf{r}) n(\mathbf{r}')}} d\tau d\tau'$$

☞ XC in terms of the **pair correlation function** $g_\lambda([n];\mathbf{r},\mathbf{r}')$

☞ XC in terms of the **adiabatic connection** integrand
(scaled e-e potential energy)



- may distinguish exchange and correlation, e.g. $E_{xc} = E_x + E_c$

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[1] *cf. DFT books by Dreizler and Gross & Yang and Parr*

. . . coupling constant averaged XC hole

- λ-integration implies coupling constant averaged pair correlation function

$$\tilde{g}([n];\mathbf{r},\mathbf{r}') = \int_0^1 g_\lambda([n];\mathbf{r},\mathbf{r}')d\lambda$$

Identify the XC energy as

$$E_{xc}[n] = \frac{1}{2}\int d\tau n(\mathbf{r}) \int d\tau' n(\mathbf{r}')\{\tilde{g}([n];\mathbf{r},\mathbf{r}') - 1\} \times w(\mathbf{r},\mathbf{r}')$$

- interpretation: the electron density $n(\mathbf{r})$ interacts with the electron density of the XC hole

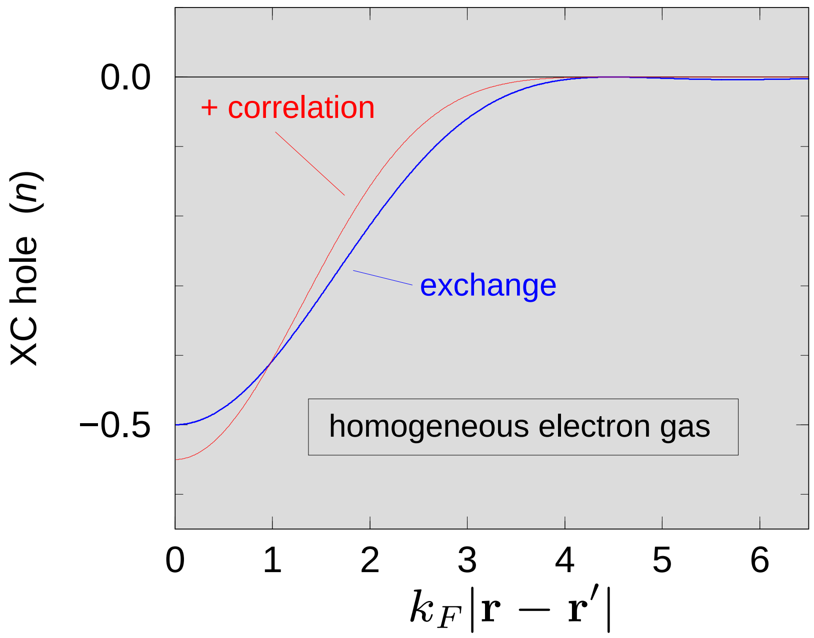
  $n_{xc}([n];\mathbf{r},\mathbf{r}') = n(\mathbf{r}')\{\tilde{g}([n];\mathbf{r},\mathbf{r}') - 1\}$

  ➥ Pauli exclusion principle & Coulomb repulsion

- local density approximation corresponds to

$$n_{xc}([n];\mathbf{r},\mathbf{r}') = n(\mathbf{r})\{\tilde{g}^{hom}(n(\mathbf{r});|\mathbf{r}-\mathbf{r}'|) - 1\}$$

  ➥ always centered at reference electron & spherical



(NB: correlation part varies with k_F)

From the XC hole to the XC energy

Focus on $E_{xc}[n] = \int n(\mathbf{r}) e_{xc}([n];\mathbf{r}) d\tau$ (... component of the total energy) $w = \frac{1}{|\mathbf{r}-\mathbf{r}'|} = \frac{1}{|\mathbf{u}|}$

- for e_{xc} only the angle averaged XC hole matters (and LDA hole is always spherical)

$$n_{xc}(\mathbf{r}, \mathbf{r}+\mathbf{u}) = \sum_{lm} n_{lm}^{xc}(\mathbf{r}, u) Y_{lm}(\Omega_{\mathbf{u}})$$

$$E_{xc}[n] = \frac{1}{2} \int n(\mathbf{r}) \int \frac{n_{xc}(\mathbf{r}, \mathbf{r}+\mathbf{u})}{u} d\tau_u \, d\tau \rightarrow \frac{1}{2} \int n(\mathbf{r}) \int_0^\infty \frac{n_{00}^{xc}(\mathbf{r}, u)}{u} u^2 du \, d\tau$$

- for E_{xc} only the system & angle averaged XC hole matters

$$\langle n_{xc}(u) \rangle = \frac{1}{N} \int n(\mathbf{r}) n_{00}^{xc}(\mathbf{r}, u) d\tau$$

➥ XC energy in terms of averaged XC hole[1]

$$E_{xc}[n] = \frac{N}{2} \int_0^\infty \frac{\langle n_{xc}(u) \rangle}{u} u^2 du \quad = \quad N \times \text{average XC energy per electron}$$

LDA & GGA approximate average holes rather closely ⇔ work mostly o.k.

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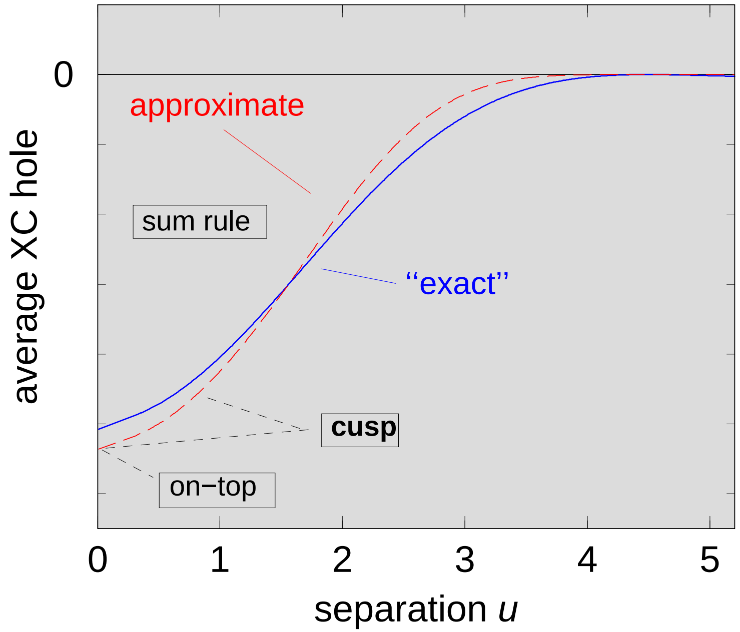
[1] *Perdew et al., J Chem Phys 108, 1552 (1998).*

Sum rule and other constraints on the XC hole

- sum rule (constrains global behavior)

$$\int n_{xc}([n];\mathbf{r},\mathbf{r}')d\mathbf{r}' = -1 \quad \text{... average hole too}$$

