FHI, Berlin, 13th July 2011

Hands-on Tutorial Workshop 2011 on Ab Initio Molecular Simulations: Toward a First-Principles Understanding of Materials Properties and Functions

Exchange-Correlation functionals for the ground state: from LDA up to the Optimized Effective Potential method

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Kohn-Sham (KS) Density Functional Theory

HK theorem $v_{ext}(\mathbf{r}) \Leftrightarrow \rho(\mathbf{r})$ (Nuclei Fixed)

$$\left[-\tfrac{1}{2}\nabla^2 + v_{\text{ext}}(\mathbf{r}) + u(\mathbf{r};[\rho]) + v_{\text{xc}}(\mathbf{r};[\rho])\right]\phi_i^{\text{KS}}(\mathbf{r}) = \varepsilon_i^{\text{KS}}\phi_i^{\text{KS}}(\mathbf{r}).$$

KS equations

SCF

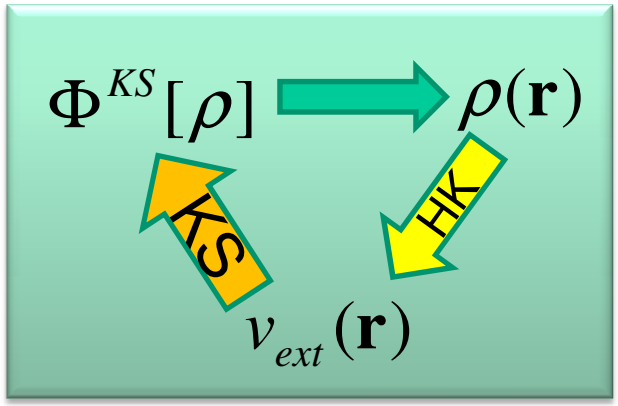
Coulomb Potential: $u(\mathbf{r};[\rho]) = \dfrac{\delta E_J[\rho]}{\delta\rho(\mathbf{r})} = \int d\mathbf{r}' \dfrac{\rho(\mathbf{r}')}{\|\mathbf{r}-\mathbf{r}'\|}$

Exchange Correlation Potential: $v_{\text{xc}}(\mathbf{r};[\rho]) = \dfrac{\delta E_{\text{xc}}[\rho]}{\delta\rho(\mathbf{r})}$

Electronic Density: *(n_s=2, closed-shell)*

$$\rho(\mathbf{r}) = \sum_a^{occ.} n_s \left|\phi_a^{KS}(\mathbf{r})\right|^2 \rightarrow \rho^{exact}(\mathbf{r})$$

Density of a single Slater-determinant Φ^{KS}
(non-interacting electrons)



Kohn-Sham Total Energy

$$E^{v_{\text{ext}}}[\rho] = T_{\text{ni}}[\rho] + \int \rho(\mathbf{r}) v_{\text{ext}}(\mathbf{r}) d\mathbf{r} + E_J[\rho] + E_{\text{xc}}[\rho]$$

Coulomb Energy: $E_J[\rho] = \frac{1}{2}\int\int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{\|\mathbf{r}-\mathbf{r}'\|} d\mathbf{r} d\mathbf{r}'$

Exchange-Correlation Energy:

$$E_{xc}[\rho] = \underbrace{(V_{ee}[\rho] - E_J[\rho])}_{U_{xc}} + \underbrace{(T[\rho] - T_{ni}[\rho])}_{T_c}$$

"Exact"

$$E_{xc}[\rho] = ?$$

$$F^{HK}[\rho] = V_{ee}[\rho] + T[\rho] = \min_{\Psi^{MB}\to\rho} \left\langle \Psi^{MB} \middle| \hat{T} + \hat{V}_{ee} \middle| \Psi^{MB} \right\rangle$$

Kinetic Energy:

$$T_{ni}[\rho] = ?? \longrightarrow \sum_a^{occ.} n_s \left\langle \phi_a \middle| -\frac{1}{2}\nabla^2 \middle| \phi_a \right\rangle = \int d\mathbf{r}\tau(\mathbf{r})$$

KS kinetic energy is an orbital-dependent functional

$$\tau(\mathbf{r}) = \frac{n_s}{2}\sum_a^{occ} |\nabla\phi_a(\mathbf{r})|^2$$

Outline

Section I

- ❑ Exact definitions / Functional Form
- ❑ Uniform Electron Gas (LDA)
- ❑ Gradient Expansion (PBE-like functionals)

Section II

- ❑ Orbital Dependent Functional
- ❑ Exact Exchange

Section III

- ❑Hybrid Functionals / Generalized KS

Summary

Purpose: Introduction to XC functional performance and development

Not covered: VDW, Magnetism, RPA (see other talks)

Exchange Functional

$$E_{xc}[\rho] = E_x[\rho] + E_c[\rho]$$

Exact Exchange

$$E_x^{EXX}[\rho] = \left\langle \Phi^{KS}[\rho] \middle| V_{ee} \middle| \Phi^{KS}[\rho] \right\rangle - E_J[\rho] =$$

$$= -\sum_a^{occ.} \sum_b^{occ.} \frac{n_s}{2} \iint \frac{\phi_a^{KS}(\mathbf{r})\phi_a^{KS}(\mathbf{r}')\phi_b^{KS}(\mathbf{r})\phi_b^{KS}(\mathbf{r}')}{\|\mathbf{r}-\mathbf{r}'\|} d\mathbf{r}d\mathbf{r}'$$

*as in Hartree-Fock but with **KS orbitals***

$$= -\frac{n_s}{2} \iint \frac{\left|\gamma^{KS}(\mathbf{r},\mathbf{r}')\right|^2}{\|\mathbf{r}-\mathbf{r}'\|} d\mathbf{r}d\mathbf{r}'$$

1e- Density Matrix

Ex is a KS-*Density Matrix* Functional
(implicit density functional $\gamma^{KS} = \gamma^{KS}[\rho]$)

$$E_x[\rho] = \int \rho(\mathbf{r})\varepsilon_x(\mathbf{r})d\mathbf{r} = \frac{1}{2}\iint \frac{\rho(\mathbf{r})h_x(\mathbf{r},\mathbf{r}')}{\|\mathbf{r}-\mathbf{r}\|} d\mathbf{r}d\mathbf{r}'$$

Exchange-energy density:

$$\varepsilon_x(\mathbf{r}) = \frac{1}{2}\int \frac{h_x(\mathbf{r},\mathbf{r}')}{\|\mathbf{r}-\mathbf{r}'\|} d^3\mathbf{r}'$$

Exact exchange-hole:

$$h_x^{EXX}(\mathbf{r},\mathbf{r}') = -n_s \frac{\left|\gamma^{KS}(\mathbf{r},\mathbf{r}')\right|^2}{\rho(\mathbf{r})} \leq 0$$

Correlation Functional

$$E_c^{DFT}[\rho] = \min_{\Psi^{MB}\to\rho} \left\langle \Psi^{MB} \middle| \hat{T} + \hat{V}_{ee} \middle| \Psi^{MB} \right\rangle - \left\langle \Phi^{KS}[\rho] \middle| \hat{T} + \hat{V}_{ee} \middle| \Phi^{KS}[\rho] \right\rangle \le 0$$

MB wavefunction *KS single Slater-Det.*

As in Many-Body theory (where there are different densities)

$$E_c^{MB} = \left\langle \Psi^{MB} \middle| \hat{T} + \hat{V}_{ext} + \hat{V}_{ee} \middle| \Psi^{MB} \right\rangle - \left\langle \Phi^{HF} \middle| \hat{T} + \hat{V}_{ee} \middle| \Phi^{HF} \right\rangle$$

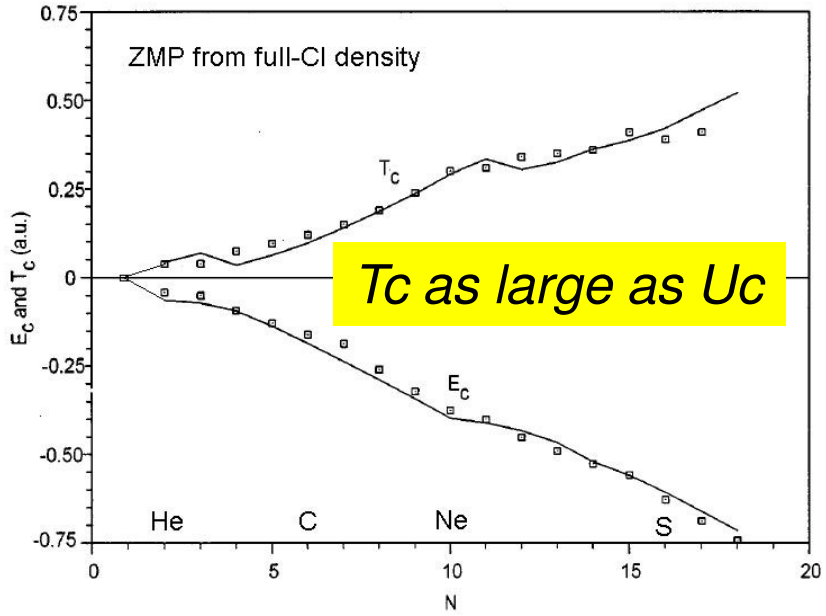
U_c : Potential contribution

$$E_c[\rho] = \frac{1}{2}\iint \frac{\Gamma(\mathbf{r},\mathbf{r}') - \Gamma^{KS}(\mathbf{r},\mathbf{r}')}{\|\mathbf{r}-\mathbf{r}''\|} d\mathbf{r}d\mathbf{r}'$$

$$-\frac{n_s}{2}\iint \left(\nabla_{\mathbf{r}'}\cdot\nabla_{\mathbf{r}}\right)\left[\gamma(\mathbf{r},\mathbf{r}') - \gamma^{KS}(\mathbf{r},\mathbf{r}')\right] d\mathbf{r}$$

T_c : Kinetic contribution

$\Gamma(\mathbf{r},\mathbf{r}')$ **: Pair-Density**



Tc as large as Uc

$$E_c[\rho] = \int \rho(\mathbf{r})\varepsilon_c(\mathbf{r})d\mathbf{r} = \frac{1}{2}\iint \frac{\rho(\mathbf{r})h_c(\mathbf{r},\mathbf{r}')}{\|\mathbf{r}-\mathbf{r}\|} d\mathbf{r}d\mathbf{r}'$$

Jacob's Ladder (Perdew)

Computational cost

Accuracy

5. All orbitals/eigenvalues (RPA,GLPT, double hybrid) $E_{xc}[\rho] = \int d^3\mathbf{r}\rho(\mathbf{r})\varepsilon_{xc}(...,\{\phi_i\ ,\varepsilon_i\}^{ALL})$

4. Hyper-GGA, EXX, Hybrid, local hybrid $E_{xc}[\rho] = \int d^3\mathbf{r}\rho(\mathbf{r})\varepsilon_{xc}(...,\varepsilon_x^{EXX}(\mathbf{r}))$

3. Meta-GGA (TPSS) $E_{xc}[\rho] = \int d\mathbf{r}\rho(\mathbf{r})\varepsilon_{xc}(...,\tau(\mathbf{r}))$

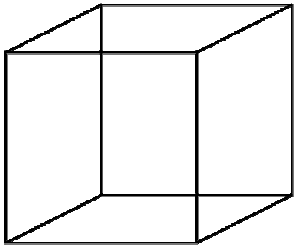
2. Gener. Gradient Approx. (GGA) $E_{xc}[\rho] = \int d\mathbf{r}\rho(\mathbf{r})\varepsilon_{xc}(...,\nabla\rho(\mathbf{r}))$

