

## Density functionals for exchange and correlation: From LDA to GGA and beyond

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### Density-Functional Theory

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

$$E_0 = \min_{n \rightarrow N} E_v[n] \Leftrightarrow E_0 = \min_{\Psi \rightarrow N} \langle \Psi | \hat{H}_v | \Psi \rangle \text{ by Hohenberg-Kohn theorem: } v(\mathbf{r}) \rightarrow v[n(\mathbf{r})]$$

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

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

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

$$\boxed{F[n]} \rightarrow \min_{\Phi \rightarrow n} \langle \Phi | \hat{T} | \Phi \rangle = \langle \Phi[n] | \hat{T} | \Phi[n] \rangle = T_s[n] \quad \underbrace{\Phi \dots \text{Slater determinant}}$$

$$\text{density: } n(\mathbf{r}) = \sum_i^{\infty} f_i |\phi_i(\mathbf{r})|^2, \quad \langle \phi_i | \phi_j \rangle = \delta_{ij}$$

Interacting case rewritten:

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

XC energy functional: exchange, Coulomb correlations & correlated kinetic energy

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

Quality of DFT in practice exclusively depends on XC functional

## Kohn-Sham scheme

Minimisation of  $E_v[n]$  with  $n(\mathbf{r}) \rightarrow N$ :

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

... groundstate for non-interacting case  $\rightarrow$  Kohn-Sham equations

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

and  $\epsilon_i < \mu : f_i = 1, \quad \epsilon_i = \mu : 0 \leq f_i \leq 1, \quad \epsilon_i > \mu : f_i = 0.$

- non-interacting particle kinetic energy treated exactly  $T_s[n] = \int \sum_i f_i |\nabla \phi_i(\mathbf{r})|^2 d\mathbf{r}$
- "classical" electrostatics ( $e - n + e - e$ ) treated exactly
- "only" need to approximate  $E_{xc}[n], \quad \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})} = v_{xc}([n]; \mathbf{r})$

... as sum of exchange and correlation terms

$$E_{xc}[n] = E_x[n] + E_c[n], \quad E_x[n] = \langle \Phi[n] | \hat{W} | \Phi[n] \rangle - \frac{1}{2} \int n(\mathbf{r}) w(\mathbf{r}, \mathbf{r}') n(\mathbf{r}') d\mathbf{r} d\mathbf{r}'$$

beware:  $F[n]$  may be approximated directly as  $\hat{F}[\Phi]$

... within DFT, but leading to generalized Kohn-Sham scheme<sup>1</sup>, e.g. Hartree-Fock eqs.

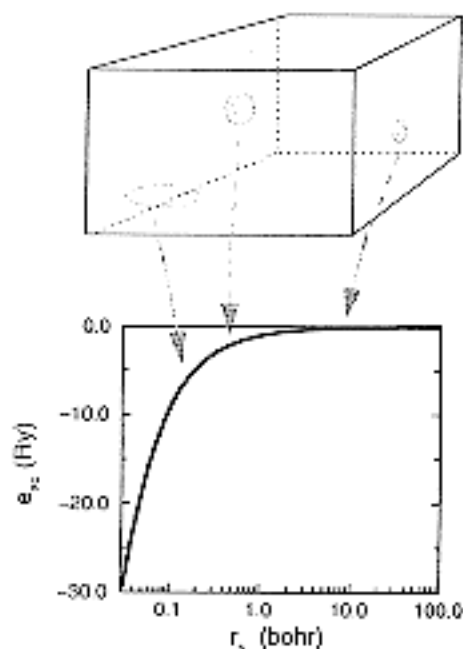
<sup>1</sup> Seidl, Gorling, Vogl, Majewski, Levy, *Phys Rev B* 53, 3764 (1996).

## Local-density approximation

$$E_{xc}^{LDA}[n] = \int n(\mathbf{r}) e_{xc}^{hom}(n(\mathbf{r})) d\mathbf{r} \quad (+ \text{gradient terms} = E_{xc}^{GGA}[n] \text{ see below})$$

- local dependence on density or Wigner-Seitz radius  $r_s = \left(\frac{4\pi}{3}n\right)^{-1/3}$
- 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  $e_c^{hom}(n)$  known
    - \* analytically for  $r_s \rightarrow 0$  and  $r_s \rightarrow \infty$
    - \* numerically "exact" for  $2 < r_s < 100$  from Quantum Monte Carlo data<sup>1</sup>
- ... as parametrization interpolating over all  $r_s$ 
  - "PW91", "Perdew-Zunger", "VWN"<sup>2</sup>

- a "workhorse" in DFT applications
- real systems far from homogeneity
  - ... why does LDA work at all?
  - ... neither slowly varying, why should GGA work?



<sup>1</sup> Ceperley, Alder, *Phys Rev Lett* 45, 566 (1980).

<sup>2</sup> Perdew, Wang, *Phys Rev B* 45, 13244 (1992); Perdew, Zunger (1980); Vosko, Wilk, Nussair (1980).

# View on XC through the XC hole

Definition of the XC hole by a coupling constant integration<sup>1</sup>

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

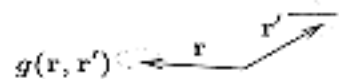
- by Hohenberg-Kohn theorem:  $n(\mathbf{r}) \leftrightarrow v_\lambda([n]; \mathbf{r})$  for any  $0 \leq \lambda \leq 1$
- $\lambda = 0 \rightarrow$  non-interacting case/ Kohn-Sham potential,  $v_{\lambda=0}([n]; \mathbf{r}) = v^{KS}([n]; \mathbf{r})$
- $\lambda = 1 \rightarrow$  external potential,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

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

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

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

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



<sup>1</sup> cf. DFT books by Dreizler and Gross & Yang and Parr

if  $e^-$  at  $r$ , what is the probability of finding one at  $r'$ ?

## ... coupling constant integration

- $\lambda$ -integration implies coupling constant averaged pair correlation function

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

Identify the XC energy density-functional as

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

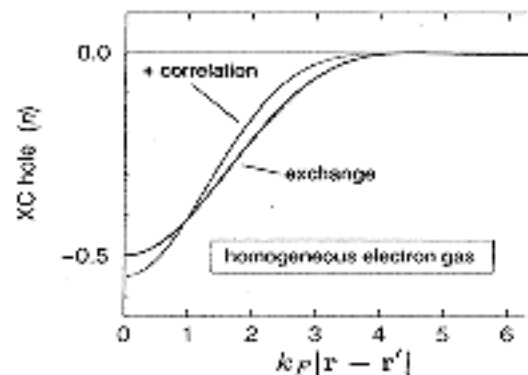
- interpretation: the electron density  $n(\mathbf{r})$  interacts with the electron density of the XC hole

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

→ Pauli exclusion principle & Coulomb repulsion

- local density approximation corresponds to

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



(NB: correlation part varies with  $k_F$ )

## From the XC hole to the XC energy

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

- for  $e_{xc}$  only the angle averaged XC hole matters

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

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

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

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

- XC energy in terms of averaged XC hole<sup>1</sup>

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

LDA & GGA approximate average holes rather closely  $\Leftrightarrow$  work mostly o.k.