✓ LDA: $\int n(\mathbf{r}) n_{xc}^{hom}(n(\mathbf{r}),\mathbf{r},\mathbf{r}')d\mathbf{r}' = -1$



- on-top hole $\langle n_{xc}(0)\rangle$ (fixes value at $u=0$)

✓ LDA: accurate (exact in some limits) for correlation, exact for exchange

- cusp condition (constrains behavior around $u=0$)

$$\left.\frac{\partial\langle n_{xc}(u)\rangle}{\partial u}\right|_{u=0} = \langle n_{xc}(0)\rangle + \langle n(0)\rangle$$

✓ LDA: correct

- LDA works well because the LDA (average) XC hole is that of a physical system, jellium

Beware:
- pointwise behavior of $n_{xc}^{LDA}(\mathbf{r},\mathbf{r}')$ may be incorrect (e.g. outside metal surface), system averaging unweights tail and near-nucleus regions
- XC potential $v_{xc}([n];\mathbf{r})$ for LDA can be locally poor, but again less so for the system average

Generalized Gradient Approximation for E_{xc}

❶ Gradient expansion of XC energy and (later) hole: $n_{xc}([n];\mathbf{r},\mathbf{u}) \longrightarrow n_{xc}(\mathbf{r},\mathbf{u}=0) + \nabla_{\mathbf{u}} n_{xc}|_{\mathbf{u}=0} + \ldots,$
and generalized to imposing **constraints** to meet

- ✓ e.g. $n_x(\mathbf{r},\mathbf{u}) < 0$, $\int n_x(\mathbf{r},\mathbf{u}) d\mathbf{r} = -1$, by real space cutoffs ⟶ numerical GGA
- ✓ scaling relations and bounds on E_{xc} by analytic approximation to numerical GGA
  - ➥ parameter-free GGA by Perdew-Wang PW91
  - ➥ simplified in **PBE** GGA
- ✓ contains LDA & retains all its good features

❷ Earlier: analytic model or ansatz + empirical parameter(s)
➥ Langreth-Mehl (C), Becke 86(X) + Lee-Yang-Parr(C) **BLYP**, ...

❸ Alternative: analytic ansatz + (many) fitted parameters (e.g. fit to thermochemical data)
☞ see accuracy limit of GGA functionals, can be better & worse than PBE

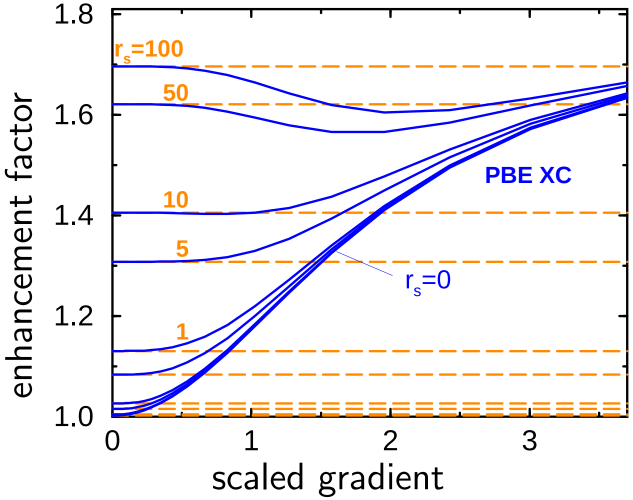
Generic GGA XC functional

$$E_{xc}^{GGA}[n] = \int n\, e_x^{LDA}(n) \boxed{F_{xc}^{GGA}(n, s)}\,\Big|_{n=n(\mathbf{r})} d\tau, \qquad s = \left.\frac{|\nabla n|}{2k_F n}\right|_{n=n(\mathbf{r})}$$

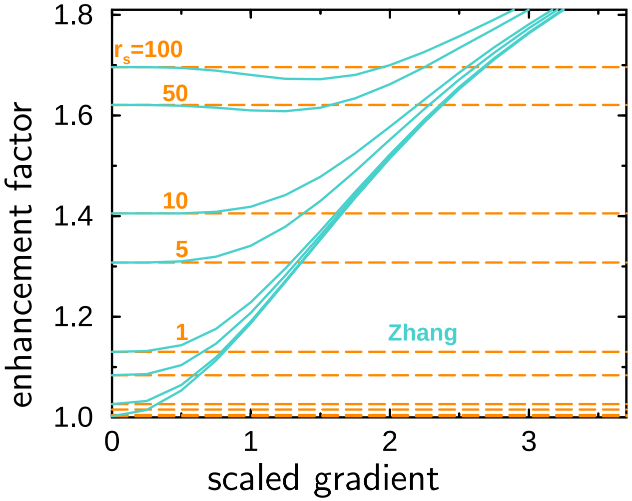
- Enhancement factor $F_{xc}(n,s)$ over LDA exchange: function of density and scaled gradient
⟶ "understanding" how GGA's work
- Calculations with GGA's are not more involved than with LDA,
except that $v_{xc}[n;\mathbf{r}] = v_{xc}(n, \nabla_i n, \nabla_i \nabla_j n)|_{n(\mathbf{r})}$

Differences in present GGA's

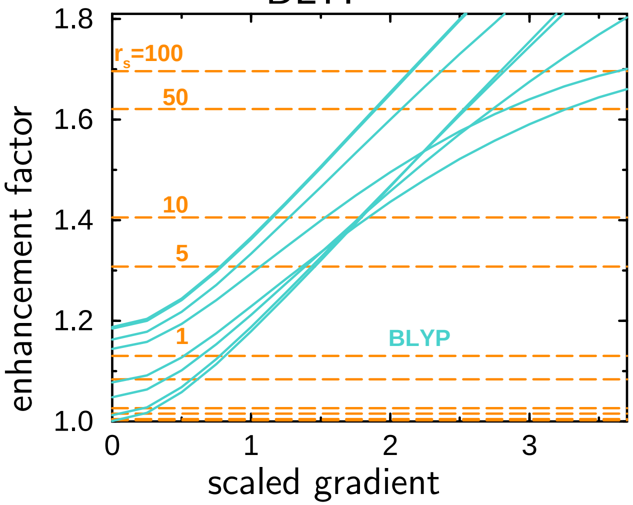
PBE



Zhang et al. "revised" revPBE



BLYP



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WC-PBE	Wu & Cohen '05
xPBE	Xu & Goddard '04
HCTH	Handy et al. '01
RPBE	Hammer et al. '99
revPBE	Zhang et al. '98
PBE GGA	Perdew et al. '96
PW91	Perdew & Wang '91
PW91	Perdew & Wang '91
BP	Becke & Perdew '88
BLYP	Becke & Lee et al. '88
. . .	