1. Local Density Approx. (LDA) $E_{xc}[\rho] = \int d\mathbf{r}\rho(\mathbf{r})\varepsilon_{xc}(\rho(\mathbf{r}))$

0. Hartree $E_{xc}[\rho] = 0$

Uniform Electron Gas (UEG, HEG, Jellium)

$V \to \infty$



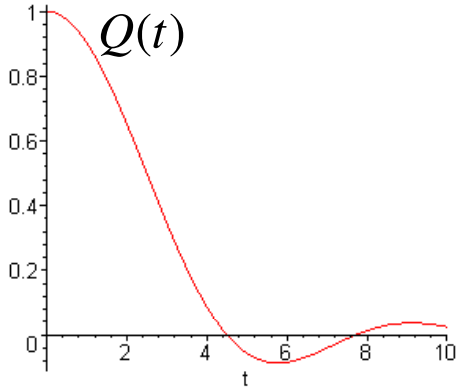
Uniform background (positive) density

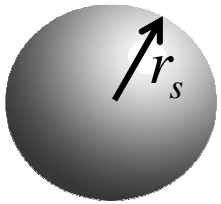
$$\phi_{\mathbf{k}}(\mathbf{r}) = \frac{\exp(i\mathbf{k}\cdot\mathbf{r})}{\sqrt{V}}$$

Density Matrix:

$$\gamma^{KS}(\mathbf{r}_1,\mathbf{r}_2) = \sum_{\mathbf{k}}^{occ.} \phi_{\mathbf{k}}(\mathbf{r}_1)\phi_{\mathbf{k}}^{*}(\mathbf{r}_2) = \frac{1}{V}\sum_{\mathbf{k}}^{occ.} \exp(i\,\mathbf{k}\cdot\mathbf{r}_{12}) =$$

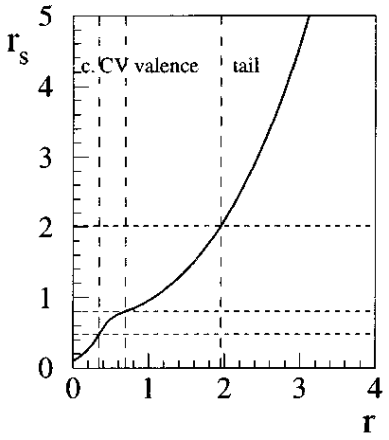
$$= \frac{1}{(2\pi)^3}\int_0^{k_F} dk\, k^2 \iint_{\hat{\mathbf{k}}} \exp(ik\hat{\mathbf{k}}\cdot\mathbf{r}_{12}) d^2\hat{\mathbf{k}} = \left(\frac{k_F^3}{6\pi^2}\right) Q(k_F r_{12})$$





$$\rho = \frac{3}{4\pi(r_s)^3}$$

Seitz Radius
(in real metals, rs=2..5)



ρ / n_s

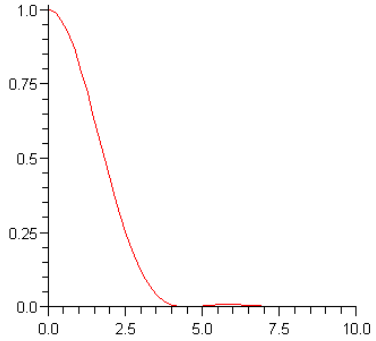
Electron density
is uniform

Fermi wavevector

$$k_F = \left(6\pi^2 \frac{\rho}{n_s}\right)^{1/3}$$

LDA Exchange

$$h_x^{LDA}(\mathbf{r}_1,\mathbf{r}_2) = -n_s \frac{\left|\gamma^{KS}(\mathbf{r},\mathbf{r}')\right|^2}{\rho(\mathbf{r})} = -\frac{\rho(\mathbf{r})}{n_s}\left(Q(k_F r_{12})\right)^2$$



$$\varepsilon_x^{LDA}([\rho];\mathbf{r}) = \frac{1}{2}\int \frac{h_x(\mathbf{r},\mathbf{r}')}{\|\mathbf{r}-\mathbf{r}'\|}d\mathbf{r}' = -\frac{1}{2}\frac{\rho(\mathbf{r})}{n_s}\int \frac{\left|Q(k_F r_{12})\right|^2}{r_{12}}d\mathbf{r}' =$$

$$= -\frac{1}{2}\frac{\rho(\mathbf{r})}{n_s}\left[\frac{9\pi}{k_F(\mathbf{r})^2}\right] = -\underbrace{\frac{3}{2}\left(\frac{3}{4n_s\pi}\right)^{1/3}}_{A_x=0.7386}\rho(\mathbf{r})^{1/3}$$

Dirac-Exchange 1930

$$E_x^{LDA}[\rho] = -A_x\int \rho(\mathbf{r})^{4/3}d\mathbf{r}$$

$$\varepsilon_x^{LDA}([\rho];\mathbf{r}) \rightarrow \varepsilon_x^{LDA}(\rho(\mathbf{r}))$$

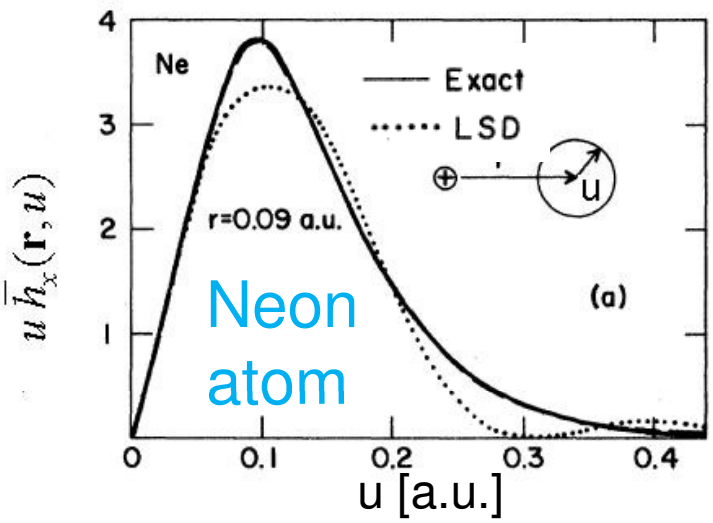
simple function
(not a functional) of the density

	E_x^{exact}		E_x^{LSD}
H	0.3125	>	0.2680
He	1.0258	>	0.8840
Li	1.7807	>	1.5379
Be	2.6658	>	2.3124
N	6.6044	>	5.9008
Ne	12.1050	>	11.0335
Na	14.0131	>	12.7859
Mg	15.9884	>	14.6117
P	22.6341	>	20.7931
Ar	30.1747	>	27.8632
Kr	93.8330	>	88.6245
Xe	179.0635	>	170.5660
mare (in %)			9.8

Quite good performance (underestimation)
for atoms where the density is not uniform !

Exchange Hole

$$\varepsilon_x([\rho];\mathbf{r}) = \frac{1}{2}\int \frac{h_x(\mathbf{r},\mathbf{r}')}{\|\mathbf{r}-\mathbf{r}'\|} d^3\mathbf{r}' = \frac{1}{2}\int \frac{h_x(\mathbf{r},\mathbf{r}+\mathbf{u})}{u} d^3\mathbf{u} = \frac{1}{2}\int du\, u 4\pi\, \bar{h}_x(\mathbf{r},u)$$



Ex depends only on spherically-averaged exchange hole :

$$\bar{h}_x(\mathbf{r},u) = \frac{\int d^2\hat{\mathbf{u}}\, h_x(\mathbf{r},\mathbf{r}+u\hat{\mathbf{u}})}{4\pi}$$

Exact Conditions for the exchange hole:

$$h_x(\mathbf{r},\mathbf{r}'=\mathbf{r}) = -n_s \frac{\left|\gamma^{KS}(\mathbf{r},\mathbf{r})\right|^2}{\rho(\mathbf{r})} = -\frac{\rho(\mathbf{r})}{n_s}$$

Satisfied by LDA!

$$\int h_x(\mathbf{r},\mathbf{r}')d^3\mathbf{r}' = -\frac{n_s}{\rho(\mathbf{r})}\int \left|\gamma^{KS}(\mathbf{r},\mathbf{r}')\right|^2 d^3\mathbf{r}' \xrightarrow{\text{idempotency}} \frac{n_s}{\rho(\mathbf{r})}\frac{\rho(\mathbf{r})}{n_s} = -1$$

UEG correlation

High Density $r_s \to 0$

$$\varepsilon_c(\rho,\zeta) = a_0(\zeta)\ln r_s - b_0(\zeta) + \left(a_1(\zeta)\ln r_s - b_1(\zeta)\right) r_s + \ldots$$

$\zeta = \frac{\rho_\alpha - \rho_\beta}{\rho_\alpha + \rho_\beta}$ Spin polarization

Low Density $r_s \to \infty$

$$\varepsilon_c(\rho,\zeta) = -\frac{f_0 - c_x(\zeta)}{r_s} + \frac{f_1}{(r_s)^{3/2}} + \frac{f_2 - c_s(\zeta)}{r_s} + \ldots$$

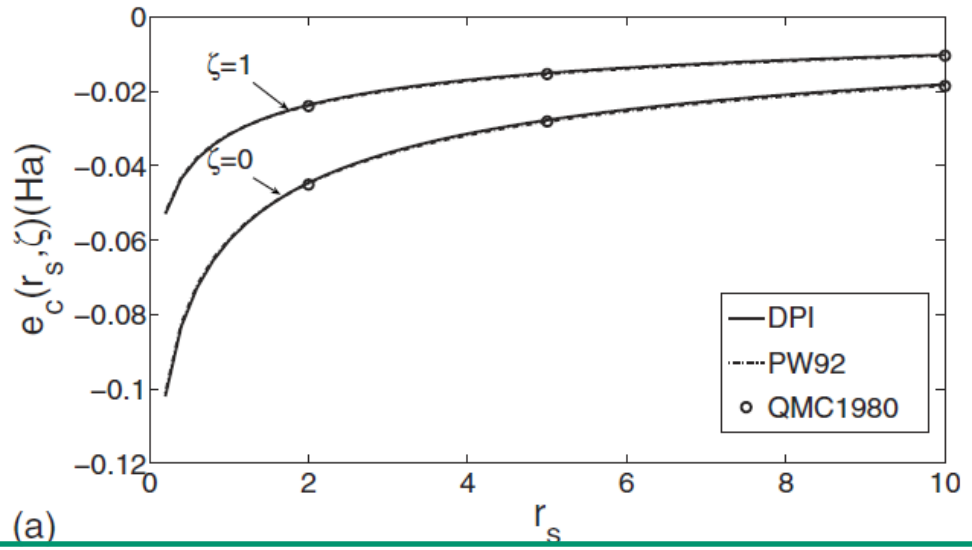
Fits between the two limits

Vosko,Wilk,Nusair 1980

Perdew, Wang 1992

Perdew, Zunger 1981

Sun, Perdew, Seidl 2010



	E_c^{exact}		E_c^{LSD}
H	0.0000	<	0.0222
He	0.0420	<	0.1125
Li	0.0455	<	0.1508
Be	0.0950	<	0.2240
N	0.1858	<	0.4268
Ne	0.3929	<	0.7428
Na	0.3988	<	0.8010
Mg	0.4424	<	0.8874
P	0.5446	<	1.1127
Ar	0.7314	<	1.4242
Kr			3.2693
Xe			5.1773
mare (in %)			128.3

Overestimation for atoms:
Error cancellation with exchange !