<sup>1</sup> Perdew et al., J Chem Phys 108, 1552 (1998).

## Sum rule and other constraints on the XC hole

- sum rule (constrains global behavior)

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

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

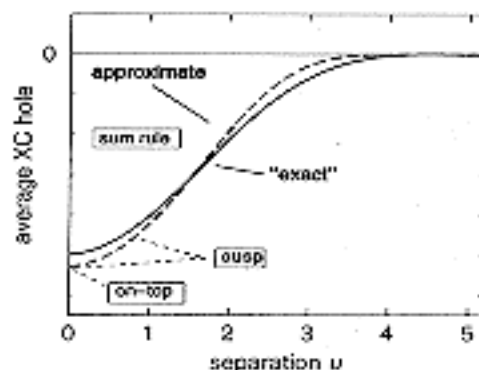
- on-top hole  $\langle n_{xc}(0) \rangle$  (fixes value at  $u = 0$ )

✓ accurately (exactly in some limits) for correlation, exactly for exchange

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

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

✓ exactly



- Beware:*
- pointwise behavior of  $n_{xc}^{\text{LDA}}(\mathbf{r}, \mathbf{r}')$  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 & GGA can be locally poor, but again less so for the system average

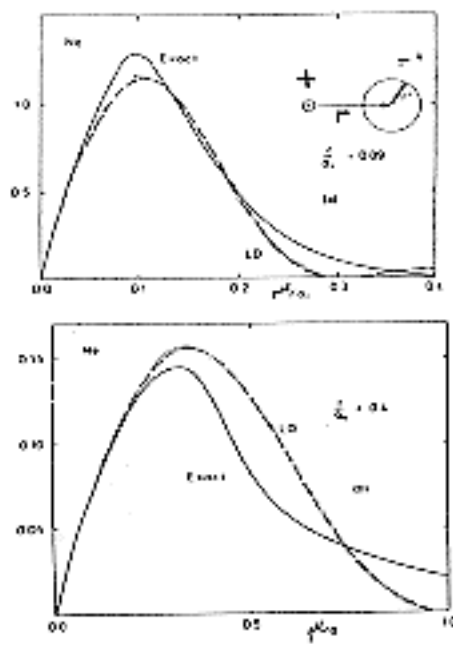


FIG. 8.2 Spherical average of the neon atom exchange hole (lines  $r'$ ) for (a)  $r = 0.09 a_0$  (b)  $r = 0.4 a_0$ . The full curves give the exact results and the dashed curves are obtained by LD approximation. (From Gunnarsson, Jonson, and Lundqvist 1979.)

spherical average

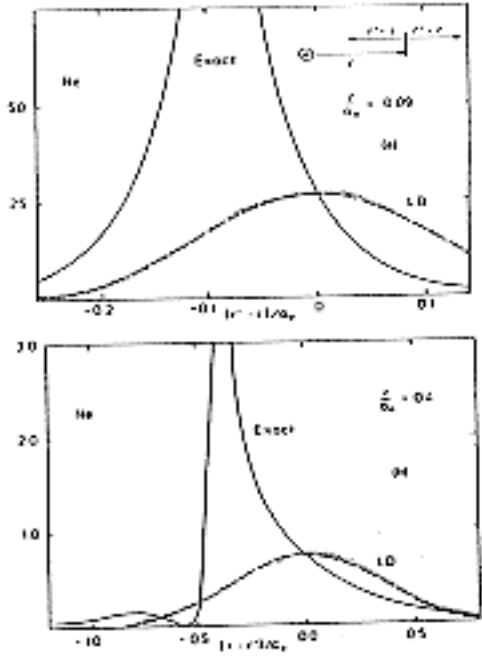


Figure 8.3 Exchange hole  $\rho(r, r')$  for a neon atom. The full curves show exact results and broken curves show the results in the LD approximation. The curves in (a) and (b) are for two different values of  $r$ . (From Gunnarsson, Jonson, and Lundqvist 1979.)

pointwise  
(Gunnarsson) c.f. [Parr & Yang]

On-top hole  $n_{XC,\lambda}(r, r)$

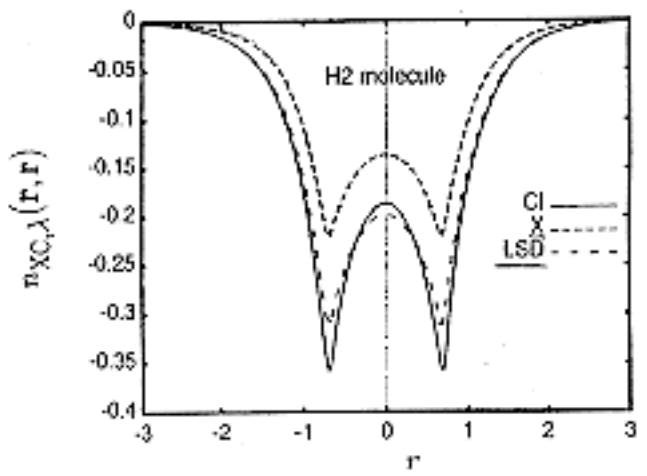


FIG. 1. On-top hole in  $H_2$  molecule ( $\lambda = 1$ ).

Burke et al., J Chem Phys 109, 3760 (1998)

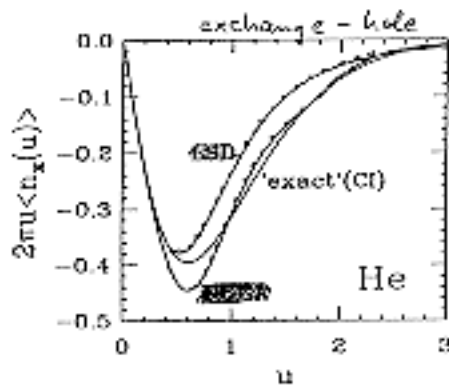
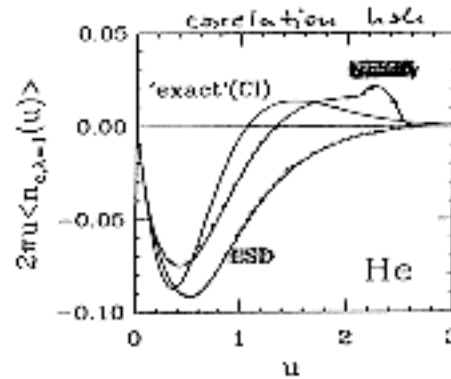
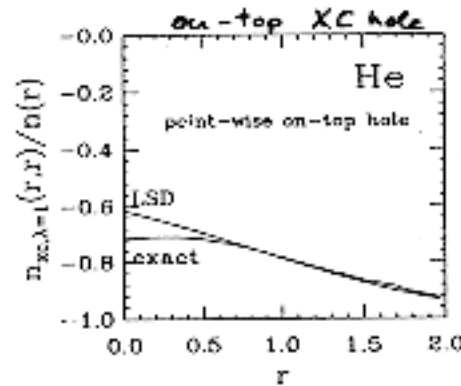


FIG. 4. System-averaged exchange hole density (in atomic units) in the He atom, in LSD, numerical GGA, and exactly (CI). The area under each curve is the exchange energy.