- revPBE & BLYP more nonlocal than PBE GGA
  - molecules: more accurate atomization energies
  - solids: bondlengths too large, cohesive energies too small
  - LYP correlation incorrect for jellium

- more local GGAs will make lattice constants smaller (e.g. Tinte et al. PRB 58, 11959 (1998)), but make binding energies more negative

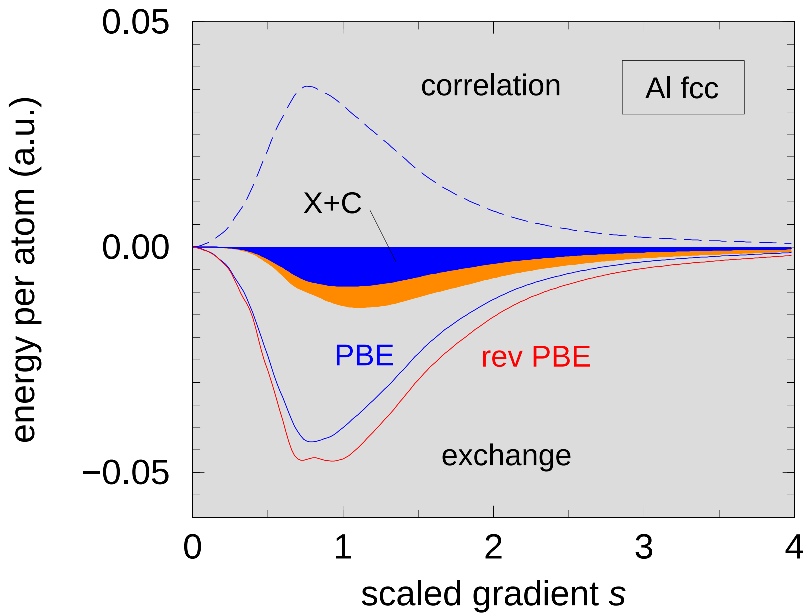
… how GGA's change total energies

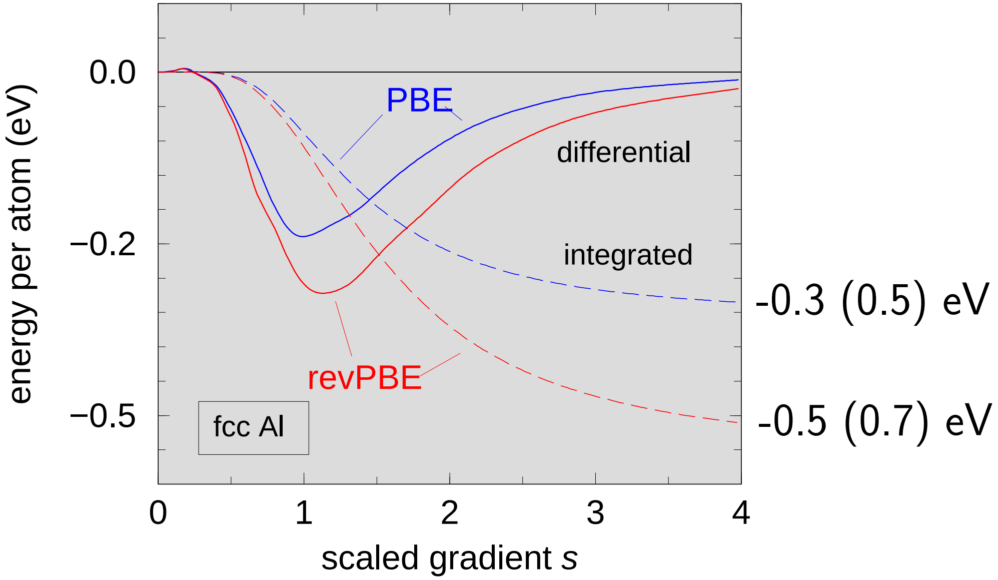
Analysis in terms of selfconsistent LDA density shows how GGAs work:

$$E_{tot}^{GGA}[n^{GGA}] = E_{tot}^{LDA}[n^{LDA}] + \boxed{E_{xc}^{GGA}[n^{LDA}] - E_{xc}^{LDA}[n^{LDA}]} + \mathcal{O}(n^{GGA} - n^{LDA})^2$$

"Spectral decomposition" in terms of s:

$$E_{xc}^{GGA} - E_{XC}^{LDA} = \int\!\!\int_{s=0}^{\infty} \left[e_{xc}^{GGA}(\mathbf{r}) - e_{xc}^{LDA}(\mathbf{r})\right] \delta(s - s(\mathbf{r}))d\tau ds$$





➥ only $0 \leq s \leq 4$ contribute, similar analysis can be made for $n(\mathbf{r})$

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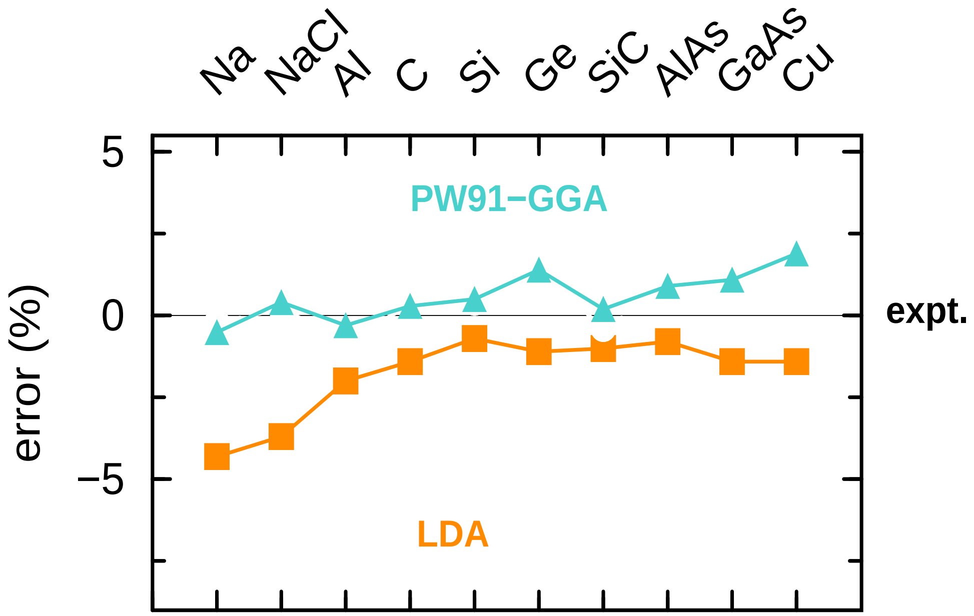
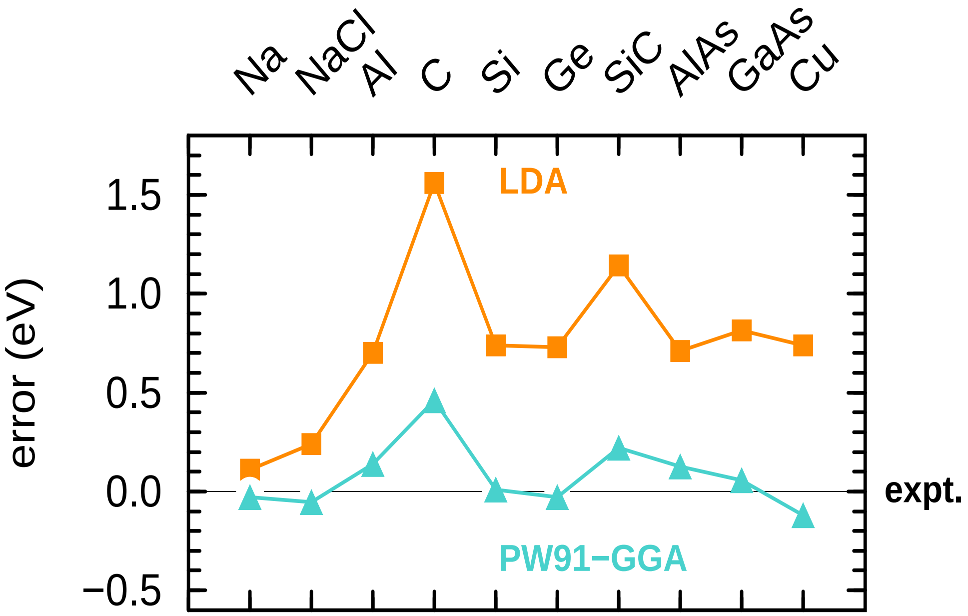
for more see e.g. *Zupan et al., PRB 58, 11266 (1998)*