Rung 2: Gradient Expansion

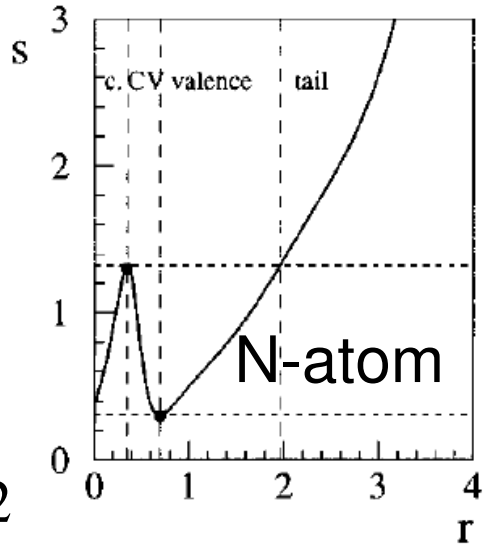
$$E_x[\rho] = \int \rho(\mathbf{r})\varepsilon_x^{LDA}[\rho]\left(1+\mu_x s^2+\ldots\right)d\mathbf{r}$$

$$s = \frac{\|\nabla\rho\|}{2(3\pi^2)^{1/3}\rho^{4/3}} = \frac{\|\nabla\rho\|}{2k_F(\rho)\rho}$$ Reduced gradient (adimensional)

Exact second order (GE2) $\mu_x = \frac{10}{81}$

Antoniewicz, Kleiman 1985

In solids $0.8 \le s_{\max} \le 2.2$



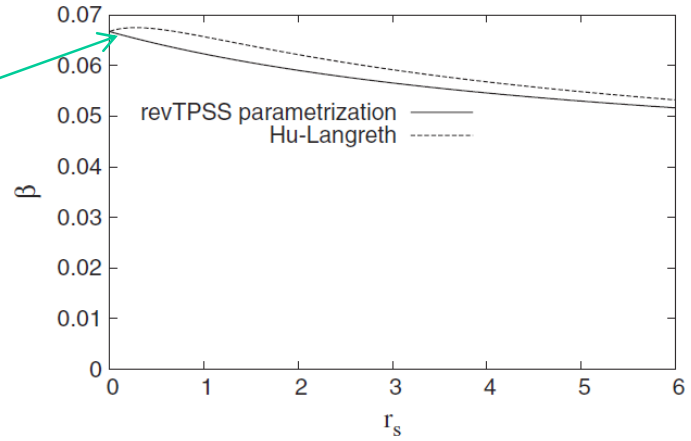
$$E_c[\rho] = \int \rho(\mathbf{r})\left(\varepsilon_c^{LDA}[\rho]+\beta_c(\rho)t^2+\ldots\right)d\mathbf{r}$$

$$t = \frac{\|\nabla\rho\|}{2k_s(\rho)\rho} = \frac{\|\nabla\rho\|}{4\left(\frac{3}{\pi^2}\right)^{1/6}\rho^{7/6}}$$

Reduced gradient for correlation

$$\beta(r_s \to 0) = 0.066725$$

Ma,Brueckner 1968



Gradient Expansion (GE2, GE4..) works badly ….

Generalized Gradient Expansion

$$E_x^{GGA}[\rho] = \int \rho(\mathbf{r})\varepsilon_x^{LDA}(\rho(\mathbf{r}))F_x(s)d^3\mathbf{r}$$

Exchange Enhancement Factor

PW86	**Perdew Wang 1986**	**8148 cit.**
B86	Becke 1986	917 cit.
B88	Becke 1988	19414 cit.
PW91	Perdew Wang 1991	2817 cit.
PBE	**Perdew, Burke, Ernzerhof 1996**	**20630 cit.**
revPBE	Zhang Yang 1998	521 cit.
RPBE	Hammer, Hansen Norskov 1999	1678 cit.
AM05	Armiento Mattsson 2005	105 cit.
WC	Wu Cohen 2006	244 cit.
PBEsol	Perdew el at 2008	208 cit.
SOGGA	Zhao Truhlar 2008	42 cit.
RGE	Ruzsinszky Csonka Scuseria 2009	
PBEint	Fabiano Constantin Della Sala 2010	
APBE	**Constantin Fabiano Laricchia Della Sala 2011**	

(Citations from google-schoolar)

Few are not empirical

Many are optimized for certain properties

Fx Limits

Becke88

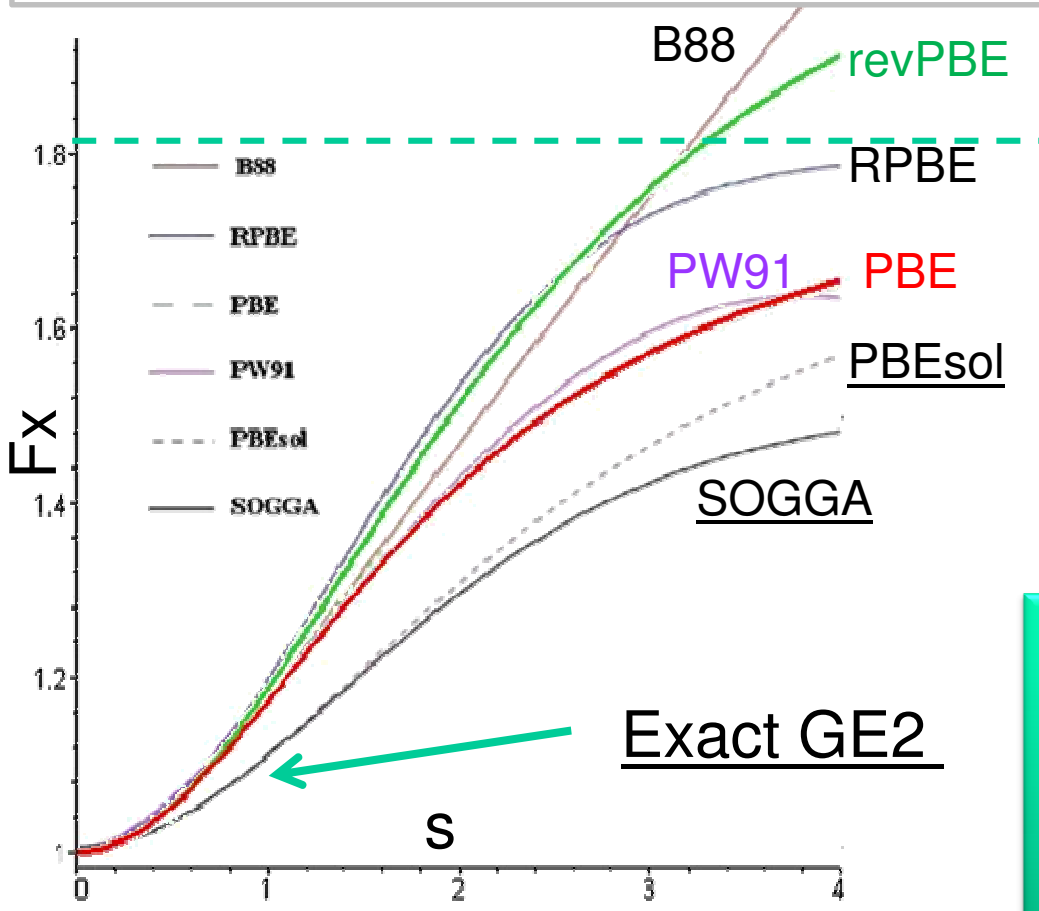
$$F_x^{B88}(s) = 1 + \frac{\beta c_2 (c_1 s)^2}{1 + 6\beta (c_1 s)\sinh^{-1}(c_1 s)}$$

$$c_2 = 2(6\pi^2)^{1/3} \quad c_2 = (2^{1/3} A_x)^{-1}$$

$\beta = 0.0042$ (fitted on atoms)

$$\varepsilon_x(\mathbf{r}) = \frac{1}{2}\int \frac{h_x(\mathbf{r},\mathbf{r}')}{\|\mathbf{r}-\mathbf{r}'\|} d^3\mathbf{r}' \xrightarrow[r\to 0]{} \frac{1}{2}\frac{\rho(\mathbf{r})}{r}$$

Exact asymptotic property



$$F_x(s) < 1.804$$

$$E_x[\rho] \geq E_{xc}[\rho] \geq 2.273 E_x^{LDA}[\rho]$$

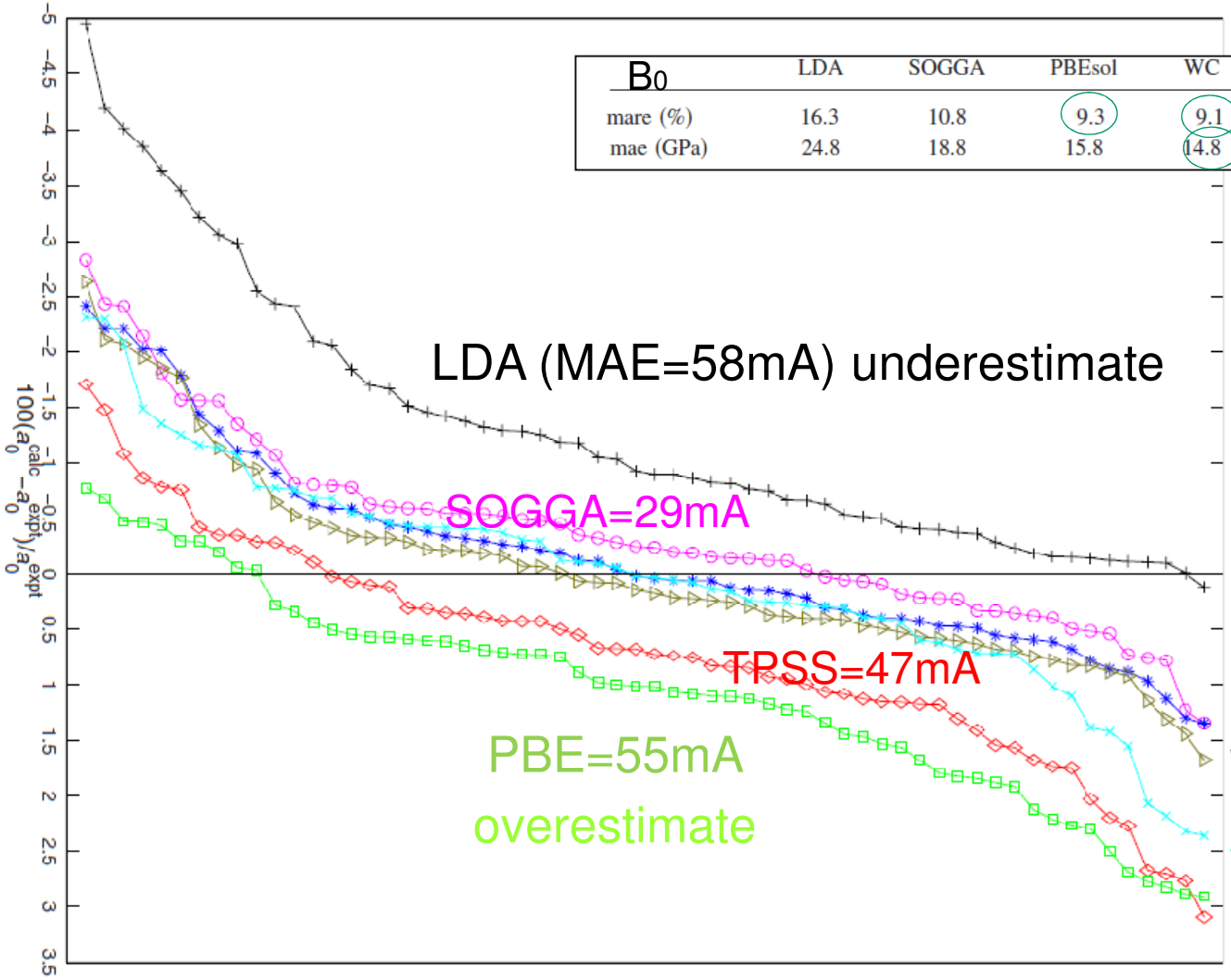
Lieb-Oxford bound

MARE(%) for atoms

LDA	9.8
PBE	0.8
B88	**0.2**

GGA performance

Lattice constants for 60 solids



B_0	LDA	SOGGA	PBEsol	WC	AM05	TPSS	PBE
mare (%)	16.3	10.8	9.3	9.1	10.6	9.9	9.5
mae (GPa)	24.8	18.8	15.8	14.8	16.7	13.7	12.8