[Burke et al.]



spherical & system-averaged



pointwise

FIG. 7. Local on-top exchange-correlation hole at full coupling strength divided by density as a function of  $r$  in the

## Performance of the LDA

- bulk lattice constants accurate to within 1...3%, usually underestimated
- binding energies are too large (overbinding)
  - X molecular dissociation energies
  - X cohesive energies of solids
  - ✓ but formation enthalpies often o.k.
- activation energies in chemical reactions
  - X too small for  $H_2$  on various surfaces (Al, Cu, Si, ...)
  - X  $H_3$  molecule predicted to be stable
- bulk equation of state inaccurate
  - X qualitative:  $SiO_2$  at high pressure < at zero pressure
  - X quantitative: underestimated transition pressure for diamond  $\leftrightarrow$   $\beta$ -tin phase transitions in Si & Ge
- band structure mostly correct, except band gap not just an LDA problem (at least in Si, Ge, GaN, ...)

# Generalized Gradient Approximation

- ① Gradient expansion of XC hole  $v_{xc}(n; r, u) \rightarrow v_{xc}^{LDA}(n; r, u) + \nabla u, \dots$   
and constraints to meet
  - ✓ e.g.  $v_{xc}(r, u) < 0$ ,  $\int v_{xc}(r, u) dr = -1$ , by real space cutoffs  $\rightarrow$  numerical GGA
  - ✓ scaling relations and bounds on  $F_{xc}$  by analytic approximation to numerical GGA
    - parameter-free GGA by Perdew-Wang "PW91"
    - simplified in **PBE** GGA
- ② Earlier: analytic model or ansatz + empirical parameter(s)
  - Becke 86(X), Langreth-Mehl(C), Lee-Yang-Parr(C), ...
- ③ Alternative: analytic ansatz + (many) fitted parameters ( $\rightarrow$  fit to atomization energies)
  - see accuracy limit of GGA functionals

PBE: Perdew, Burke, Ernzerhof  
*Phys Rev Lett 77, 3855 (1996)*

Generic GGA functional

$$E_{xc}^{GGA}[n] = \int v_{xc}^{LDA}(n(r)) \underbrace{F_{xc}^{GGA}(n(r); s(r))}_{\text{enhancement factor}} d\tau, \quad s(r) = \frac{|\nabla n(r)|}{2k_F n(r)}$$

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

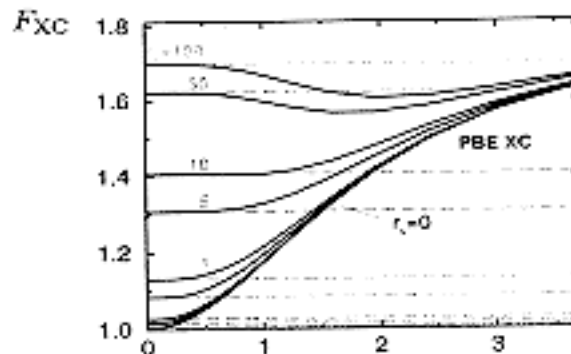
## Generalized gradient approximation: Nutshell view

Exchange-correlation density functional

$$E_{XC}^{GGA}[n] = \int \epsilon_X^{LDA}(n(r)) \underbrace{F_{XC}^{GGA}(n(r), |\nabla n(r)|, \dots)}_{\text{enhancement factor (over local exchange)}} d^3r$$

"Catalogue:"

HCTH	Handy et al.
RPBE	Hammer et al. '99
revPBE	Zhang et al. '98
<b>PBE GGA</b>	Perdew et al. '96
PW91	Perdew & Wang '91
PW91	Perdew & Wang '91
BP	Becke & Perdew '88
BLYP	Becke & Lee et al. '88



## Performance of PBE GGA vs. LDA

- ✓ atomic & molecular total energies are improved
- ✓ GGA corrects for the LDA overbinding  
mean error for a set of small molecules:  
-3.1 eV (HF) → +1.4 eV (LSDA)  
→ 0.5 eV (GGA) → 0.05 eV (goal)  
better cohesive energies of solids
- ✓ improved activation energy barriers in chemical reactions (but still too low)
- ✓ improved description of relative ordering of bulk phases

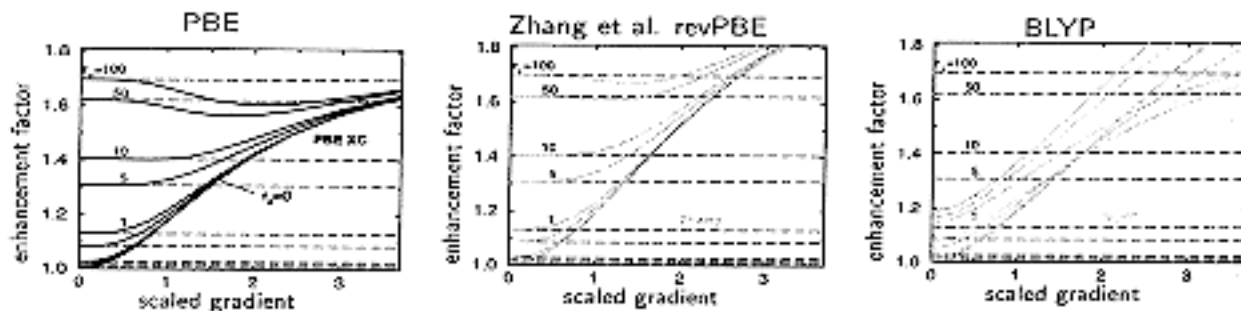
- ✗ GGA softens the bonds (in solids)  
increasing lattice constants  
decreasing bulk moduli  
↳ no consistent improvement
- ✗ LDA yields good bond energies for highly coordinated atoms,  
e.g. surface energies, diffusion barriers on surfaces  
↳ significance of GGA?
- ✗ GGA workfunctions for several metals turn out somewhat smaller than in LDA
  - one-particle energies/bands close to LDA

Analysis in terms of self-consistent LDA density possible:

$$E_{\text{tot}}^{\text{GGA}}[\pi^{\text{GGA}}] = E_{\text{tot}}^{\text{LDA}}[\pi^{\text{LDA}}] + \underbrace{\left[ E_{\text{xc}}^{\text{GGA}}[\pi^{\text{LDA}}] - E_{\text{xc}}^{\text{LDA}}[\pi^{\text{LDA}}] \right]}_{\text{LDA} + \Delta E_{\text{xc}}[\pi^{\text{LDA}}]} + \mathcal{O}(\pi^{\text{GGA}} - \pi^{\text{LDA}})^2$$

U.B.: GGA's are used self-consistently, how we want to understand the effect of GGA's in the total energy at the same density (to 2nd order this gives the energy difference between self-consistent LDA and GGA)

## Differences in present GGA's



- 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 [Tinte et al. PRB 58, 11959 (1998)], but likely increase binding energies.

