

Lecture on First-principles Computations (16): Hybrid Density Functionals

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Hefei, 2018.11.09

Kohn-Sham DFT

The Kohn-Sham energy functional

$$E_{\text{KS}}[\{\psi_l\}] = - \sum_l \langle \psi_l | \frac{\nabla^2}{2m} | \psi_l \rangle + E_{\text{ext}}[n] + E_H[n] + E_{xc}[n]$$

$$\left(-\frac{1}{2m} \nabla^2 + V_{\text{eff}}(\mathbf{r}) \right) \psi_l(\mathbf{r}) = \epsilon_l \psi_l(\mathbf{r})$$

$$V_{\text{eff}}(\mathbf{r}) = V_{\text{ext}}(\mathbf{r}) + V_H(\mathbf{r}) + \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})}$$

$E_{xc}[n]$: unknown exchange-correlation functional

The exchange-correlation (XC) hole

The XC energy functional

$$E_{xc}[n] = \int d^3 r n(\mathbf{r}) \epsilon_{xc}(\mathbf{r}, [n]) = \frac{1}{2} \int d^3 r n(\mathbf{r}) \int d^3 r' \frac{\bar{n}_{xc}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

The XC energy density

The averaged XC hole

$$\bar{n}_{xc}(\mathbf{r}, \mathbf{r}') = \int_0^1 d\lambda n_{xc}^\lambda(\mathbf{r}, \mathbf{r}')$$

The XC hole with the Coulomb interaction scaled by λ

LDA and GGAs

- Local spin density approximation (LSDA)

$$E_{xc}^{\text{LDA}}[n] = \int d^3 r n(\mathbf{r}) \epsilon_{xc}^{\text{HES}}(n_{\uparrow}(\mathbf{r}), n_{\downarrow}(\mathbf{r}))$$

$\epsilon_{xc}^{\text{HES}}(n_{\uparrow}, n_{\downarrow})$: Exchange-correlation energy per electron for **homogeneous electron gas (HEG)**

- Generalized gradient approximation (GGA)

$$E_{xc}^{\text{GGA}}[n_{\uparrow}, n_{\downarrow}] = \int d^3 r f(n_{\uparrow}(\mathbf{r}), n_{\downarrow}(\mathbf{r}), \nabla n_{\uparrow}(\mathbf{r}), \nabla n_{\downarrow}(\mathbf{r}))$$