Cohesive properties in GGA

Bulk lattice constants GGA increase due to more repulsive core-valence XC.



Cohesive energies GGA reduction mostly valence effect.



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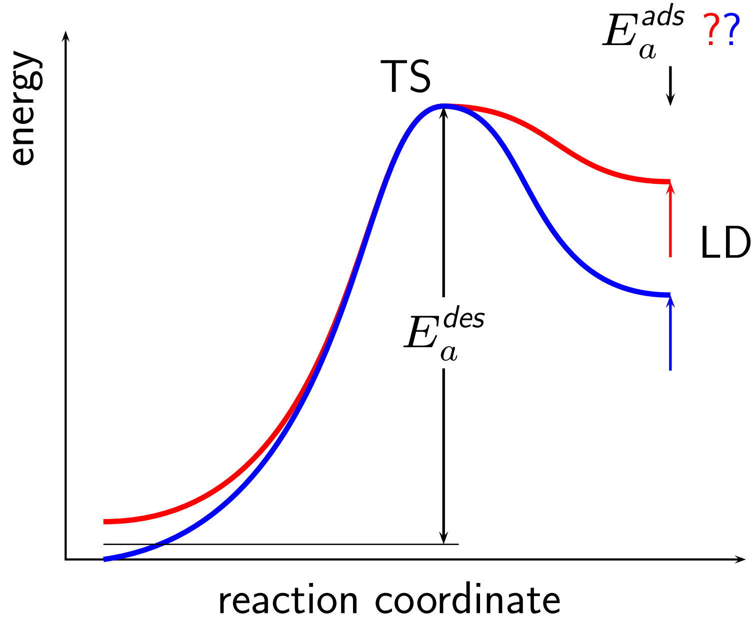
for comparison of LDA, GGA, and Meta-GGA see *Staroverov, Scuseria, Perdew, PRB 69, 075102 (2004)*

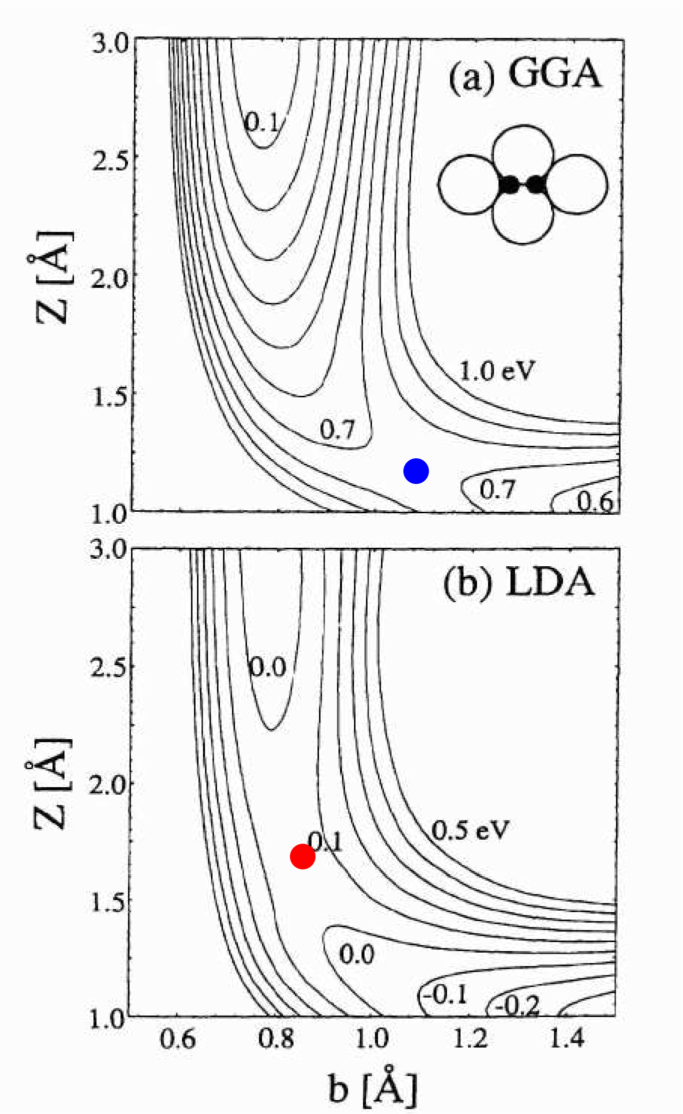
… energy barriers: H_2 on Cu(111)

barrier to dissociative adsorption
- PW91-GGA ≈ 0.7 eV
- LDA <0.1 eV

total energy of free H_2
- PW91-GGA -31.8 eV ($\approx$ expt.)
- LDA -30.9 eV

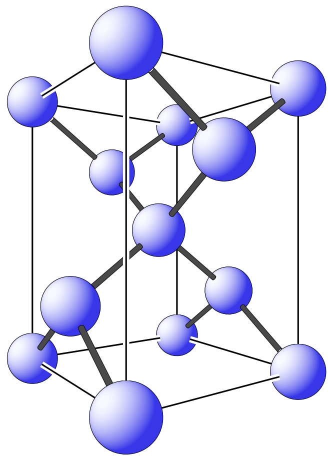


Cu + H_2:
LDA-GGA ≈ 1 eV

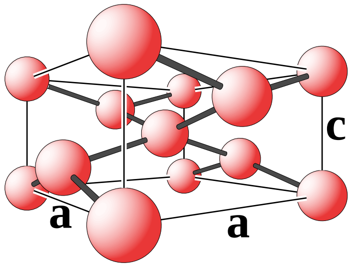


Hammer et al. PRL 73, 1400 (1994)