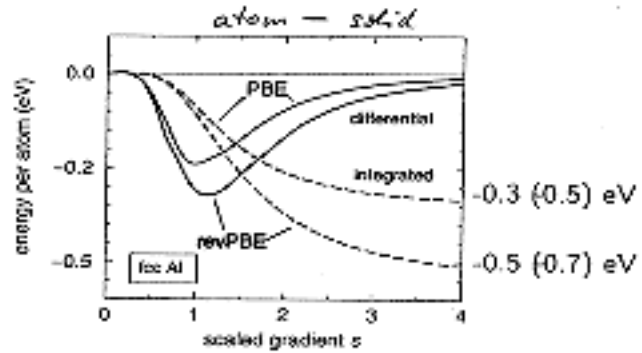
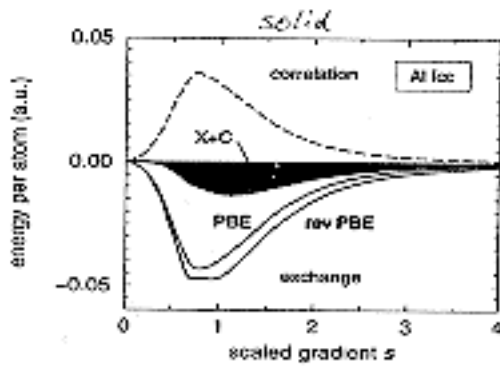
Zhang, Yang, Phys Rev Lett 80, 290 (1998) → revPBE  
 Becke Phys Rev A 38, 3098 (1988); Lee, Yang, Parr  
 Phys Rev B 37, 785 (1988) → BLYP



## ... how GGA's change binding energies

"Spectral decomposition" in terms of  $s$ :

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

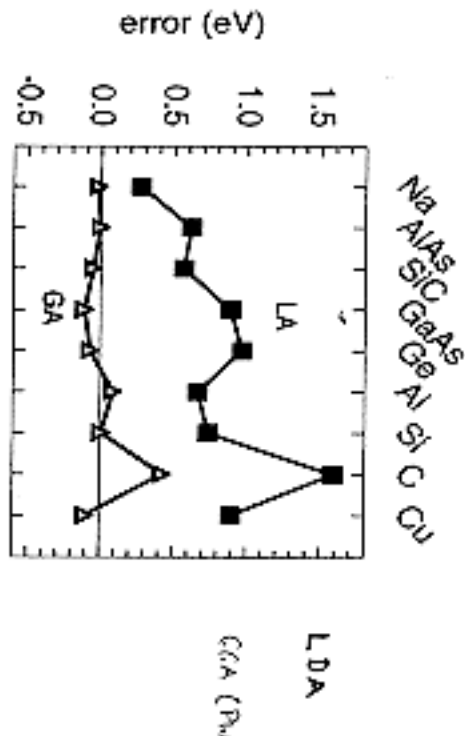


- only  $0 \leq s \leq 4$  contribute
- similar analysis can be made for  $n(r)$

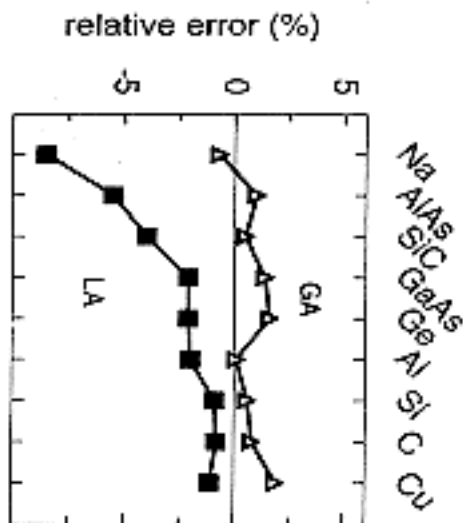
see Zupan et al. J Chem Phys 106, 10424 (1997)  
Zupan, Blaha, Schwarz, Padeau, Phys Rev B 58, 11200 (1998)

## Cohesive properties in GGA

- binding energy: LDA overbinding corrected

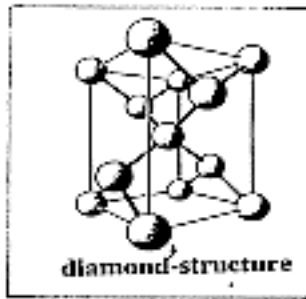


- GGA induced lattice expansion

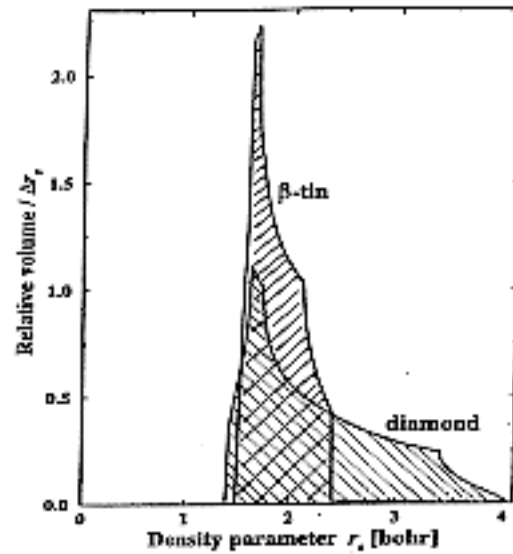
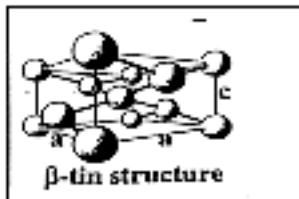


## LDA vs. GGA: Phase transition $\beta$ -tin - diamond in Si

$$a_0 = 5.43 \text{ \AA}$$



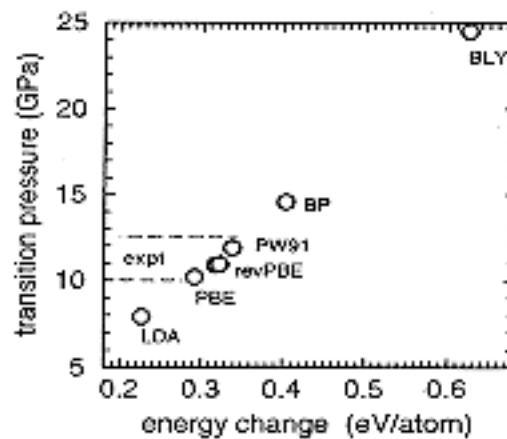
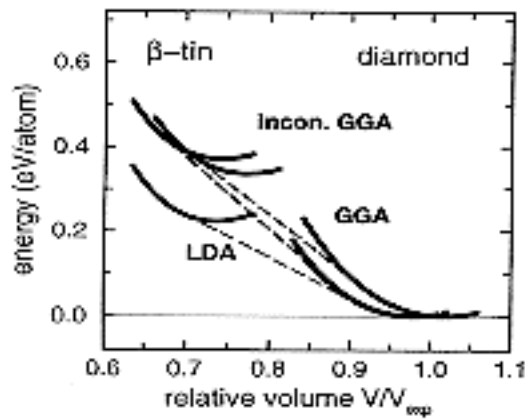
$$c/a = 0.552$$



Moll et al.