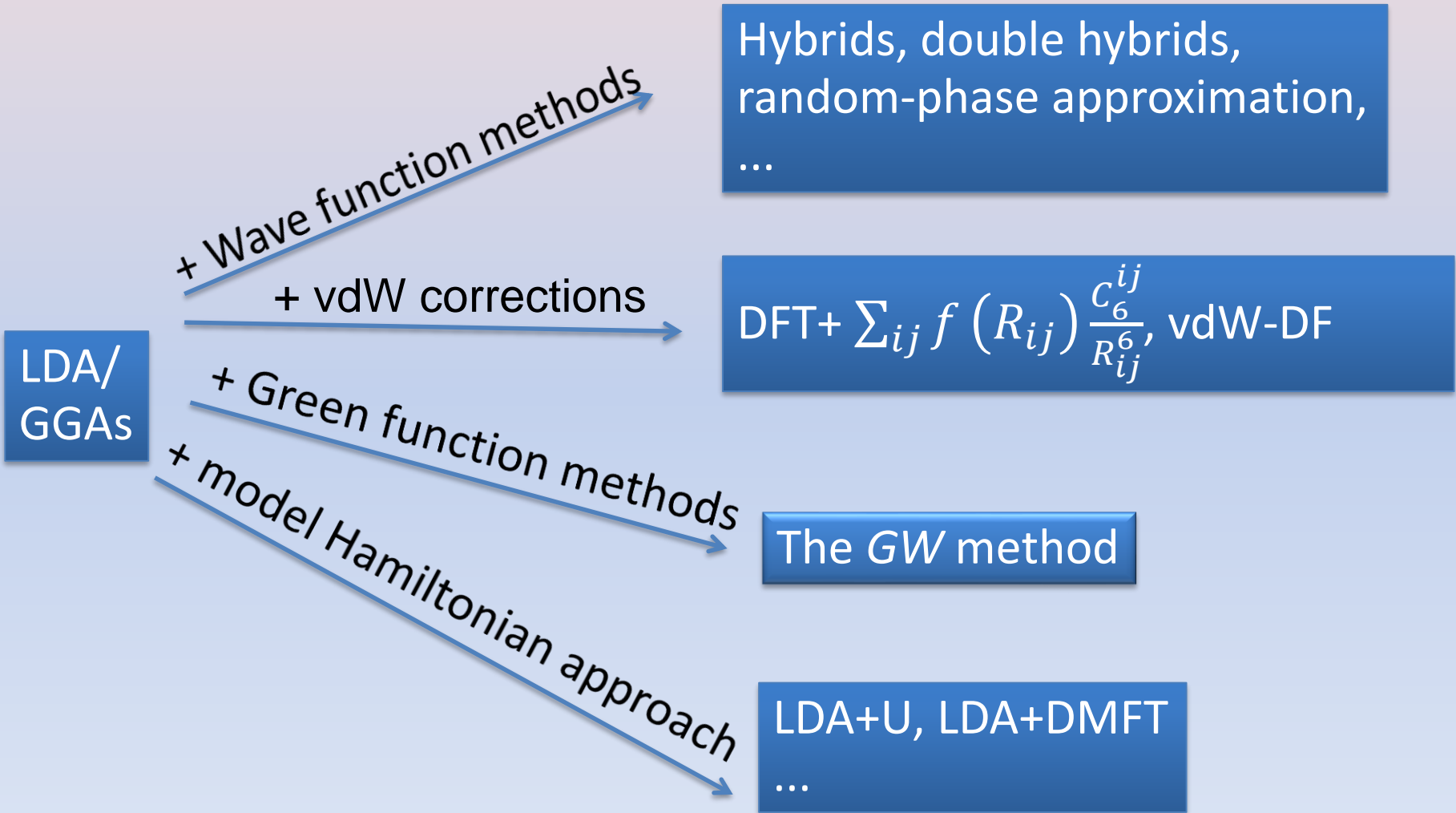
Deficiencies of LDA and GGAs

- Self-interaction error (delocalization error)
 - Too small band gaps
 - Underestimated reaction barrier heights
 - Unable to describe localized electronic states
 - Overestimated polarizability
 - The XC potential decays too fast
(no negative ions, no Rydberg states)

Cohen, Mori-Sánchez, and Yang, Science **321**, 792 (2008).