Phase transition β-tin - diamond in Si

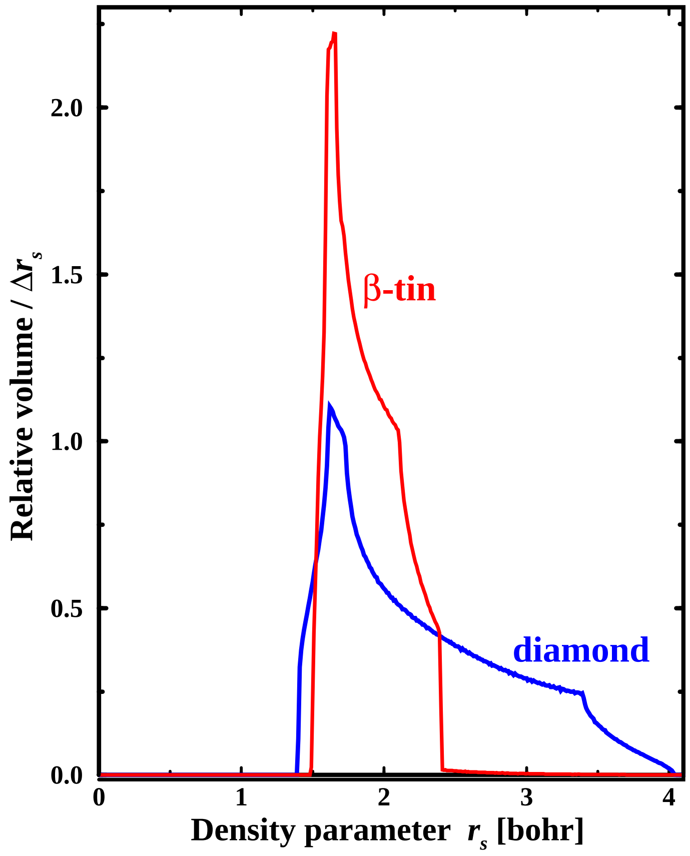


diamond-structure



β-tin structure

“Spectral decomposition” in terms of n

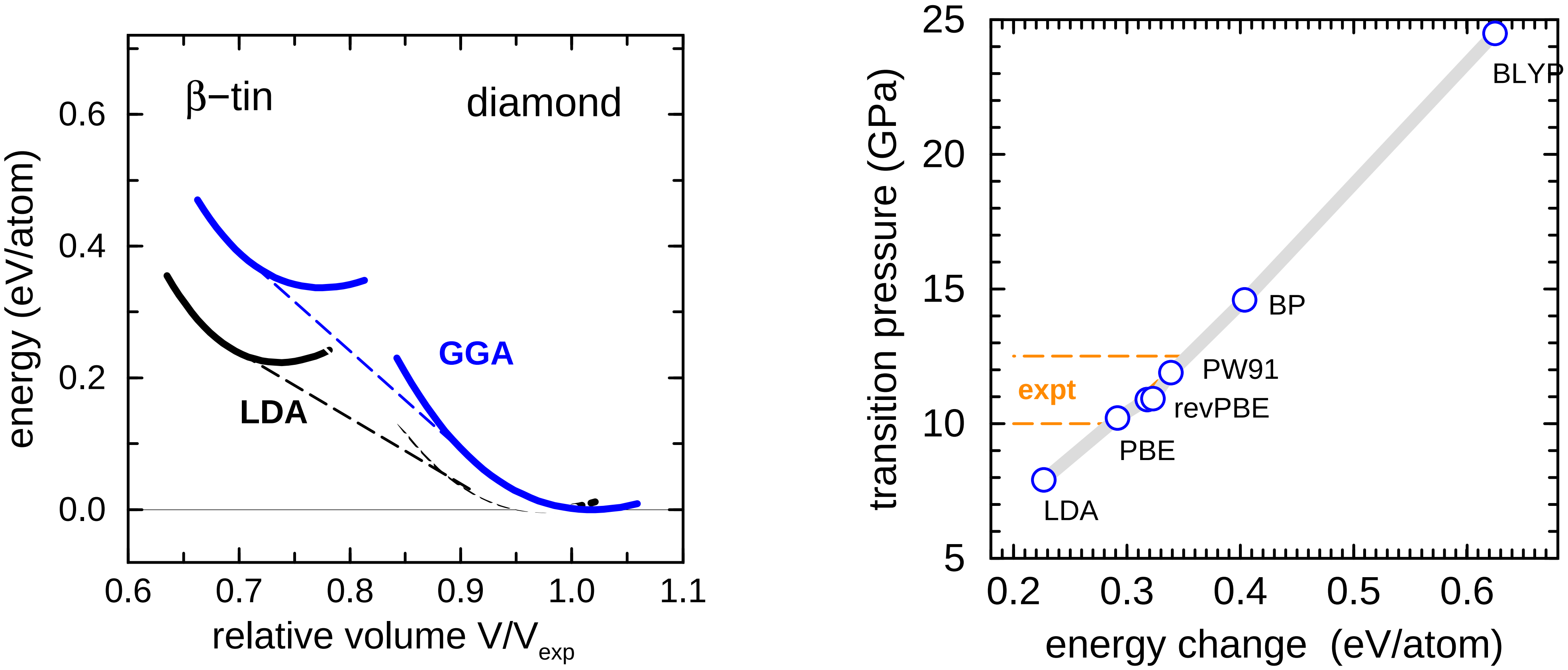


diamond: $a_0 = 10.26$ bohr, semiconductor

β-tin: $c/a = 0.552$, metallic

Phase transition β-tin - diamond in Si

Gibbs construction: $E_t^{\beta} + p_t V_t^{\beta} = E_t^{dia} + p_t V_t^{dia}, \quad p_t^{exp} = 10.3 \ldots 12.5$ GPa



- GGA increases transition pressure, “inhomogeneity effect”
- use of LDA-pseudopotentials insufficient

Moll et al, PRB 52, 2550 (1995); DalCorso et al, PRB 53, 1180 (1996); McMahon et al, PRB 47, 8337 (1993).

Performance of PBE GGA vs. LDA

✓ atomic & molecular total energies are improved

✓ **GGA corrects the LDA overbinding**:

average error for G2-1 set of molecules:

+6 eV	HF
−1.5 eV	LSDA
−0.5 eV	PBE-GGA
0.2 eV	PBE0 hybrid
±0.05 eV	goal,

better cohesive energies of solids

✓ improved activation energy barriers in chemical reactions (but still too low)

✓ improved description of relative stability of bulk phases

✓ more realistic for magnetic solids

✓ useful for “electrostatic” hydrogen bonds

✗ GGA softens the bonds
increasing lattice constants
decreasing bulk moduli
➥ no consistent improvement

○ LDA yields good relative bond energies for highly coordinated atoms,
e.g. surface energies, diffusion barriers on surfaces

○ GGA favors lower coordination (larger gradient!),
not always enough where LDA has a problem,
e.g. CO adsorption sites on transition metal surfaces
➥ significance of GGA ?