Philipp Haas, Fabien Tran, and Peter Blaha PHYSICAL REVIEW B **79**, 085104 (2009)

PBE: quest for parameters

$$F_x^{PBE}(s) = 1 + \kappa - \frac{\kappa}{1 + \frac{\mu s^2}{\kappa}}$$

$$s \to \infty \Rightarrow F_x = 1 + \kappa$$

$$s \to 0 \Rightarrow F_x = 1 + \mu s^2$$

PBE correlation

$$E_c[\rho,\zeta] = \int \rho(\mathbf{r}) \left(\varepsilon_c^{LDA}[\rho,\zeta] + H_0(\rho,\zeta,t)\right) d\mathbf{r}$$

$$H_0(r_s,\zeta,t) = \gamma\phi^3(\zeta) \ln\left[1 + \frac{\beta_{\mathrm{MB}}}{\gamma} t^2 \left(\frac{1 + At^2}{1 + At^2 + A^2t^4}\right)\right]$$

$\mu_x^{PBE} = \beta_{MB}(\pi^2/3) \approx 0.21961$

To satisfy the LDA response

$\mu_x = \frac{10}{81} \approx 0.1234$ (PBEsol)

$\mu_x = 0.26$ Semiclassical neutral atom: asymptotic-Z expansion (APBE)

$\kappa^{PBE} = 0.804$ (LO bound)

κ large (≈ 1.2 as in revPBE) improoves atoms

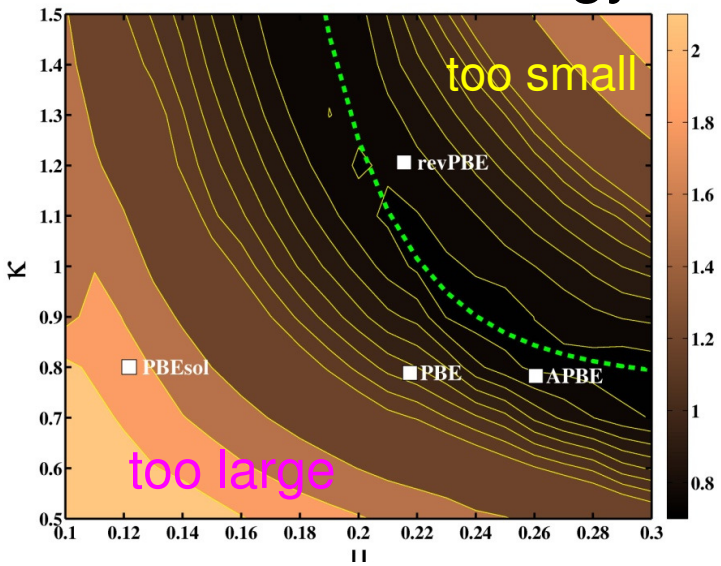
κ small (≈ 0.5 as in SOGGA) improoves solid

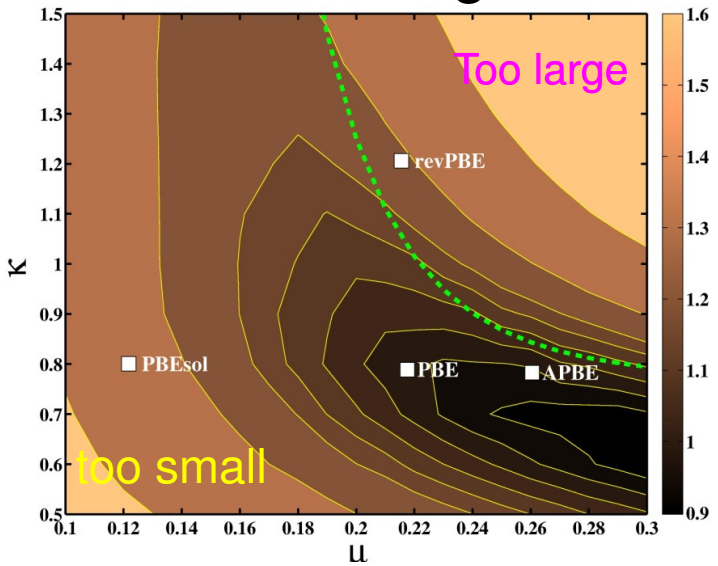
APBE: Constantin,Fabiano,Laricchia, Della Sala, Phys. Rev. Lett. *106, 186406* (2011)

Atomiz. Energy

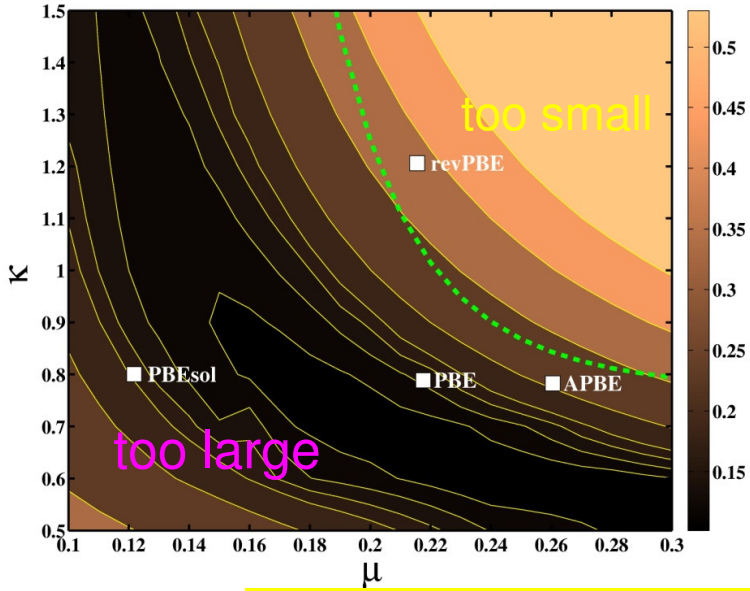
Bond-lenghts

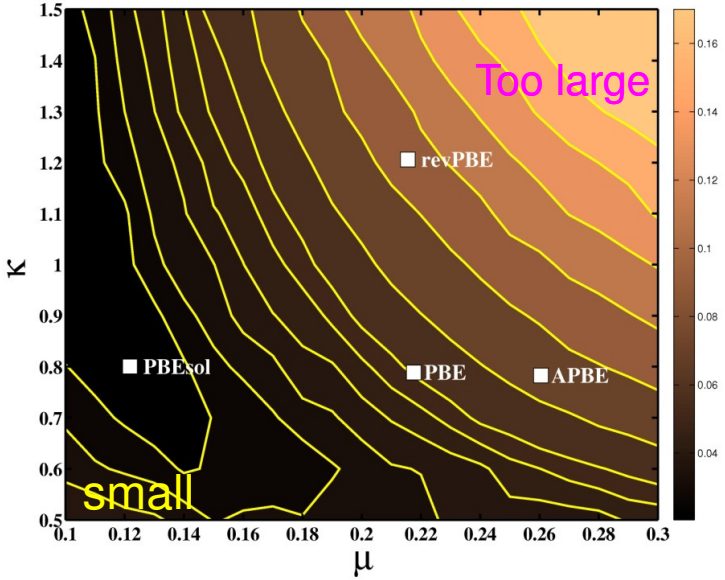
Molecules





Solids





Two dimensional PBE scan: Fabiano, Constatin, Della Sala submitted

(Perdew) GGA cannot be exact for solid and molecules: PBE (APBE) best on the average

We need to go beyond GGA : meta-GGA, OEP, hybrids ...

Section II

Orbital Dependent Functional
Exact Exchange

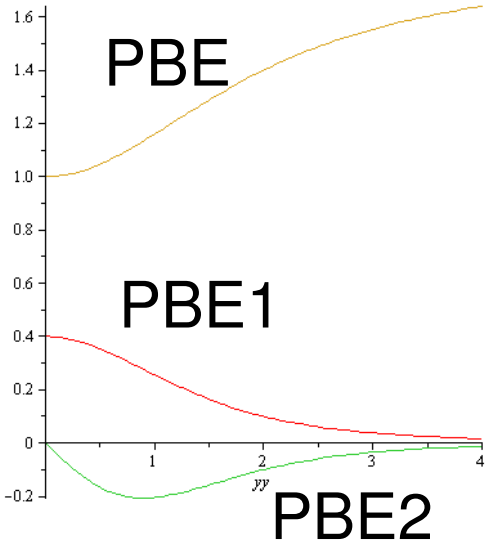
Exchange potential for Hydrogen atom

$$v_x(\mathbf{r}) = \frac{\delta E_x^{GGA}}{\delta \rho(\mathbf{r})} = -A_x \frac{4}{3} n^{1/3} \left(F_x - \frac{3}{4} t \underbrace{\left(s^{-1} \frac{dF_x}{ds} \right)}_{PBE1} - \left(\frac{3}{4} u - s^3 \right) \underbrace{\frac{d}{ds} \left(s^{-1} \frac{dF_x}{ds} \right)}_{PBE2} \right)$$

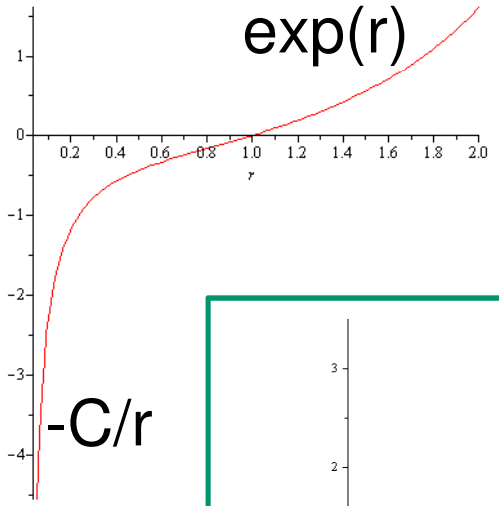
$$u = (2k_F)^{-3} n^{-2} \times \nabla n \cdot \nabla |\nabla n| \Rightarrow = \frac{C}{n}$$

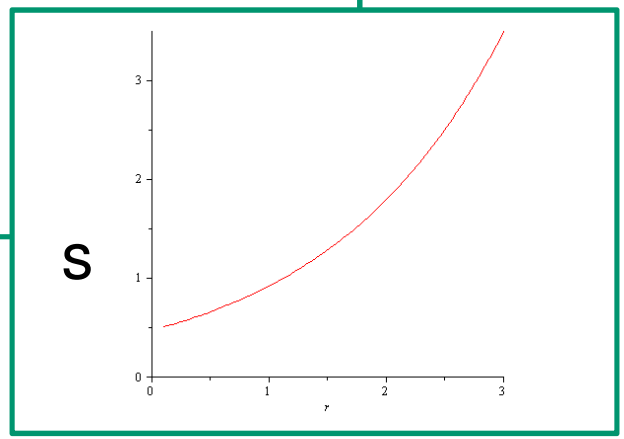
$$n = \frac{\alpha^3}{\pi} e^{-2\alpha r}$$