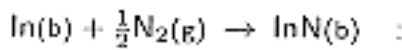
## Phase transition $\beta$ -tin - diamond in Si

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

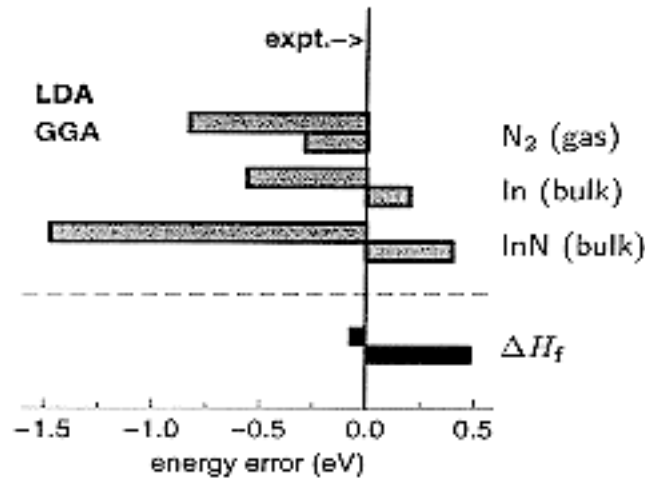


- GGA increases transition pressure, "inhomogeneity effect"
- use of LDA-pseudopotentials insufficient

## ... InN



$$\text{formation enthalpy } \Delta H_f = H_{\text{InN}} - [H_{\text{N}}^{\text{gas}} + H_{\text{In}}^{\text{bulk}}] < 0$$



- PBE GGA    ✓ improves cohesive energy of each constituent (N<sub>2</sub>, In, InN)  
               ✗ but **not** formation enthalpies → InN is endothermic

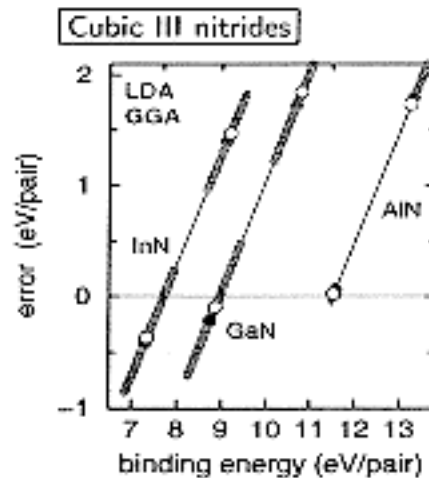
## Thermodynamic stability: GGA vs. LDA

Binding energies improved by GGA → formation enthalpies too?

Formation enthalpy (eV/unit)

	LDA	PW91	expt.
AlAs	-1.01	-1.05	-1.20 ... 1.25
GaAs	-0.67	-0.64	-0.74 ... 0.94

- GGA ~ LDA



- PBE GGA corrects cohesive energies

## Dissociation of H<sub>2</sub> over Cu(111)<sup>1</sup>

barrier to dissociation

- GGA  $E_a \approx 0.7$  eV •
- LDA  $E_a < 0.1$  eV •

total energy of free H<sub>2</sub>

- GGA  $E_{H_2} \approx -31.8$  eV
- LDA  $E_{H_2} \approx -30.9$  eV
- (expt.  $-31.7$  eV)

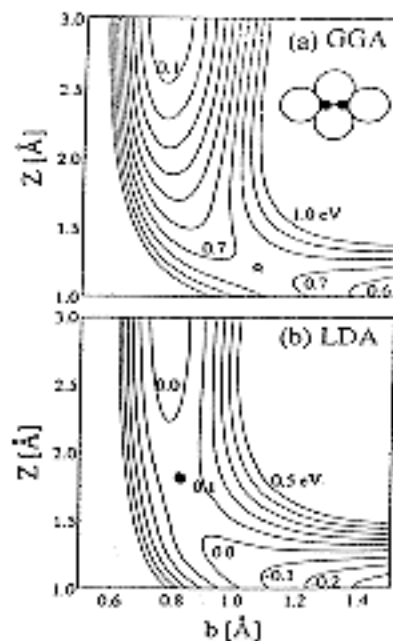
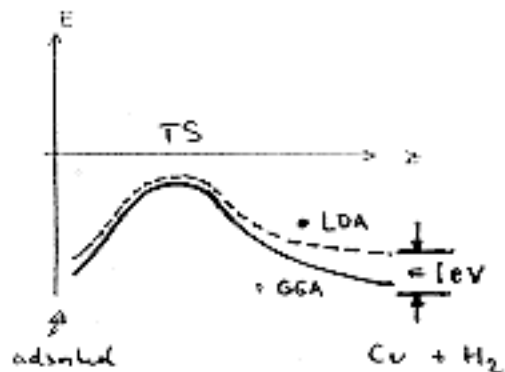
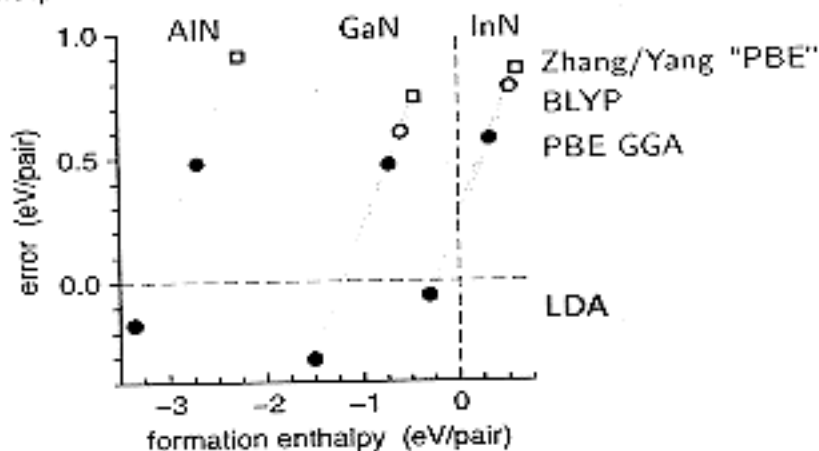


FIG. 1. (a) The PES for H<sub>2</sub> dissociation over Cu(111) calculated within the GGA. The inset shows the dissociation geometry. (b) Same as (a) but calculated with the LDA only.

<sup>1</sup> [Hammer et al., Phys Rev Lett 73, 1400 (1994).]