✗ GGA workfunctions for several metals turn out somewhat smaller than in LDA

○ one-particle energies/bands close to LDA

✗ Van der Waals (dispersion) forces not included!

Comparing LDA and (different) GGAs gives an idea about possible errors!

Beyond GGA: orbital dependent XC functionals

Kohn-Sham non-interacting system make $\phi_i[n]$ density-functionals: $n \leftrightarrow v^{KS}[n;\mathbf{r}] \Rightarrow \phi_i$

- LDA and GGA are explicit density-functionals $E_{xc}[n]$
- Implicit density-functionals formulated in terms of $\phi_i[n]$?

  ⟶ more flexible for further improvements

  self-interaction free: $E_{xc}[n]|_{N=1} = 0$,

  $v_{xc}(|\mathbf{r}| \to \infty) = -\frac{1}{r}$,

  nonspherical $n_{xc}(\mathbf{r}, \mathbf{r}')$ ... ?

➥ Start with exact exchange:

Exchange-energy $E_x[\{\phi_i\}] = \frac{1}{2}\int \frac{\sum_{i,j} \bar{\phi}_i(\mathbf{r})\bar{\phi}_j(\mathbf{r}')\phi_i(\mathbf{r}')\phi_j(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|} d\tau d\tau'$

▲ same as in Hartree-Fock, **but** $-\frac{\nabla^2}{2} - v^{KS}(\mathbf{r})|\phi_i(\mathbf{r}) = \epsilon_i\phi_i(\mathbf{r})$ KS and HF orbitals different!

- Groundstate ...

  in KS-DFT: optimized effective potential **OEP** method, local KS potential

  in Hartree-Fock: variation with respect to orbitals yield HF eqs., nonlocal effective potential

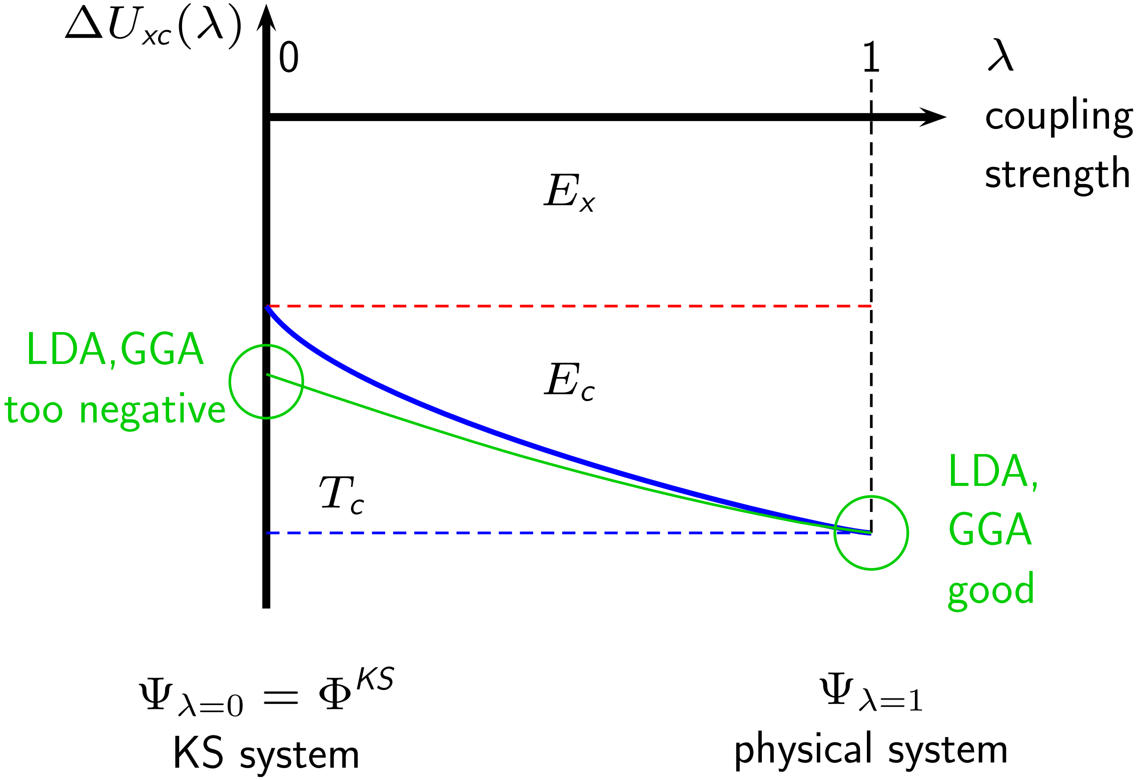
  $E_0^{HF} \le E_0^{KS-EXX}$

Hybrid functional: mixing exact exchange with LDA/GGA

- XC = EXX + LDA correlation is less accurate (underbinds) than XC = LDA for molecules
- challenge: correlation functional that is **compatible with exact exchange**?
- **hybrid functionals** to "interpolate" adiabatic connection, $U_{xc}^{\lambda}[n]$

$$E_{xc}[n] = \int_0^1 \boxed{U_{xc}[n](\lambda)} d\lambda \quad U_{xc}[n](\lambda) = \langle \Psi_\lambda[n] | \hat{W} | \Psi_\lambda[n] \rangle - U_{Hartree}[n]$$

- molecular dissociation: ΔU_{xc} = molecules - atoms ... looks like



. . . hybrid functionals

How they are defined:

- use exact exchange for $\lambda = 0$
  and a “local” functional for $\lambda = 1$

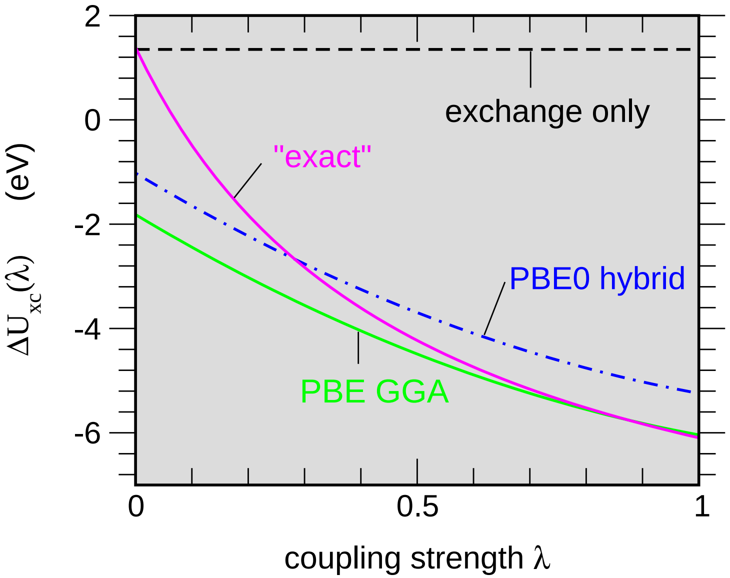
  Hybrid functional $=$ “interpolation”

  $$E_{xc}^{hyb} = E_{xc}^{GGA} + a\left\{E_x - E_x^{GGA}\right\}$$

  - mixing parameter $a = 0.16 \ldots 0.3$
    from fitting thermochemical data
  - $a = 1/4$ by 4th order perturbation theory
    $\longrightarrow$ **PBE0** $=$ PBE1PBE
- **B3LYP** 3-parameter combination of
  Becke X-GGA, LYP C-GGA, and LDA
- molecular dissociation energies on average
  within $\approx$3 kcal/mol $\approx$ 0.1 eV
  (but 6 times larger errors can happen)