Hydrogenic density

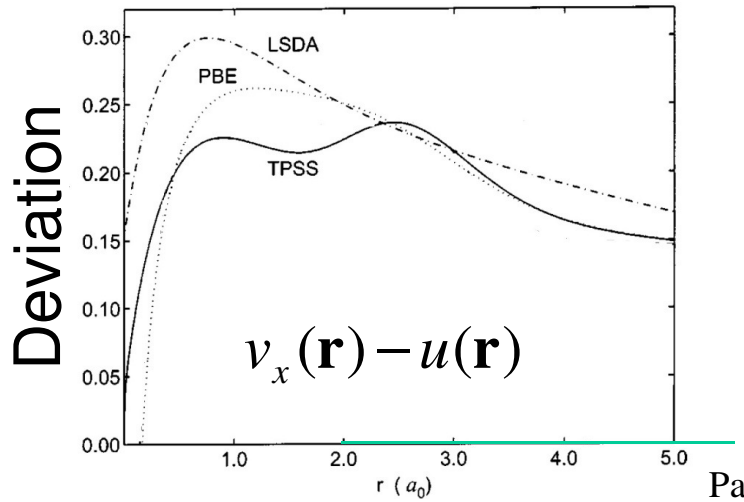


$$t = (2k_F)^{-2} n^{-1} \nabla^2 n$$





- PBE **diverges** at nucleus (LDA,TPSS ok)
- PBE asymptotically **exponentially decreasing** (TPSS,LDA too; B88 $\rightarrow -\frac{a}{r^2}$)



1-e Self-interaction

1-electron (ns=1) or 2-electron (ns=2) systems

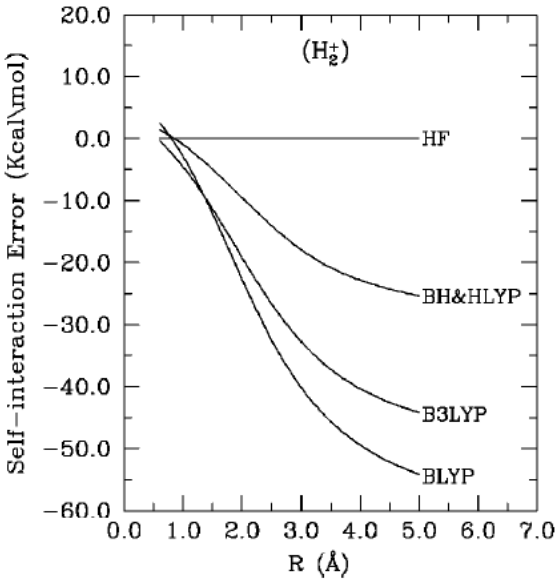
$$h_x^{EXX}(\mathbf{r},\mathbf{r}') = -n_s \frac{\left|\gamma^{KS}(\mathbf{r},\mathbf{r}')\right|^2}{\rho(\mathbf{r})} = -\frac{\rho(\mathbf{r}')}{n_s}$$

$$\varepsilon_x(\mathbf{r}) = -\frac{1}{2n_s}\int \frac{\rho(\mathbf{r}')}{\|\mathbf{r}-\mathbf{r}'\|} d^3\mathbf{r}' = -\frac{1}{2n_s} u(\mathbf{r})$$

$$E_x[\rho] = -\frac{1}{2n_s}\iint \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{\|\mathbf{r}-\mathbf{r}'\|} d^3\mathbf{r} d^3\mathbf{r} = -\frac{E_c}{n_s}$$

$$v_x(\mathbf{r}) = \varepsilon_x(\mathbf{r}) + \int d\mathbf{r}\rho(\mathbf{r}')\frac{\delta\varepsilon_x(\mathbf{r}')}{\delta\rho(\mathbf{r})} = -\frac{u(\mathbf{r})}{n_s}$$

For 1-e systems exchange cancels coulomb exactly



GGA/Hybrid functionals: large self-interaction erroor

1) Perdew,Zunger (SIC) 9517 cit.

2) Orbital dependent Functionals

Almbladh, von Barth 1985 (atoms)

$$\rho^{exact}(\mathbf{r}) \xrightarrow{r\to\infty} \exp(-2\sqrt{2I}\,r) \Rightarrow \begin{cases} v_x^{exact}(\mathbf{r}) \xrightarrow{r\to\infty} -\dfrac{1}{r} \\ v_c^{exact}(\mathbf{r}) \xrightarrow{r\to\infty} -\dfrac{\alpha}{r^4} \\ \varepsilon_{\mathrm{H}}^{\mathrm{KS,exact}} = -I \end{cases}$$

1-e Self-interaction-free

Perdew, Levy 1997

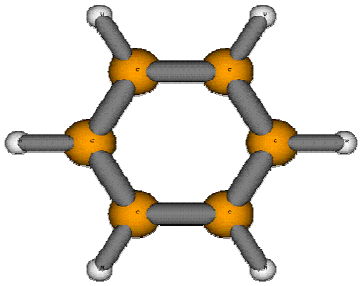
Della Sala, Gorling 2002 (molecules)

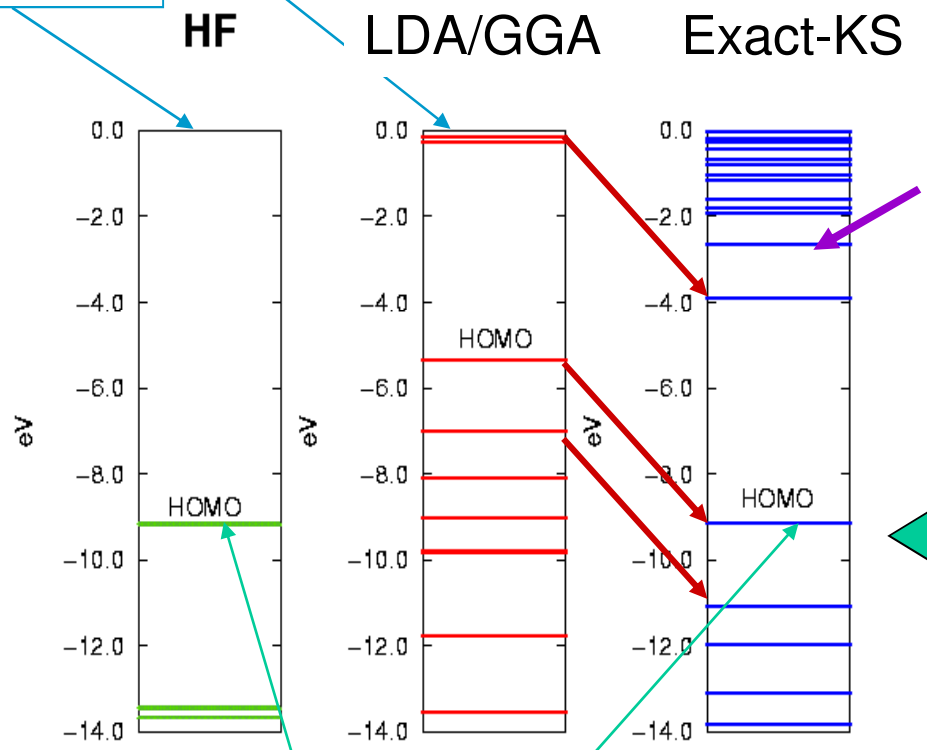
Kohn-Sham Eigenvalues

Difficulties in representing virtual unbound orbital in local basis sets

Common LDA/GGA gives largely incorrect absolute eigenvalues (3eV), but acceptable energy differences (ok for solid-state). **LDA/GGA LUMO more diffuse**

Rydberg series of virtual orbitals





Exp. I.P.

HOMO energy in HF and Exact-KS is similar and close to the Exp. I.P.

Exact KS eigenvalues:
Response properties (TD-DFT, NMR,...)

-1/r corrected Functional

Leeuwen, Baerends 1994 (LB94) 714 cit.

$$v_{xc}(\mathbf{r}) = v_{xc}^{LDA}(\mathbf{r}) - \beta\rho^{1/3}\frac{x^2}{1+3\beta\, x\,\mathrm{arcsinh}(x)} \xrightarrow{r\to\infty} -\frac{1}{r} \qquad \beta = 0.05;\ \mathrm{x} = \frac{|\nabla\rho|}{\rho^{4/3}}$$

Becke, Roussel 1989 (BR) 193 cit.

$$E_x = \frac{1}{2}\int \rho(\mathbf{r}) v_{slat}(\mathbf{r}) d\mathbf{r}$$

$$v_{slat}(\mathbf{r}) = -n_s \sum_{ab}^{\text{occ.}} \frac{\phi_a(\mathbf{r})\phi_b(\mathbf{r})}{\rho(\mathbf{r})} \int \frac{\phi_a(\mathbf{r}')\phi_b(\mathbf{r}')}{\|\mathbf{r}-\mathbf{r}'\|} d^3\mathbf{r}' \xrightarrow{r\to\infty} -\frac{1}{r}$$

$$v_x(\mathbf{r}) = \frac{\delta E_x}{\delta\rho(\mathbf{r})} = v_{slat}(\mathbf{r}) + v_{resp}(\mathbf{r})$$

$$v_{slat}^{UEG}(\mathbf{r}) = \frac{3}{2} v_x^{LDA}(\mathbf{r})$$

$$v_{slat}(\mathbf{r}) \approx \int du\, u 4\pi\, \bar{h}_x^{\text{exp.dens.}}(\mathbf{r},u) = -\frac{(8\pi\rho)^{1/3}}{x\exp(-x/3)}\left(1-\exp(-x)-\frac{1}{2}x\exp(-x)\right) \xrightarrow{r\to\infty} -\frac{1}{r}$$

Meta-GGA: $x = x[\rho, \nabla\rho, \nabla^2\rho, \tau]$

$E_{xc}(\mathbf{r})$ 1e-self interaction free $\Rightarrow$ $v_{xc}(\mathbf{r}) \xrightarrow{r\to\infty} -\frac{1}{r}$

$\Leftarrow$ X

Orbital-Dependent Functionals

Energy Functional of the Rung 4-5 are *orbital dependent functional* (implicit density functional of the form)

$$E_{xc}[\{\phi\}])$$

Exact Exchange

$$E_x[\{\phi\}] = -\frac{n_s}{2}\sum_{a,b}^{\text{occ.}}\iint \frac{\phi_a(\mathbf{r})\phi_b(\mathbf{r})\phi_a(\mathbf{r}')\phi_b(\mathbf{r}')}{\|\mathbf{r}-\mathbf{r}'\|}d\mathbf{r}d\mathbf{r}'$$

EXX: self-interaction-free, exactly !

How to obtain KS equations with a **local** xc-potential ?