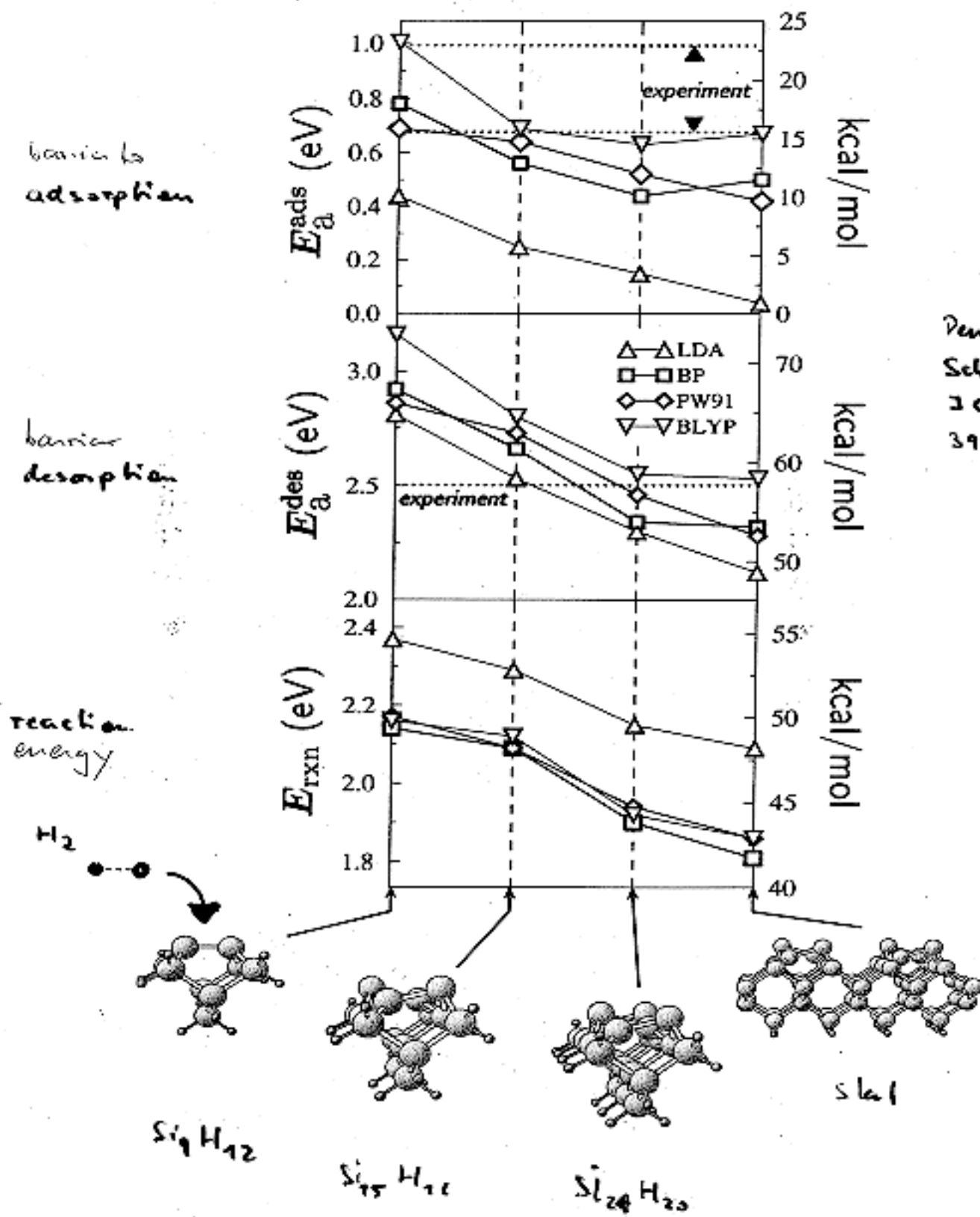
## ... alternative GGA functionals

Formation enthalpies



- similar trend as for PBE GGA, underestimate of  $\Delta H_f$  even more pronounced
  - GGA's not always improving over LDA (here: N<sub>2</sub> not perfect in GGA
    - ... still worse in LDA
    - ... but better error cancellation)
- Zhang, Yang, PRL 80 890 (1998) "revised PBE".

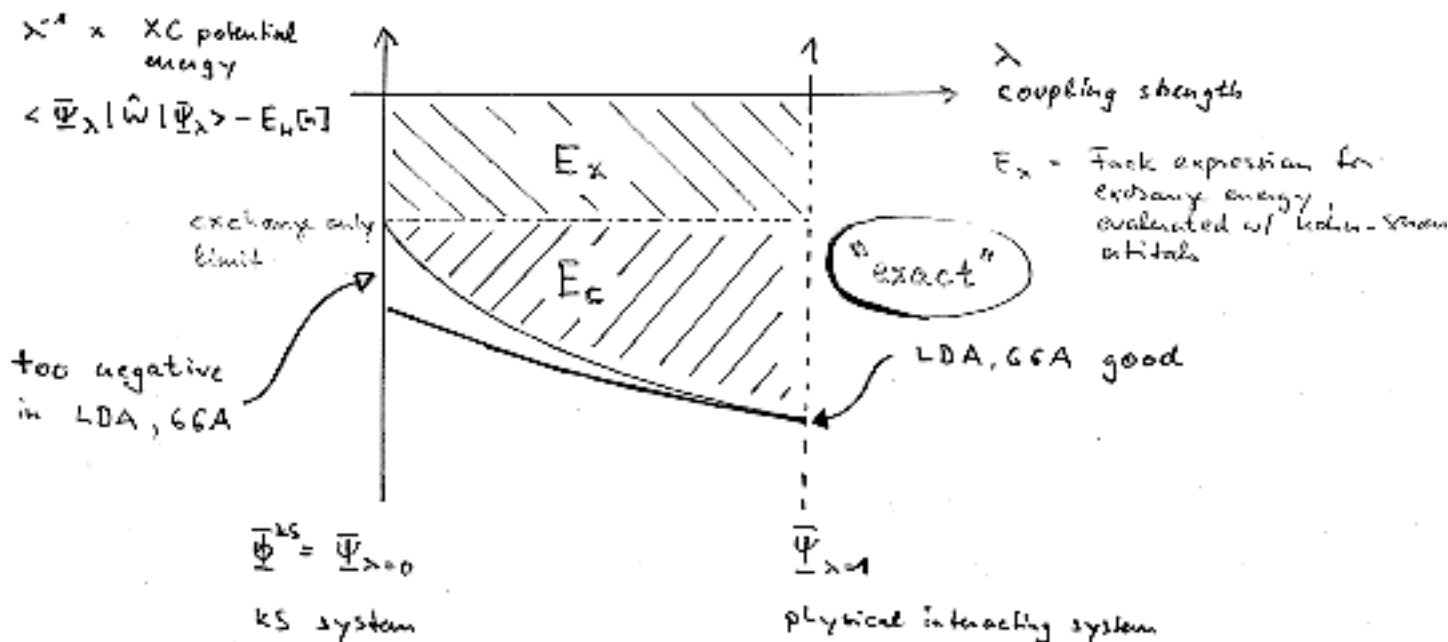
Comparison of different GGA's gives ...