How hydbrids and GGAs work:

Adiabatic connection $N_2 \longrightarrow 2N$



XC contributions to binding:

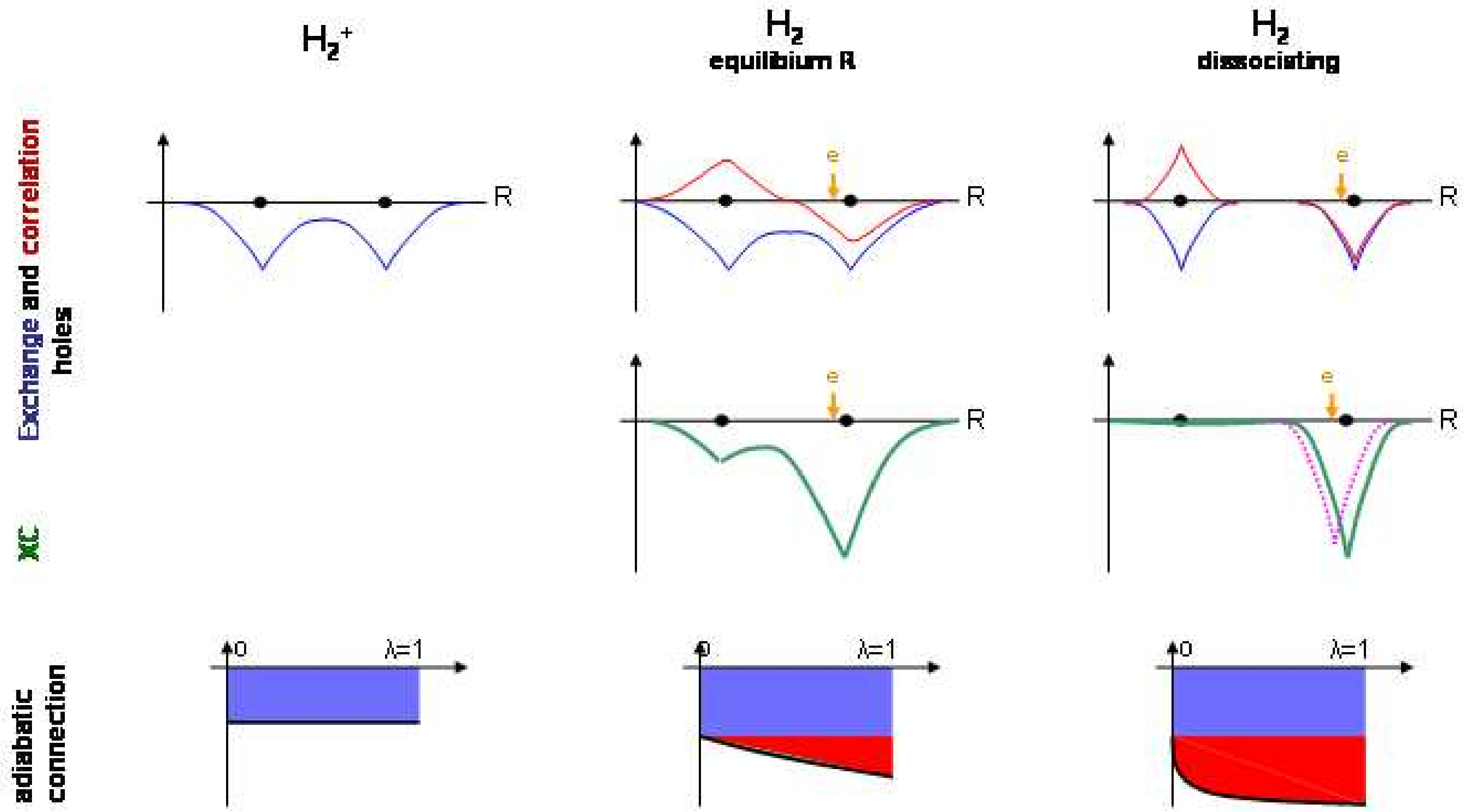
(eV)	E_b	ΔE_x	ΔE_c
PBE	-10.58	-1.82	-2.49
PBE0	-9.62	-1.01	-2.49
exact	-9.75	1.39	-5.07

... X and C errors tend to cancel!

Becke, J Chem Phys 98, 5648 (1993); Perdew et al, J Chem Phys 105, 9982 (1996).
comprehensive comparison: *Staroverov, Scuseria, Tao, Perdew, J Chem Phys 119, 12129 (2003)*

XC revisited: role of error cancellation between X and C

… or: when GGAs or hybrids are not enough



- need 100% exchange mixing
- LDA/GGA self-interaction error!

- "normal" case for LDA/GGA/hybrids
- mostly "dynamical correlation"

- 0% exchange mixing better
- strong "left-right (static) correlation" simulated by LDA/GGA exchange (& more so if spin-polarized)

see e.g. *Baerends and Gritsenko, JCP 123, 062202 (2005)*

… orbital dependent functionals

- Meta-GGA's

XC energy functional

$$E_{xc}^{MGGA}[n] = \int n(\mathbf{r}) e_{xc}^{MGGA}(n, \nabla n, t_s)\Big|_{n(\mathbf{r})} d\tau$$

kinetic energy density of non-interacting electrons $t_s(\mathbf{r}) = \frac{1}{2}\sum_i^{occ} f_i |\nabla\phi_i(\mathbf{r})|^2$

- OEP or HF style treatment of $\dfrac{\delta E_{xc}^{MGGA}[\phi_i]}{\delta\phi_i(\mathbf{r})} = \ldots - \dfrac{1}{2}\nabla \dfrac{\partial e_{xc}}{\partial t_s}\nabla\phi_i$

- **TPSS**: Tao, Perdew, Stavroverov, Scuseria, Phys Rev Lett 91, 146401 (2003): + v_x finite
  PKZB: Perdew, Kurth, Zupan, Blaha, Phys Rev Lett 82, 2544 (1999): XC "non-empirial", LDA limit
  Van Voorhis, Scuseria, J Chem Phys 109, 400 (1998): XC "highly fitted", no LDA limit
  Colle, Salvetti, Theoret Chim Acta 53, 55 (1979): C, no LDA limit → BLYP GGA
  Becke, J Chem Phys 109, 2092 (1998): XC + exact exchange "fitted"

- TPSS accomplishes a consistent improvement over (PBE) GGA
- PKZB improved molecular binding energy, but worsened bond lengths in molecules & solids
- hybrid functionals on average still more accurate for molecular binding energies
- TPSS provides sound, nonempirical basis for new hybrids "TPSSh"
  → next step: MGGA correlation compatible with exact exchange?