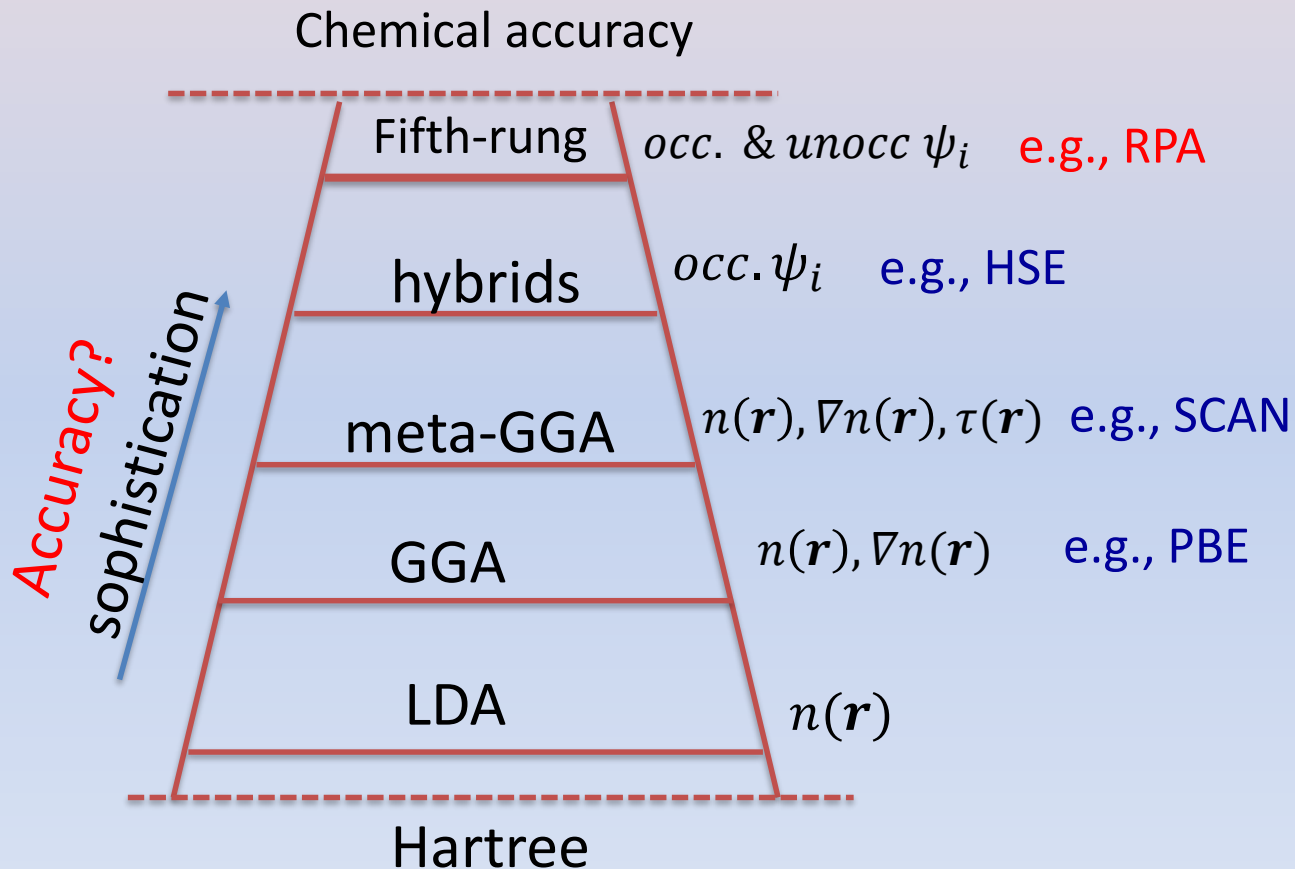
- Unable to describe “strong correlation”
(open-shell d and f electron systems)
- Absence of van der Waals interactions

Computational schemes beyond LDA and GGAs



Hybrid functionals

Jacob's ladder in DFT



J. Perdew & K. Schmidt, in Density functional theory and its application to materials, edited by Van Doren et al. (2001).

Underlying principle for hybrid functionals

The adiabatic connection

Design a path connecting the KS state and the full many-body state

$$\hat{H}_\lambda = \hat{T} + \lambda \hat{V}_{ee} + \hat{V}_{aux}^\lambda, \quad \hat{V}_{aux}^\lambda = \int d^3 r v_{aux}^\lambda(\mathbf{r}) \hat{n}(\mathbf{r}) \quad \text{and} \quad \hat{V}_{ee} = \sum_{i < j}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

$v_{aux}^\lambda(\mathbf{r})$ is chosen such that :

$$\hat{H}_{\lambda=0} = \hat{H}_{KS} = \hat{T} + \int d^3 r v_{eff}(\mathbf{r}) \hat{n}(\mathbf{r}) \quad (\text{the KS system})$$

$$\hat{H}_{\lambda=1} = \hat{H} = \hat{T} + \hat{V}_{ee} + \int d^3 r v_{ext}(\mathbf{r}) \hat{n}(\mathbf{r}) \quad (\text{the Interacting system})$$

The electron density is kept fixed at the physical $n(\mathbf{r})$ for $0 < \lambda < 1$.