Pencer, Kral  
Schaffler,  
J Chem Phys  
3986 (199

# Hybrid functionals - adiabatic-connection

... or "why GGA's are not enough"



Adiabatic connection = device to get  $\bar{\Psi}_\lambda$  many- $e^-$  wavefunction @ fixed  $\lambda$  than we analyse e.g.  $E_\lambda = \langle \bar{\Psi}_\lambda | \hat{H} | \bar{\Psi}_\lambda \rangle$  or  $\langle \bar{\Psi}_\lambda | \hat{W} | \bar{\Psi}_\lambda \rangle$   
 ↑ Hamiltonian of physical system      ↑  $e^-e^-$  interaction

## ... hybrid functionals

Expect ...<sup>1</sup>

- = 1 LDA and GGA quite accurate
- = 0 but off in exchange limit ... overestimated dissociation energies

→ should use exact exchange for  $\lambda = 0$  and a local functional for  $\lambda = 1$

Hybrid functional = "interpolation"

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

mixing parameter  $a = 0.16 \dots 0.3$  by fitting dissociation energies of molecules  
 $a = 1/4$  by 4th order perturbation theory

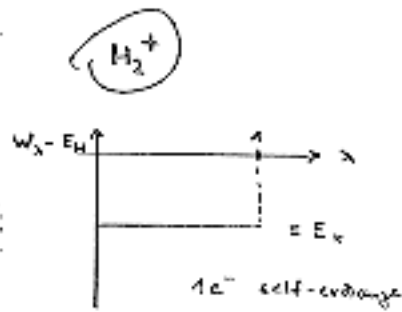
- B3LYP: 3-parameter combination of Becke X-GGA, LYP C-GGA, LDA ... molecular dissociation energies within 3 kcal/mol

U.B.  
 $E_x + E_c^{LDA/GGA}$   
 - disaster for molecules,  
 - a.k. for several solids' binding energies  
 ... we cannot mix in 100% exact exchange

<sup>1</sup> Becke. J Chem Phys 98, 5648 (1993); Perdew et al, J Chem Phys 105, 9982 (1996).

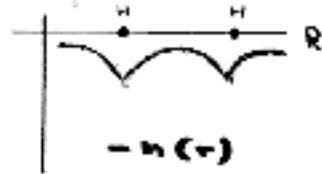
# XC revisited : "Error Cancellation between X and C"

... or "why hybrids are not enough"

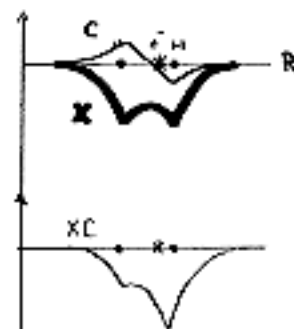
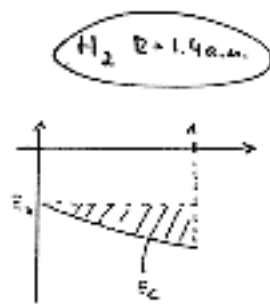


need 100% mixing

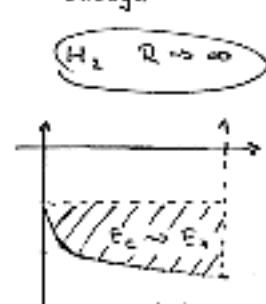
$u_{xc}(r, r')$  (XC holes)



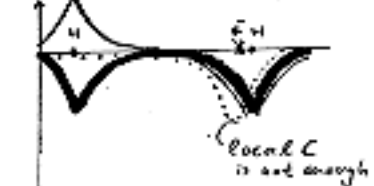
...  $e^-$  delocalized over nuclei  $\rightarrow$  radicals etc.



NORMAL CASE



no mixing needed, spin-GGA, LDA fine



left-right or static correlation simulated by LSDA, S-GGA... XC

## Orbital dependent XC density-functionals

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

- LDA and GGA are explicit density-functionals  $E_{xc}[n]$
- Implicit density-functionals formulated in terms of  $\phi_i[n]$ ?
  - $\rightarrow$  more flexible for further improvements
  - self-interaction free:  $E_{XC}[n]_{N=1} = 0$ ,  $v_{xc}(|r| \rightarrow \infty) = -\frac{1}{r}$
  - nonspherical  $n_{xc}(r, r')$

$\rightarrow$  Example I: Exact exchange

Exchange-energy

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

$\blacktriangle$  looks like in Hartree-Fock, but  $-\frac{\nabla^2}{2} - v^{KS}(r) \phi_i(r) = \epsilon_i \phi_i(r)$  KS and HF orbitals different!

How to calculate the exchange potential?

### ... exact Kohn-Sham exchange

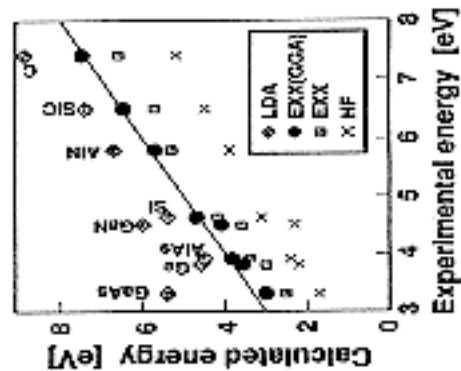
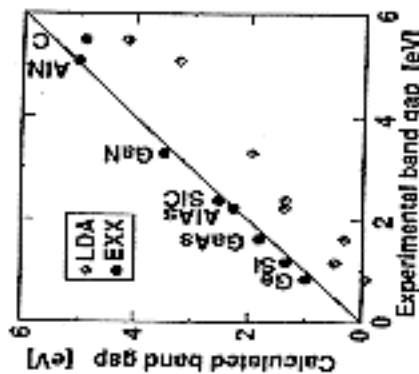
$$v_x[n; \mathbf{r}] = \frac{\delta E_x[n]}{\delta n(\mathbf{r})} = \int \frac{\delta E_x[\phi_i]}{\delta \phi_i(\mathbf{r}_1)} \frac{\delta \phi_i(\mathbf{r}_1)}{\delta v^{KS}(\mathbf{r}_2)} \frac{\delta v^{KS}(\mathbf{r}_2)}{\delta n(\mathbf{r})} d\mathbf{r}_1 d\mathbf{r}_2 + \text{c.c.} \dots \text{chain rule}$$

1)
2)
3)

where

- 1)  $\frac{\delta E_x[\phi_i]}{\delta \phi_i(\mathbf{r})}$  gives Fock exchange potential (dependent on  $i$ )
- 2)  $\frac{\delta \phi_i(\mathbf{r})}{\delta v^{KS}(\mathbf{r}')}$  from first order perturbation theory
- 3)  $\frac{\delta v^{KS}(\mathbf{r})}{\delta n(\mathbf{r}')} = \chi_{KS}^{-1}(\mathbf{r}, \mathbf{r}')$  from linear response theory