ACFDT XC: including unoccupied Kohn-Sham states

- Adiabatic connection: KS system $\lambda = 0$ $\longrightarrow$ physical system $\lambda = 1$

  $$E_{xc}[n] = \int_0^1 \langle \Psi_\lambda | \hat{W}_{ee} | \Psi_\lambda \rangle d\lambda - U[n]$$

- Fluctuation-dissipation theorem:

$$W_{xc}(\lambda) =: \langle \Psi_\lambda | \hat{W}_{ee} | \Psi_\lambda \rangle = \frac{1}{2} \int \frac{e^2}{|\vec{r} - \vec{r}'|} \left[-\frac{\hbar}{\pi} \int_0^\infty \chi_\lambda(iu, \vec{r}, \vec{r}')\, du - n(\vec{r}) \delta(\vec{r} - \vec{r}') \right] d\vec{r} d\vec{r}'$$

…using dynamical density response

- From noninteracting Kohn-Sham to interacting response by TD-DFT

$$\chi_0(iu, \vec{r}, \vec{r}') = 2\Re \sum_{i,j}^{\infty} \frac{\varphi_i^*(\vec{r})\varphi_j(\vec{r})\varphi_j^*(\vec{r}')\varphi_i(\vec{r}')}{i\hbar u - (\epsilon_j - \epsilon_i)}$$

$\epsilon_i[n]$ …KS eigenvalues

$\varphi_i([n], \vec{r})$ …KS orbitals

$$\chi_\lambda(iu) = \chi_0(iu) + \chi_0(iu) \cdot K_\lambda^{hxc}(iu) \cdot \chi_\lambda(iu)$$

"Dyson equation" 6dim.

…using Coulomb and XC kernel from TD-DFT

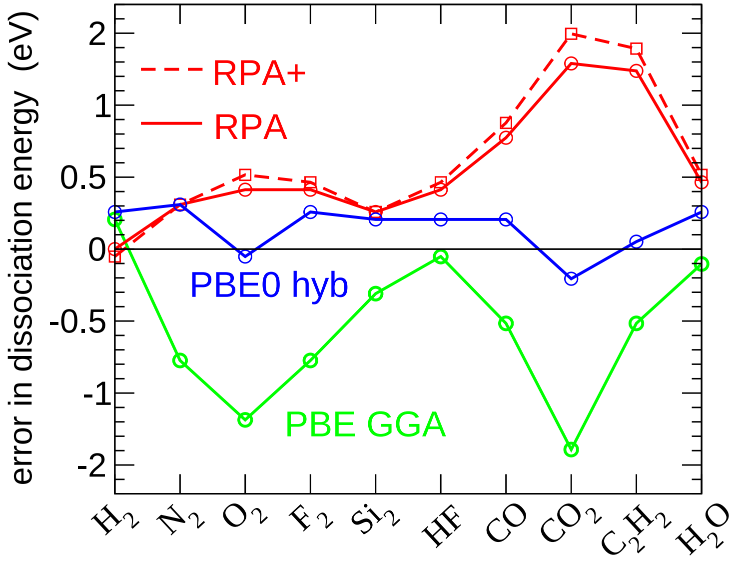
In principle ACFDT formula gives exact XC functional

In practice starting point for fully nonlocal approximations

- **RPA**: $K_\lambda^{hxc} = \lambda |\mathbf{r} - \mathbf{r}'|^{-1}$ and zero XC kernel ... yields exact exchange and London dispersion forces
- combine with XC kernels, hybrids with usual XC functionals, split Coulomb interaction …

Status of RPA type functionals

Molecular dissociation energies
"RPA for all e-e separations"



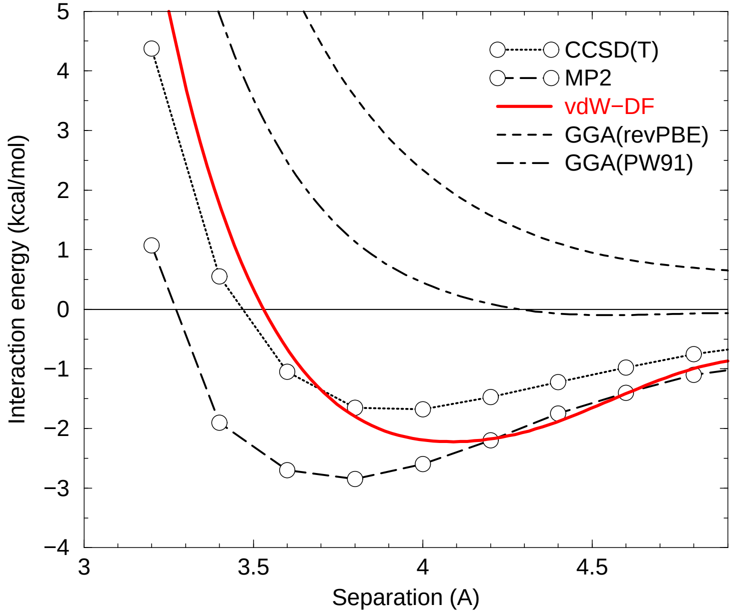
... no consistent improvement over GGA

... not too bad, without X and C error cancellation

... better TD-DFT XC kernels needed!

Furche, PRB 64, 195120 (2002),
Fuchs and Gonze, PRB 65, 235109 (2002)

Stacked benzene dimer
(Van der Waals complex)
"short-range: GGA + long-range: RPA"



... includes dispersion forces!

Dion et al., PRL 92, 246401 (2004)

Summary

- LDA & GGA are *de facto* controlled approximations to the average XC hole

- GGA remedies LDA shortcomings w.r.t. total energy differences but may also overcorrect (e.g. lattice parameters)

- still can & **should** check GGA induced corrections for plausibility by
  . . . simple arguments like homogeneity & coordination
  . . . results from "quantum chemical" methods (Quantum Monte Carlo, CI, . . .)
  . . . depends on actual GGA functional

- hybrid functionals mix in exact exchange (B3LYP, PBE0, ... functionals)

- orbital dependent, implicit density functionals:
  exact Kohn-Sham exchange, Meta-GGA & OEP method,
  functionals from the adiabatic-connection fluctuation-disspation formula

- Always tell what XC functional you used,
  e.g. PBE-GGA (not just GGA)
  ... helps others to understand your results
  ... helps to see where XC functionals do well or have a problem