The exact XC energy: $E_{xc}^{\text{exact}} = \int_0^1 d\lambda U_{xc}^\lambda$

$$U_{xc}^\lambda = \langle \Psi_0^\lambda | \hat{V}_{ee} | \Psi_0^\lambda \rangle - \frac{1}{2} \iint d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \quad \text{where} \quad \hat{H}_\lambda | \Psi_0^\lambda \rangle = E_\lambda^0 | \Psi_0^\lambda \rangle$$

Two limits in the adiabatic connection path

- $\lambda = 0, v_{aux}^{\lambda=0}(r) = v_{KS}(r), |\Psi_0^{\lambda=0}\rangle = |\Psi_{KS}\rangle$ (the KS system)

$$\begin{aligned} U_{xc}^{\lambda=0} &= \langle \Psi_{KS} | \hat{V}_{ee} | \Psi_{KS} \rangle - \frac{1}{2} \iint d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \\ &= -\frac{1}{2} \sum_{i,j}^{occ.} \iint d\mathbf{r} d\mathbf{r}' \frac{\psi_i^*(\mathbf{r})\psi_j(\mathbf{r})\psi_j^*(\mathbf{r}')\psi_i(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} := E_x^{\text{exact}} \end{aligned}$$

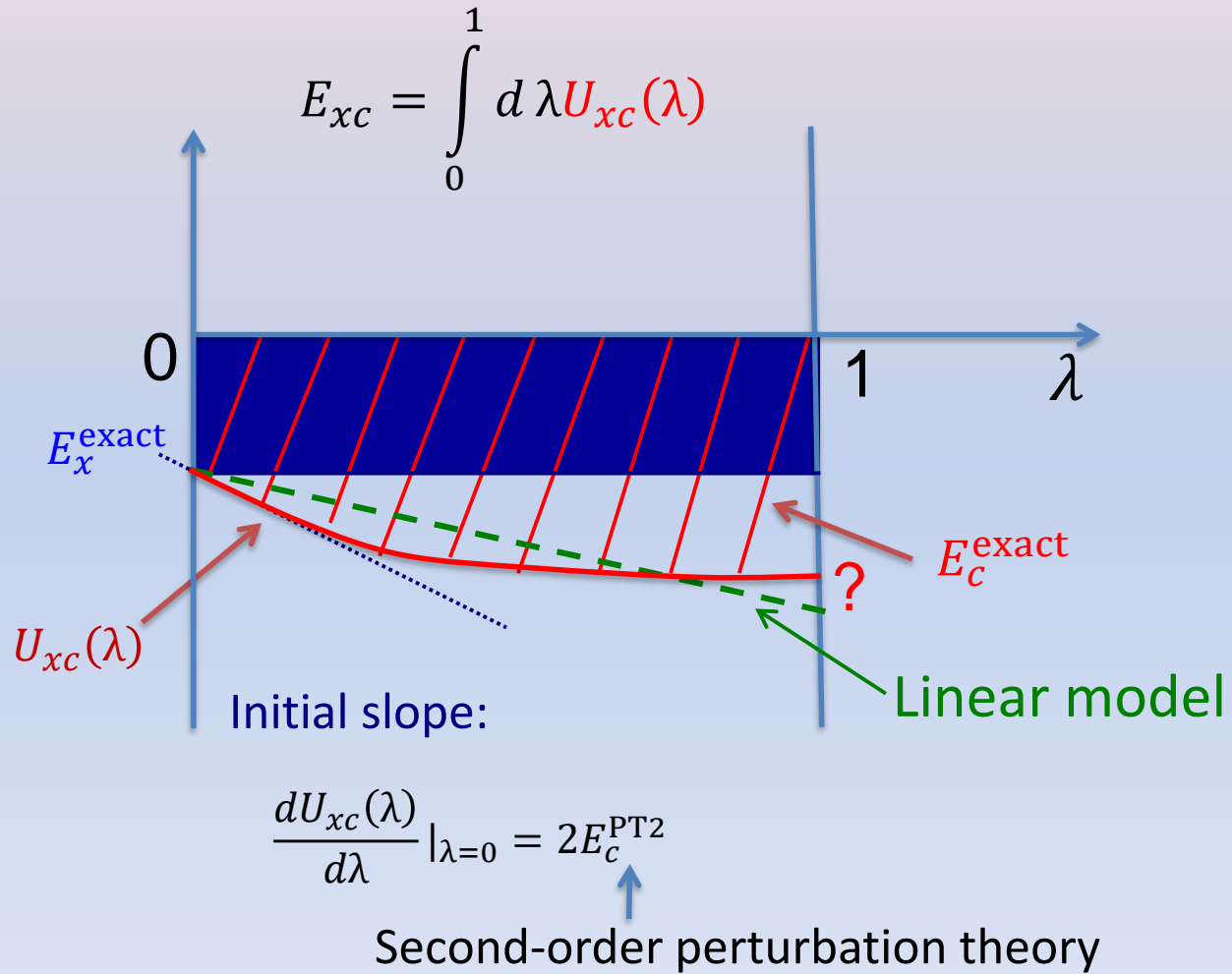
Exchange-only limit, where LDA/GGAs are least accurate => exact exchange is needed.