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

Chain-Rule: Density Response

$$\underbrace{\frac{\delta E_{xc}[\{\phi\}]}{\delta v_s(\mathbf{r})}}_{d_{xc}(\mathbf{r})} = \int \underbrace{\frac{\delta E_{xc}}{\delta\rho(\mathbf{r}')}}_{v_{xc}(\mathbf{r}')} \underbrace{\frac{\delta\rho(\mathbf{r}')}{\delta v_s(\mathbf{r})}}_{\chi_s(\mathbf{r}',\mathbf{r})} d\mathbf{r}'$$

$$-\frac{1}{2}\nabla^2\phi_i(\mathbf{r}) + v_s(\mathbf{r})\phi_i(\mathbf{r}) = \varepsilon_i\phi_i(\mathbf{r})$$

Green's functions

$$\frac{\delta\phi_i(\mathbf{r}')}{\delta v_s(\mathbf{r})} = \sum_{j\neq i}^{all} \phi_i(\mathbf{r})\frac{\phi_j(\mathbf{r}')\phi_i(\mathbf{r}')}{\varepsilon_i - \varepsilon_j}$$

Density response

Only virtual

$$\chi_s(\mathbf{r},\mathbf{r}') = \frac{\delta\rho(\mathbf{r})}{\delta v_s(\mathbf{r})} = 2n_s\sum_a^{occ}\phi(\mathbf{r})\frac{\delta\phi(\mathbf{r})}{\delta v_s(\mathbf{r})} = 2n_s\sum_a^{occ}\sum_s^{virt}\frac{\phi_a(\mathbf{r})\phi_s(\mathbf{r})\phi_a(\mathbf{r}')\phi_s(\mathbf{r}')}{\varepsilon_a - \varepsilon_s}$$

Integral equation for the exchange-correlation potential

$$\int \chi_s(\mathbf{r},\mathbf{r}')v_{xc}(\mathbf{r}')d\mathbf{r}' = d_{xc}(\mathbf{r})$$

Chain Rule: RHS term

$$d_{xc}(\mathbf{r}) = \frac{\delta E_{xc}}{\delta v_s(\mathbf{r})} = \int \sum_i \frac{\delta E_{xc}[\{\phi\}]}{\delta \phi_i(\mathbf{r}')} \frac{\delta \phi_i(\mathbf{r}')}{\delta v_s(\mathbf{r})} d\mathbf{r}' =$$

$$= \sum_i \sum_{j \neq a}^{all} \frac{\phi_i(\mathbf{r})\phi_j(\mathbf{r})}{\varepsilon_i - \varepsilon_j} \left\langle \frac{\delta E_{xc}[\{\phi\}]}{\delta \phi_i(\mathbf{r}')} \middle| \phi_j(\mathbf{r}) \right\rangle$$

Note that $\int d_{xc}(\mathbf{r}) d\mathbf{r} = \int\int \chi_s(\mathbf{r},\mathbf{r}') v_{xc}(\mathbf{r}') d\mathbf{r}' d\mathbf{r} = 0$

$d_{xc}(\mathbf{r})$ is an induced density

Integral equation for the EXX potential

$$\int \chi_s(\mathbf{r},\mathbf{r}') v_x^{EXX}(\mathbf{r}') d\mathbf{r}' = \frac{\delta E_{EXX}}{\delta v_s(\mathbf{r})} = 2 n_s \sum_a^{occ.} \sum_s^{virt.} \frac{\phi_a(\mathbf{r})\phi_s(\mathbf{r})}{\varepsilon_a - \varepsilon_s} \left\langle \phi_a \middle| \hat{v}_x^{NL} \middle| \phi_s \right\rangle$$

Non-local Exchange $v_x^{NL}(\mathbf{r},\mathbf{r}') = -\sum_a^{occ.} \frac{\phi_a(\mathbf{r})\phi_a(\mathbf{r}')}{\|\mathbf{r}-\mathbf{r}'\|}$

Exact-Exchange (EXX)

$$\int \chi_s(\mathbf{r},\mathbf{r}')v_x^{EXX}(\mathbf{r}')d\mathbf{r}' = \frac{\delta E_{EXX}}{\delta v_s(\mathbf{r})} = 2n_s \sum_a^{occ.} \sum_s^{virt.} \langle \phi_a | \hat{v}_x^{NL} | \phi_s \rangle \frac{\phi_a(\mathbf{r})\phi_s(\mathbf{r})}{\varepsilon_a - \varepsilon_s}$$

- 1976 (Talman) EXX for atoms (GRID) 850 cit. => ok!
- 1997 (Gorling) EXX for solids (PW) 272 cit. => ok!
- 1999 (Gorling; Ivanov) EXX in GTO 243;217 cit. => bad potential !
- 2002 (Yang) OEP iterative minimiz. in GTO 179 cit. => more stable
- 2003 (Kummel) EXX on GRID 127cit. => iterative
- **2007 (Yang)** **GTO: good potential with penalty function 43 cit.**
- **2007 (Hesselman)** GTO: "balanced" basis set

EXX is local-basis set is numerically tricky

⇨ more stable/efficient methods required for large systems

Total Energy deviation from HF (eV)

System	HF	KLI	LHF	EXX
Ne	– 3497.95	0.06	0.06	0.05[a] 0.05[b],0.05[c]
H_2O	– 2069.89	0.10	0.09	0.06[a], 0.06[b]
CO	– 3069.18	0.21	0.21	0.14[a] 0.14[b],0.16[c]

HF<EXX<LHF<KLI

Effective EXX

(KLI) Krieger, Li, Iafrate 1992 491 cit.

$$v_x^{KLI}(\mathbf{r}) = \underbrace{-n_s \sum_{ab}^{\text{occ.}} \frac{\phi_a(\mathbf{r})\phi_b(\mathbf{r})}{\rho(\mathbf{r})} \int \frac{\phi_a(\mathbf{r}')\phi_b(\mathbf{r}')}{\|\mathbf{r}-\mathbf{r}'\|} d^3\mathbf{r}'}_{\text{Slater Potential} = 2\varepsilon_x^{EXX}(\mathbf{r})} + \underbrace{n_s \sum_{i\neq H}^{\text{occ.}} \frac{|\phi_i(\mathbf{r})|^2}{\rho\ (\mathbf{r})} \langle \phi_i | v_x^{LHF} - \hat{v}_{NL} | \phi_j \rangle}_{\text{Response Term}}$$

Slater Potential goes asymptotically as -1/r (self-interaction free)

The (HOMO) term is removed so that v_x vanishes asymptotically

Localized Hartree-Fock (LHF) method **Della Sala, Gorling 2001 207 cit.**

$$v_x^{LHF}(\mathbf{r}) = v_{sla}(\mathbf{r}) + \underbrace{n_s \sum_{\substack{ij\neq \\ (N,N)}}^{\text{occ.}} \frac{\phi_i(\mathbf{r})\phi_j(\mathbf{r})}{\rho\ (\mathbf{r})} \langle \phi_i | v_x^{LHF} - \hat{v}_{NL} | \phi_j \rangle}_{\text{Correction Term}}$$

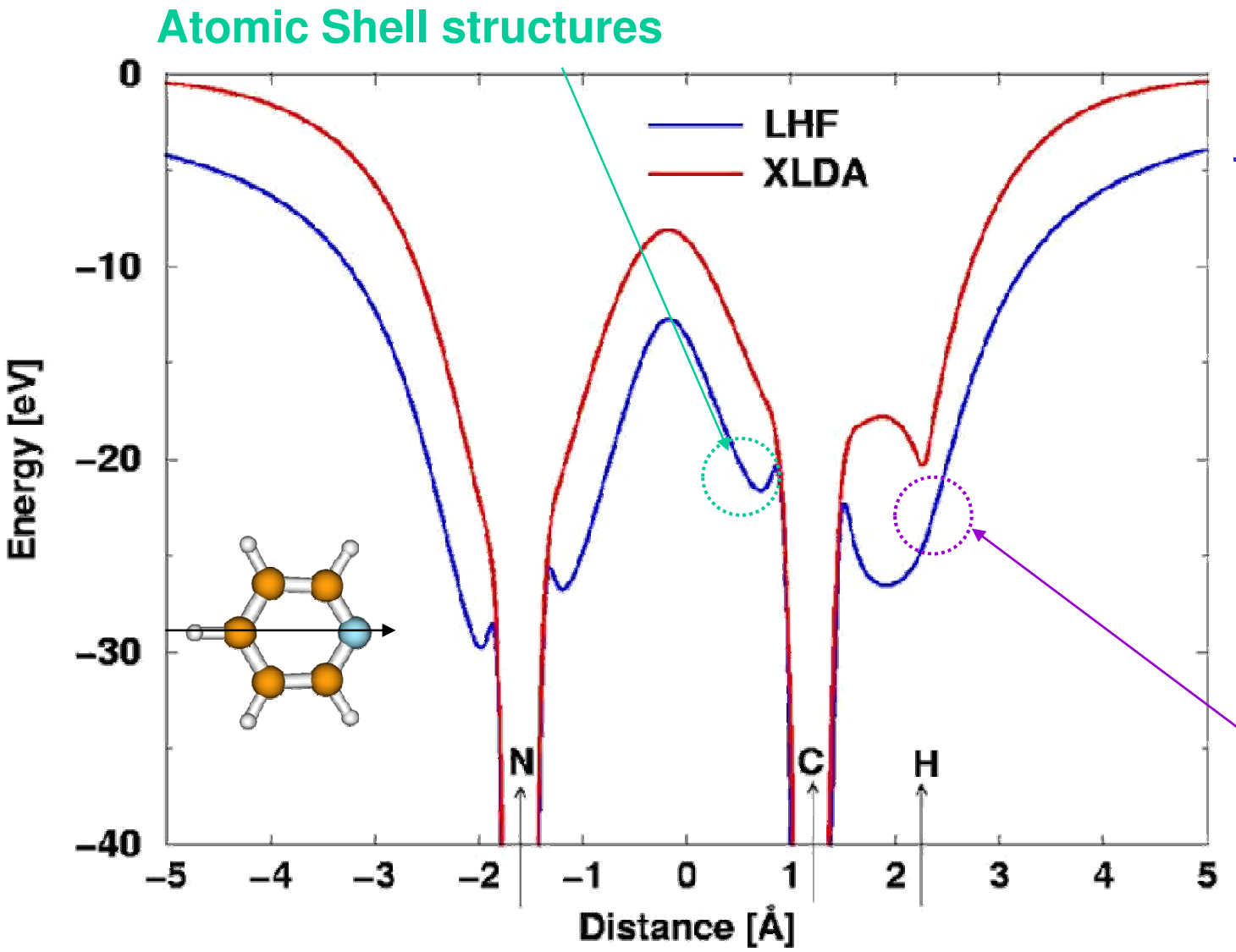
$$\begin{aligned} v_x(\mathbf{r}) = &-\frac{n_s}{\rho(\mathbf{r})} \int d\mathbf{r}' \frac{\rho(\mathbf{r}',\mathbf{r})\rho(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \\ &+ \frac{n_s}{\rho(\mathbf{r})} \int d\mathbf{r}' \rho(\mathbf{r}',\mathbf{r})\rho(\mathbf{r},\mathbf{r}') v_x(\mathbf{r}') \\ &+ \frac{n_s}{\rho(\mathbf{r})} \int \int d\mathbf{r}' d\mathbf{r}'' \frac{\rho(\mathbf{r}'',\mathbf{r})\rho(\mathbf{r},\mathbf{r}')\rho(\mathbf{r}',\mathbf{r}'')}{|\mathbf{r}'-\mathbf{r}''|}. \end{aligned}$$

LHF potential functional of the density matrix

CEDA: Gritsenko, Baerends 2001

ELF: Staroverov, Scuseria, Davidson 2006

LHF potential



$e^{-\alpha r}$

-1/r

Different asymptotic behavior

No structure around hydrogens

Section III

Hybrid Functionals

Generalized Kohn-Sham

Non-interacting Kohn-Sham system

$$\hat{H}^{KS} = \hat{T} + \hat{V}_{ext} + \sum_{i=1}^{N}\left[u(\mathbf{r}_i) + v_{xc}(\mathbf{r}_i)\right]$$

Local potential

Single determinant Φ ; $\rho^{KS}(\mathbf{r}) = \rho^{exact}(\mathbf{r})$

$$E^{V_{ext}}[\rho] = T_{ni}[\rho] + \int \rho(\mathbf{r}) v_{ext}(\mathbf{r}) d^3\mathbf{r} + E_J[\rho] + E_{xc}[\rho]$$

Interacting MB system

$$\hat{H}^{MB} = \hat{T} + \hat{V}_{ext} + \hat{V}_{ee}$$

MB wavefunction Ψ

$$\rho^{MB}(\mathbf{r}) = \rho^{exact}(\mathbf{r})$$

$$E^{V_{ext}} = \langle \Psi | \hat{H}^{MB} | \Psi \rangle$$

Partially-interacting
Generalized Kohn-Sham(GKS) system

$$\hat{H}^{KS} = \hat{T} + \hat{V}_{ext} + \sum_{i=1}^{N}\left[u(\mathbf{r}_i) + \hat{w}_{xc}^{NL} + r_{xc}(\mathbf{r}_i)\right]$$