- Solved prior to Hohenberg-Kohn DFT for atoms (1-D integral equation):  
Optimized Effective Potential method  $\rightarrow v^{eff}(\mathbf{r}) \mid \min_{\Phi} \langle \Phi \mid \hat{H} \mid \Phi \rangle ?$
- For diatomics (2-D) & solids (in KLI approximation) to  $v_x[n; \mathbf{r}]$
- In 3-D for bulk semiconductors within plane-wave pseudopotential approach
- Bandstructure of Si (and others) superior to HF (local hamiltonian!), improved over LDA
- Self-interaction free etc. - but what is a compatible, general correlation functional?  
Solids: GGA correlation seems fine [Staedle et al. Phys Rev B 59, 10031 (1999)]  
Molecules: GGA & LDA correlation not enough [Clementi, Chakravorty, J Chem Phys 93, 2591 (1990)]
- exact exchange as a starting point for including (compatible) correlation. (see discussion of hybrids for challenges ahead)



Staedle et al., Phys Rev Lett 79, 2089 (1997);  
Phys Rev B 59, 10031 (1999)



## ... orbital dependent density-functionals

### • Example II: Meta-GGA's

XC energy functional

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

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

$$1) \frac{\delta E_{xc}^{MGGGA}[\phi_i]}{\delta \phi_i(\mathbf{r})} = \dots - \frac{1}{2} \nabla \frac{\partial e_{xc}}{\partial t_x} \nabla \phi_i$$

- "TPSS": Tao, Perdew, Staroverov, Scuseria, cond-mat/0306203 (2003)
  - "PKZB": Perdew, Kurth, Zupan, Blaha, Phys Rev Lett 82, 2544 (1999):  $\underline{XC}$  "non-empirical", LDA limit
  - Van Voorhis, Scuseria, J Chem Phys 109, 400 (1998):  $\underline{XC}$  "highly fitted", no LDA limit
  - Colle, Salvetti, Theoret Chim Acta 53, 55 (1979):  $\underline{C}$ , no LDA limit  $\rightarrow$  BLYP GGA
  - Becke, J Chem Phys 109, 2092 (1998):  $\underline{XC}$  + 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 more accurate for molecular binding energies, cohesive energies of solids up to now not reported
  - TPSS provides sound, nonempirical basis for new hybrids  
 $\rightarrow$  Next step: correlation compatible with exact exchange?

## Tests of TPSS MGGGA

3LE 1: Statistical summary of the errors of four density functionals for various properties of molecules, solids, and surfaces. aJ/mol = 0.0434 eV = 0.00159 hartree. For jellium,  $r_s = (3/4\pi n)^{1/3}$  characterizes bulk density.

Property (units)	Test set	Mean value of property	Mean absolute errors			
			LSD	PBE	PKZB	TPSS
Atomization energy $\Sigma D_0$ (kcal/mol)	G2 (148 molecules)	478	83.8	<u>17.1</u>	4.4	6.2
Bond length $r_e$ (Å)	96 molecules	1.56	0.013	0.016	<u>0.027</u>	<u>0.014</u>
Harmonic frequency $\omega_e$ (cm <sup>-1</sup> )	82 diatomics	1430	48.9	42.0	<u>51.7</u>	<u>30.4</u>
Ionization potential (eV)	G2 (86 species)	10.9	0.22	0.22	0.29	0.23
Electron affinity (eV)	G2 (58 species)	1.4	0.26	0.12	0.14	0.14
H-bond dissoc. energy $D_0$ (kcal/mol)	10 complexes	13.4	5.8	1.0	2.9	0.6
H-bond lengths $r_e$ (Å)	11 H-bonds	2.06	0.147	0.043	<u>0.179</u>	<u>0.021</u>
H-bond angles (deg)	13 angles	111	4.0	2.6	3.5	2.0
Lattice constant (Å)	17 solids	4.34	0.669	0.662	<u>0.078</u>	<u>0.037</u>
Bulk modulus (GPa)	17 solids	124	14.6	8.7	9.2	9.1
XC surface energy (erg/cm <sup>2</sup> )	$r_s = 2, 4, 6$	1245	22	<u>55</u>	5	13

Hyd-14  
1...5

?

3h Tao et al. cond-mat/0306203 (2003)

## Theory: Adiabatic-Connection Fluctuation-Dissipation Theorem

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

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

- Fluctuation-dissipation theorem:

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

... using **dynamical density response**

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

$$\chi_0(iu, \mathbf{r}, \mathbf{r}') = 2\Re \sum_{i,j} \frac{\varphi_i^*(\mathbf{r})\varphi_j(\mathbf{r})\varphi_j^*(\mathbf{r}')\varphi_i(\mathbf{r}')}{iu - (\epsilon_j - \epsilon_i)} \quad \begin{array}{l} \epsilon_i[n] \quad \dots \text{KS eigenvalues} \\ \varphi_i([n], \mathbf{r}) \quad \dots \text{KS orbitals} \end{array}$$

$$\chi_\lambda(iu) = \chi_0(iu) + \chi_0(iu) \cdot \mathbf{K}_\lambda \cdot \chi_\lambda(iu) \quad \text{"Dyson equation"} \text{ 6dim.}$$

... using **coupling between KS states**

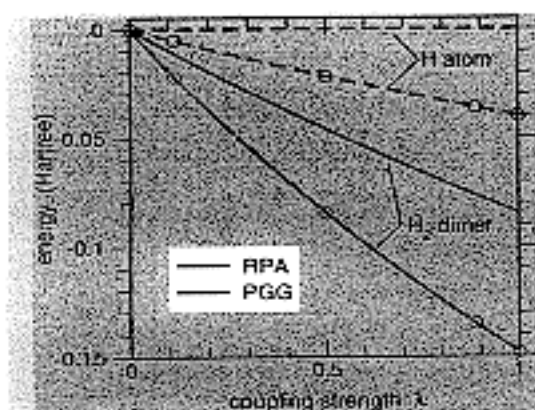
*In principle* ÁCFDT formula gives exact XC functional

*In practice* starting point for fully nonlocal approximations

Example:  $K_{\lambda}^{HXC} = \frac{\lambda}{|\mathbf{r} - \mathbf{r}'|}$  ... RPA random phase approximation  
to include van der Waals interactions (which are missed in local functionals like LDA or GGA).

## Results: H<sub>2</sub> molecule ... a simple bond

Adiabatic connection  $\frac{dE_\lambda^c}{d\lambda}$



✓ PGG self-correlation free!

Binding energy & bond length

	$E_b$ (eV)	$R_0$ (bohr)
LSDA	-4.92	1.44
PBE GGA	-4.54	1.41
xOEP	-3.64	1.38
<b>RPA</b>	<b>-4.71</b>	<b>1.39</b>
<b>RPA+</b>	<b>-4.73</b>	<b>1.40</b>
<b>PGG</b>	<b>-4.85</b>	<b>1.40</b>
expt.	-4.75	1.40

- post xOEP

- ♥ RPA and RPA+ both perform within chemical accuracy!
- ♥ Short-range errors of RPA cancel in total energy differences
- ⚠ PGG slightly overbinds  $\rightarrow$  correlation kernel needed?

## Summary

- XC hole provides some understanding of LDA & GGA
- 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 overcorrects somewhat (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, ...)
- hybrid functionals mix in exact exchange (B3LYP functional)
- orbital dependent, implicit density functionals:  
exact Kohn-Sham exchange, Meta-GGA & OEP method,  
functionals from the adiabatic-connection fluctuation-dissipation formula