- $\lambda = 1, v_{aux}^{\lambda=1}(r) = v_{\text{ext}}(r), |\Psi_0^{\lambda=1}\rangle = |\Psi_0\rangle$ (fully interacting system)

$$U_{xc}^{\lambda=1} = \langle \Psi_0 | \hat{V}_{ee} | \Psi_0 \rangle - \frac{1}{2} \iint d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} = E_x^{\text{exact}} + U_c$$

LDA/GGAs work reasonably well. The correlation effect is crucial, and exact-exchange-only treatment will not work.

Adiabatic connection path



The milestone: Becke's half-and-half theory

A. D. Becke, *JCP* **98**, 1372 (1993)

$$E_{xc} = \int_0^1 d\lambda U_{xc}^\lambda \approx 1/2 (U_{xc}^{\lambda=0} + U_{xc}^{\lambda=1})$$

$$U_{xc}^{\lambda=0} = E_x^{\text{exact}}, \quad U_{xc}^{\lambda=1} \approx U_{xc}^{\text{LSDA}}$$

Becke's half-and-half (HH) theory : 

$$E_{xc}^{\text{HH}} = 1/2 (E_x^{\text{exact}} + U_{xc}^{\text{LSDA}})$$

$$U_{xc}^{\text{LSDA}} = \int U_{xc}[n_\uparrow(\mathbf{r}), n_\downarrow(\mathbf{r})] d\mathbf{r}$$

Performance of the half-half method

TABLE I. Atomic exchange-correlation energies (a.u.).

	Exact ^a	LSDA ^b	HH ^c
H	-0.313	-0.290	-0.308
He	-1.068	-0.997	-1.045
Li	-1.827	-1.689	-1.782
Be	-2.761	-2.537	-2.671
B	-3.869	-3.563	-3.744
C	-5.202	-4.819	-5.045
N	-6.785	-6.323	-6.596
O	-8.432	-7.881	-8.201
F	-10.32	-9.70	-10.06
Ne	-12.50	-11.78	-12.19
Na	-14.42	-13.60	-14.07
Mg	-16.43	-15.50	-16.04
Al	-18.55	-17.50	-18.11
Si	-20.80	-19.63	-20.30
P	-23.19	-21.91	-22.65
S	-25.63	-24.23	-25.02
Cl	-28.22	-26.68	-27.54
Ar	-30.98	-29.29	-30.23

A. D. Becke, JCP 98, 1372 (1993)

The atomization energies obtained with the half-and-half method

TABLE II. Atomization energies D_0 (kcal/mol). Expt.: from Refs. 9 and 15. E_X^{exact} : exact exchange only. $E_X^{\text{exact}} + E_C^{\text{SPP}}$: exact exchange plus SPP correlation (Ref. 27). $E_{\text{XC}}^{\text{HH}}$: half-and-half theory, Eq. (12). $E_{\text{XC}}^{\text{SE}}$: Equation (14) with semiempirical parameters 0.332 and 0.575. Δ : average absolute deviation from experiment.