Non-Local operator

Single determinant Φ ; $\rho^{KS}(\mathbf{r}) = \rho^{exact}(\mathbf{r})$

$$E^{V_{ext}}[\Phi] = T_{wi}[\Phi] + \int \rho(\mathbf{r}) v_{ext}(\mathbf{r}) d^3\mathbf{r} + E_J[\rho] + E_w[\Phi] + R_w[\rho]$$

We are not forced to solve only the very simple KS non-interacting system.
We can solve also easily solve Hartree-Fock

Interaction included in GKS equations

$$E_w[\Phi] = \frac{n_s}{2}\sum_a \langle \phi_a | \hat{w}_{xc}^{NL} | \phi_a \rangle$$

$$\frac{\delta E_w}{\delta \phi_a(\mathbf{r})} = 2 n_s \left[\hat{w}_{xc}^{NL}\phi_a\right](\mathbf{r})$$

Residual Interaction (local potential)

$$R_w[\rho]$$

$$r_w(\mathbf{r}) = \frac{\delta R_w[\rho]}{\delta \rho(\mathbf{r})}$$

KS-DFT and beyond

Classical Electrostatic potential

Exchange-Correlation Operator

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + v_{\text{ext}}(\mathbf{r}) + u(\mathbf{r}) + \hat{\mathrm{V}}\right)\phi_i(\mathbf{r}) = \varepsilon_i\phi_i(\mathbf{r})$$

Kohn-Sham: $\hat{V} = v_{xc}(\mathbf{r})$ *(Local operator)*

Hartree-Fock (exchange-only) $\hat{V} = v_x^{NL}(\mathbf{r},\mathbf{r}') = -\sum_a^{\text{occ.}} \frac{\phi_a(\mathbf{r})\phi_a(\mathbf{r}')}{\|\mathbf{r}-\mathbf{r}'\|}$

$\hat{V} = v_x^{NL}(\mathbf{r},\mathbf{r}') + v_c(\mathbf{r})$ *(HFKS)*

Generalized KS : $\hat{V} = \alpha\, v_x^{NL}(\mathbf{r},\mathbf{r}') + r_{xc}(\mathbf{r})$ *(global. hybrid)*

$\hat{V} = w_{xc}^{NL}(\mathbf{r},\mathbf{r}') + r_{xc}(\mathbf{r})$ *(range-sep.)*

Brueckner Orbitals : $\hat{V} = v_x^{NL}(\mathbf{r},\mathbf{r}') + v_c^{BO}(\mathbf{r},\mathbf{r}')$

Self-Energy (Quasi-particle) $\hat{V} = \Sigma_{xc}(\mathbf{r},\mathbf{r}',\varepsilon_i)$ (Σ=GW)

Global Hybrid

KS

$$\hat{w}_{xc}^{NL}(\mathbf{r},\mathbf{r}') = 0 \qquad r_{xc}(\mathbf{r}) = v_{xc}^{GGA}(\mathbf{r})$$

Hybrid
1-param
(PBE0,α=1/4)

$$\hat{w}_{xc}^{NL}(\mathbf{r},\mathbf{r}') = -a_x \frac{\gamma(\mathbf{r},\mathbf{r}')}{\|\mathbf{r}-\mathbf{r}'\|} \qquad r_{xc}(\mathbf{r}) = (1-a_x)v_x^{GGA}(\mathbf{r}) + v_c^{GGA}(\mathbf{r})$$

Hybrid
3-param
(B3LYP, α=0.2)

$$\hat{w}_{xc}^{NL}(\mathbf{r},\mathbf{r}') = -a_x \frac{\gamma(\mathbf{r},\mathbf{r}')}{\|\mathbf{r}-\mathbf{r}'\|}$$

$$r_{xc}(\mathbf{r}) = (1-a_x)v_x^{LDA}(\mathbf{r}) + b_x v_x^{GGA}(\mathbf{r}) + c v_c^{GGA}(\mathbf{r})$$

B3LYP : Becke 1983 33811cit. (most cited)

M05-2X a=0.56

Zhao Thrular 2006 670 cit.

HFKS

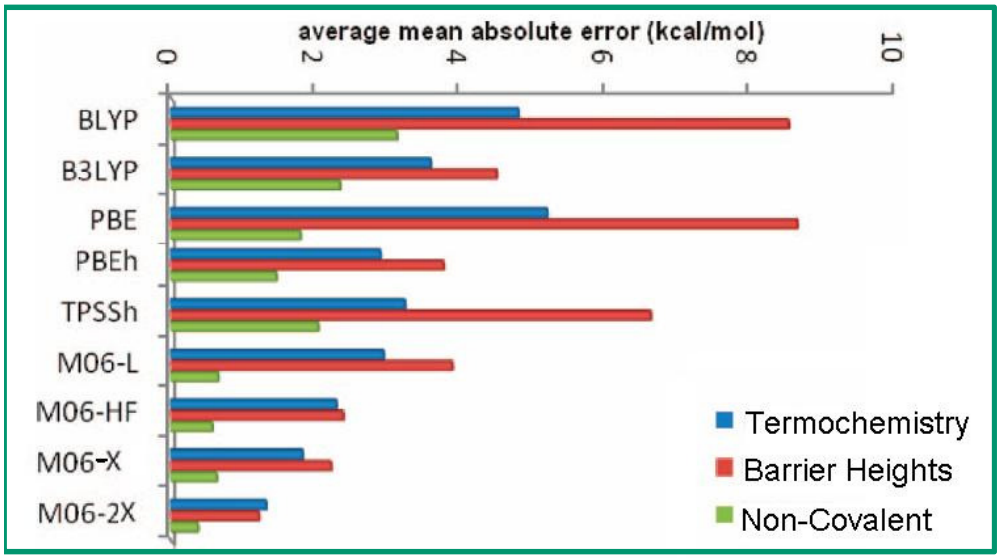
$$\hat{w}_{xc}^{NL}(\mathbf{r},\mathbf{r}') = -\sum_{a}^{occ} \frac{\phi_a(\mathbf{r})\phi_a(\mathbf{r}')}{\|\mathbf{r}-\mathbf{r}'\|} \qquad r_{xc}(\mathbf{r}) = v_c^{GGA}(\mathbf{r})$$

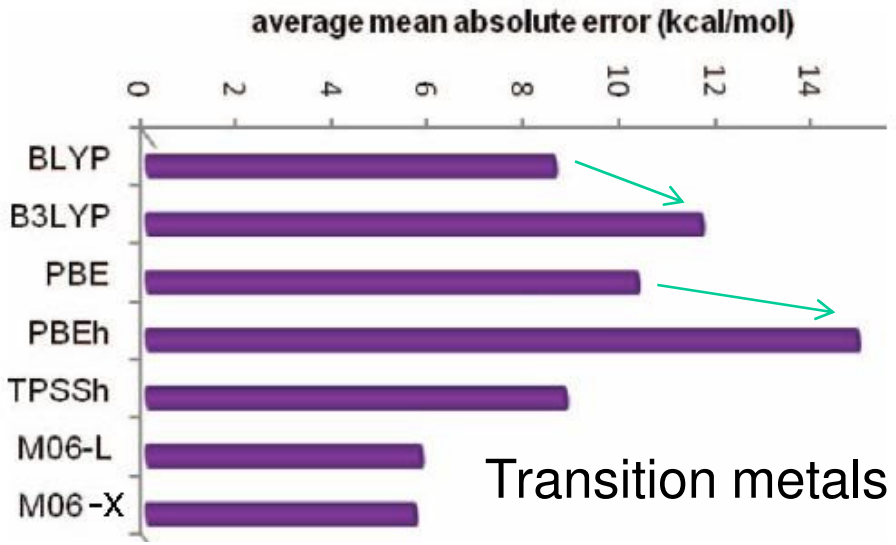
HF Fraction

Hybrid performance

Bond lengths	B3LYP	TPSS	PBE	BLYP
MSE[b]	–0.0024	0.0070	0.0094	0.0125
MUE[c]	0.0055	0.0071	0.0094	0.0125

Hybrid methods improve bond-lengths of molecules





Transition metals

	PBE	PBE0	B3YLP
Lattice const	0.044(+)	0.024(+)	0.053(+)
Bulk Moduli	12.3(-)	0.1	13.7(-)

GGA better than hybrids for transition metals

B3LYP fails for solids: PBE0 much better

Range-separated Hybrid

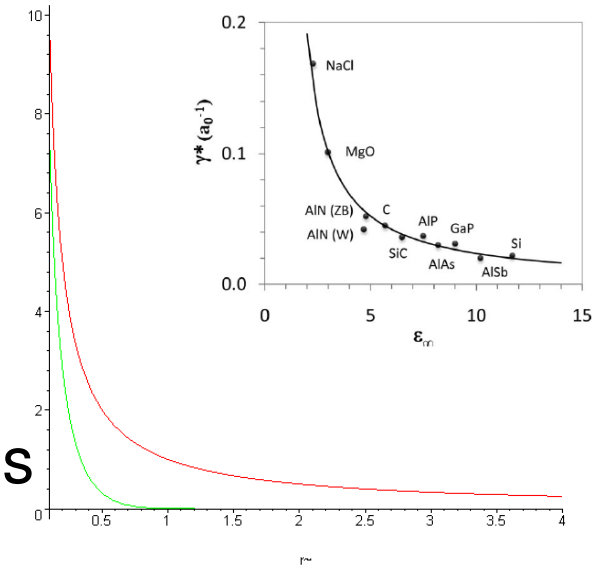
Screened hybrid

$$\hat{w}_{xc}^{NL}(\mathbf{r},\mathbf{r}') = -a\frac{erfc(\omega\|\mathbf{r}-\mathbf{r}'\|)}{\|\mathbf{r}-\mathbf{r}'\|}\gamma(\mathbf{r},\mathbf{r})$$

$$\hat{w}_{xc}^{NL}(\mathbf{r},\mathbf{r}') = -a\frac{\exp(-\omega\|\mathbf{r}-\mathbf{r}'\|)}{\|\mathbf{r}-\mathbf{r}'\|}\gamma(\mathbf{r},\mathbf{r})$$

Short-range=>a*HF
Long-range=>GGA

Efficient for solids



Heyd,Scuseria,Enzerhof (HSE) 2003 548 cit.

$$E_{xc}^{HSE} = aE_x^{HF,SR}(\omega) + (1-a)E_x^{\omega PBE,SR}(\omega) + E_x^{\omega PBE,LR}(\omega) + E_c^{PBE},$$

$$a = 1/4 \qquad \omega = 0.15\,a_0^{-1}$$

TABLE III. Bulk moduli for 21 solids (GPa).

Solid	LDA	PBE	TPSS	HSE
ME[c]	11.8	−9.2	−4.1	1.4
MAE[d]	12.6	10.1	9.9	4.4

TABLE II. Lattice constants for 21 solids (Å).

Solid	LDA	PBE	TPSS	HSE
ME[c]	−0.067	0.046	0.034	0.009
MAE[d]	0.067	0.049	0.035	0.028

TABLE IV. Band gaps for eight semiconductors (eV).