	Expt.	E_X^{exact}	$E_X^{\text{exact}} + E_C^{\text{SPP}}$	$E_{\text{XC}}^{\text{HH}}$	$E_{\text{XC}}^{\text{SE}}$
H ₂	103.5	78.4	108.7	101.8	102.7
LiH	56.0	32.2	57.6	53.1	53.1
BeH	46.9	46.1	55.2	55.9	51.8
CH	79.9	51.4	76.1	78.1	79.9
CH ₂ (³ B ₁)	179.6	143.1	176.9	185.0	180.7
CH ₂ (¹ A ₁)	170.6	115.4	162.3	167.7	169.5
CH ₃	289.2	224.8	284.9	294.1	290.5
CH ₄	392.5	300.9	383.2	396.6	392.8
NH	79.0	44.3	72.0	76.8	80.5
NH ₂	170.0	103.6	156.6	167.9	173.2
ClO	63.3	-10.6	8.0	54.5	65.9
ClF	60.3	2.0	14.5	53.7	61.7
Si ₂ H ₆	500.1	379.4	505.2	506.1	500.4
CH ₃ Cl	371.0	272.3	345.1	374.9	373.0
CH ₃ SH	445.1	320.1	416.2	448.2	447.8
HOCl	156.3	66.5	104.4	149.3	158.3
SO ₂	254.0	90.2	137.5	231.5	248.4
Δ		77.7	32.3	6.5	2.6

56 test molecules from the Pople G1 data base

Further development: the B3LYP functional

A. D. Becke, J. Chem. Phys. 98, 5648 (1993)

The original form:

Perdew-Wang 1991 GGA correlation correction

$$E_{xc}^{B3PW91} = E_{xc}^{LSDA} + a_0(E_x^{\text{exact}} - E_x^{LSDA}) + a_x \Delta E_x^{B88} + a_c \Delta E_c^{PW91}$$

Becke 1988 GGA exchange correction

$$\Delta E_x^{B88} = E_x^{B88} - E_x^{LSDA}, \quad \Delta E_c^{PW91} = E_c^{PW91} - E_c^{LSDA}$$

Empirical parameters: $a_0 = 0.20, a_x = 0.72, a_c = 0.81$

Later, implemented in **GAUSSIAN**:

$$E_{xc}^{B3LYP} = E_{xc}^{LSDA} + a_0(E_x^{\text{exact}} - E_x^{LSDA}) + a_x \Delta E_x^{B88} + a_c \Delta E_c^{LYP}$$

Lee-Yang-Parr 1991 GGA correlation correction

Simplification to one parameter

The B3LYP functional:

$$E_{xc}^{\text{B3LYP}} = E_{xc}^{\text{LSDA}} + a_0(E_x^{\text{exact}} - E_x^{\text{LSDA}}) + a_x \Delta E_x^{\text{B88}} + a_c \Delta E_c^{\text{LYP}}$$

Choosing parameters: $a_x = 1 - a_0$, $a_c = 1$

B1LYP:

$$E_{xc}^{\text{B1LYP}} = E_{xc}^{\text{BLYP}} + a_0(E_x^{\text{exact}} - E_x^{\text{B88}})$$



$$(\text{= } E_x^{\text{B88}} + E_c^{\text{LYP}})$$

In general, one-parameter hybrid functional :

$$E_{xc}^{\text{hyd}} = E_{xc}^{\text{GGA}} + a_0(E_x^{\text{exact}} - E_x^{\text{GGA}})$$


$a_0 \sim 0.25$ performs best for atomization energies!