Solid	LDA	PBE	TPSS	HSE
ME[d]	−1.30	−1.32	−1.27	−0.11
MAE[e]	1.30	1.32	1.27	0.23

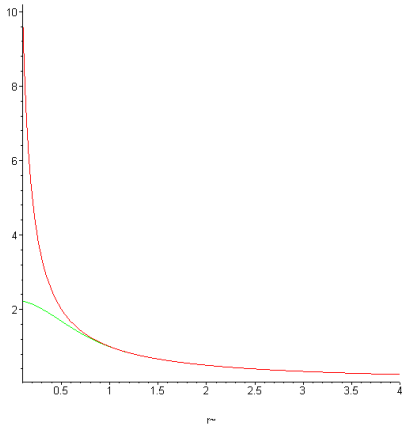
As PBE0, but more efficient

Long-range corrected Hybrid

LC-hybrid

$$\hat{w}_{xc}^{NL}(\mathbf{r},\mathbf{r}') = -\frac{erf(\omega\|\mathbf{r}-\mathbf{r}'\|)}{\|\mathbf{r}-\mathbf{r}'\|}\gamma(\mathbf{r},\mathbf{r}')$$

$$\hat{w}_{xc}^{NL}(\mathbf{r},\mathbf{r}') = -\frac{1-\exp(\omega\|\mathbf{r}-\mathbf{r}'\|)}{\|\mathbf{r}-\mathbf{r}'\|}\gamma(\mathbf{r},\mathbf{r}')$$



Short-range=>GGA
Long-range=>HF

For molecules
(charge-transfer in TD-DFT)

Yanai, Tew, Handy 2004 (CAM-B3LYP) 578 cit.
Tawada et al. (LC-BYLP) 293 cit.

Hybrid improve electronic properties (dipole, polarizability)

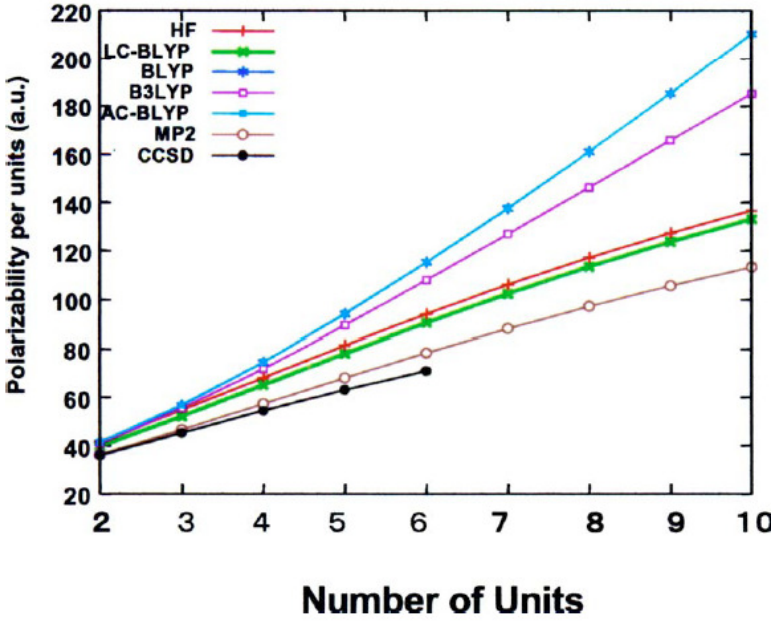
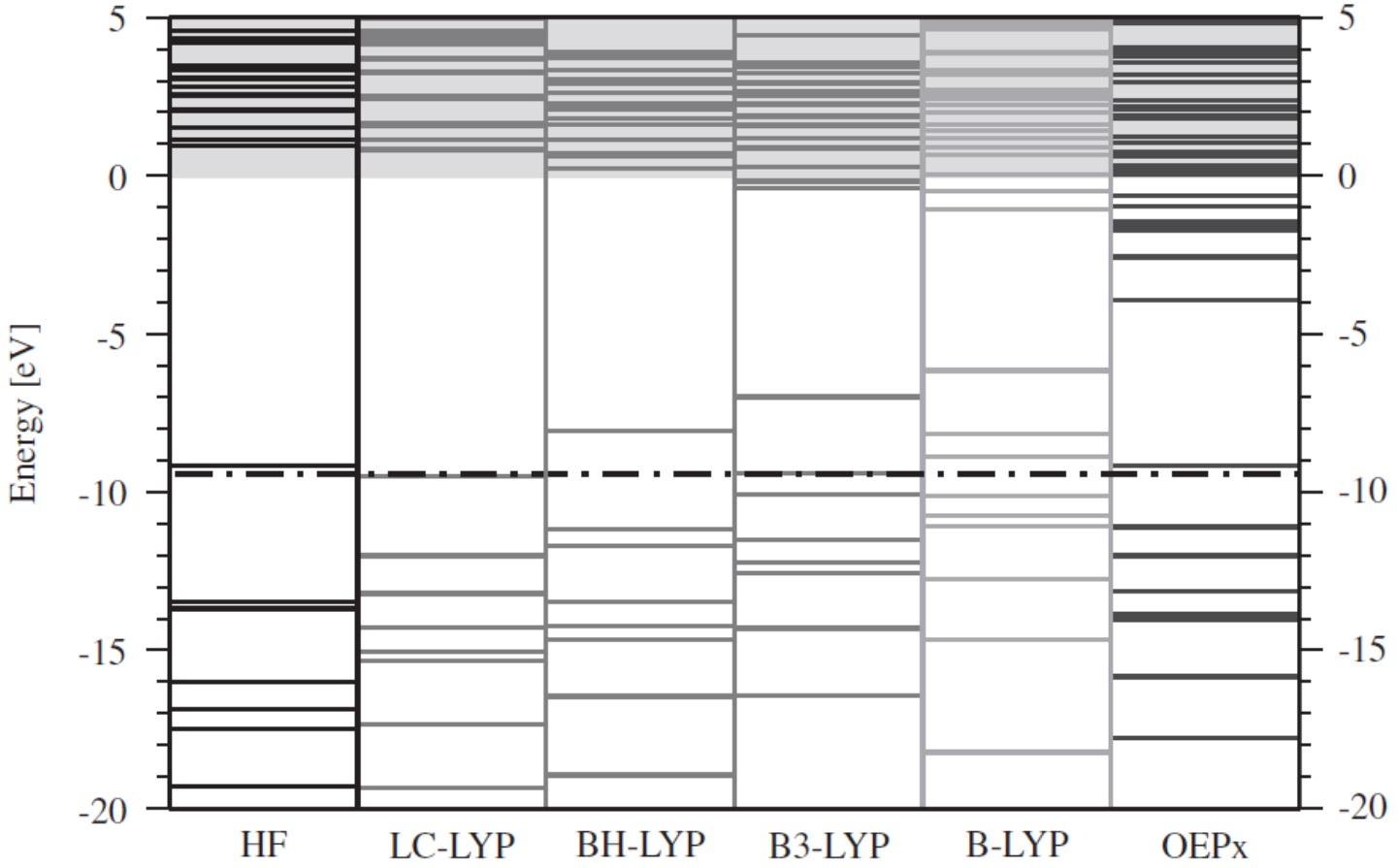


FIG. 1. Longitudinal polarizabilities of polyacetylene (in a.u.): The

Summary & Conclusions

OEP or Hybrid ?

Both OEP and hybrid methods include EXX in the total energy
However the eigenvalue spectrum is different



Hybrid (GKS) larger gap than OEPx

KS vs GKS energy gap

Many-Body Energy-Gap $E_{gap}^{MB} = \underbrace{\left(E[N+1]-E[N]\right)}_{-A} - \underbrace{\left(E[N]-E[N-1]\right)}_{-I} = I - A$

Affinity>0 (ion is more stable) Ionization>0

For an Exact Functional $E_{gap}^{deriv} = \left.\frac{\partial E}{\partial N}\right|_{N+\delta} - \left.\frac{\partial E}{\partial N}\right|_{N-\delta}$

LDA/GGA Janak 1978

$E_{gap}^{deriv} = \Delta\varepsilon^{KS} << E_{gap}^{MB}$

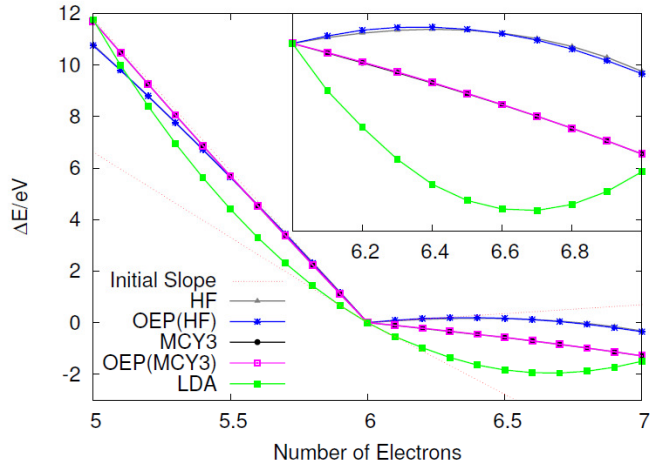
OEP Casida 1999

$$-I = \frac{\partial E}{\partial N_-} = \varepsilon_H^{KS} + \underbrace{\left\langle \phi_H \left| \Sigma_{xc}^{NL} - v_{xc} \right| \phi_H \right\rangle}_{0} = \varepsilon_H^{KS}$$

$$-A = \frac{\partial E}{\partial N_+} = \varepsilon_L^{KS} + \left\langle \phi_L \left| \Sigma_{xc}^{NL} - v_{xc} \right| \phi_L \right\rangle = \varepsilon_L^{KS} + \Delta_{xc}$$

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

GKS $E_{gap}^{deriv} = \Delta\varepsilon^{GKS}$



	LDA	HF	EXX	MCY3 GKS	MCY3 OEP	Exp
-homo	9.5	18.1	**15.9**	**15.2**	**14.6**	I=15.7
-lumo	6.1	-2.3	10.3	1.4	10.6	A=1.3
-lumo-Δxc			-2.3		1.4	
Gap	3.4	20.4	5.6	13.7	4.0	14.4

OEP: good gap for neutral excitation; GKS good MB gap

Functionals (non-local, non-linear)

$E_{xc}[\{\phi_i^{KS}\}]$ (Occupied) orbital-functional (EXX)

$E_{xc}[\rho]$ Explicit Density Functional

$$\rho(\mathbf{r}) = n_s \sum_a^{occ} |\phi_a(\mathbf{r})|^2$$

Meta-GGA

$$\tau(\mathbf{r}) = \frac{n_s}{2} \sum_a^{occ} |\nabla \phi_a(\mathbf{r})|^2$$

$$v_{ext}(\mathbf{r}) \Leftrightarrow v_{KS}(\mathbf{r}) \Leftrightarrow \{\phi_a(\mathbf{r})\}^{occ} \Leftrightarrow \varepsilon_x^{EXX}(\mathbf{r}) = -\frac{n_s}{2} \int \frac{|\gamma^{KS}(\mathbf{r},\mathbf{r}')|^2}{\rho(\mathbf{r})\|\mathbf{r}-\mathbf{r}'\|} d^3\mathbf{r}'$$

Hyper-GGA (local-hybrid)

$$\gamma^{KS}(\mathbf{r},\mathbf{r}')$$

others (unexplored)

$E_{xc}[v_{ext}]$ Potential Functional

$E_{xc}[\gamma^{KS}]$ KS Density Matrix Functional (EXX)

$$\{\phi_i(\mathbf{r})\}^{ALL}$$

$$\{\phi_i^{KS}(\mathbf{r})\}^{ALL}, \{\varepsilon_i^{KS}\}^{ALL} \leftrightarrow \chi_s(\mathbf{r},\mathbf{r}',\omega)$$

General orbital/eigenvalue functional (GLPT; double hybrid)

$E_{xc}[\chi^{KS}]$ KS Density Response Functional

References

OEP/EXX

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List of functionals (libxc)

http://www.tddft.org/programs/octopus/wiki/index.php/Libxc:manual

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