Rationale for the best mixing parameter

Perdew, Ernzerhof, Burke, *J. Chem. Phys.* **105**, 9982 (1996)

$$E_{xc,\lambda}^{\text{hyd}}(n) = E_{xc,\lambda}^{\text{DFA}} + (E_x^{\text{exact}} - E_x^{\text{DFA}})(1 - \lambda)^{n-1}$$

$$E_{xc}^{\text{hyd}}(n) = \int_0^1 E_{xc,\lambda}^{\text{DFA}}(n) + \frac{1}{n} (E_x^{\text{exact}} - E_x^{\text{DFA}})$$


 E_{xc}^{DFA}

$n=4 \iff$ The 4th-order Møller-Plesset perturbation theory

The PBE0 functional :

$$E_{xc}^{\text{PBE0}} = E_{xc}^{\text{PBE}} + 0.25(E_x^{\text{exact}} - E_x^{\text{PBE}})$$

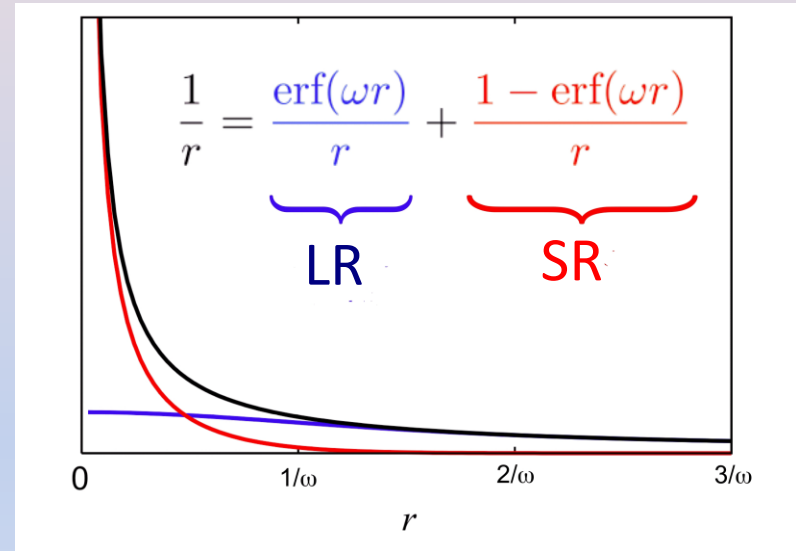
$a_0 = 0.25$ is good for atomization energies!

Application to solids: the HSE functional

Heyd, Scuseria, Ernzerhof, *J. Chem. Phys.* **118**, 8207 (2003)

$$\frac{1}{r} = \underbrace{\frac{\text{erfc}(\omega r)}{r}}_{\text{Short-range (SR)}} + \underbrace{\frac{\text{erf}(\omega r)}{r}}_{\text{Long-range (LR)}}$$

Short-range(SR) Long-range (LR)



$$E_x^{\text{exact,SR}} = - \sum_{l,m}^{\text{occ}} \int d^3 r d^3 r' \frac{\psi_l^*(\mathbf{r}) \psi_m(\mathbf{r}) \text{erfc}(\omega |\mathbf{r} - \mathbf{r}'|) \psi_m^*(\mathbf{r}') \psi_l(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

$$E_{xc}^{\text{PBE0}} = E_{xc}^{\text{PBE}} + 0.25(E_x^{\text{exact}} - E_x^{\text{PBE}}) \Rightarrow$$

$$E_{xc}^{\text{HSE}} = E_{xc}^{\text{PBE}} + 0.25(E_x^{\text{exact,SR}} - E_x^{\text{PBE,SR}})$$

Performance of the hybrid functionals

TABLE III. Summary of results for enthalpies of formation. All errors in kcal/mol.^a

Method	G2-1 set ^b			
	MAE ^d	RMS ^e	Max.(-) ^f	Max.(+) ^g
B3LYP	2.46	3.28	-8.2	9.9
PBE	8.19	10.40	-29.1	10.1
PBE0	3.01	3.76	-6.1	10.6
ω PBEh	2.93	3.78	-7.2	10.7

Method	G2-1andG2-2set ^c			
	MAE	RMS	Max.(-)	Max.(+)
B3LYP	3.04	4.40	-8.2	20.0
PBE	17.19	21.00	-50.8	10.1
PBE0	5.15	6.78	-20.8	21.7
ω PBEh	4.16	5.68	-17.4	20.5

HSE →

Heyd, Scuseria, Ernzerhof, *J. Chem. Phys.* **118**, 8207 (2003)

Lattice constants

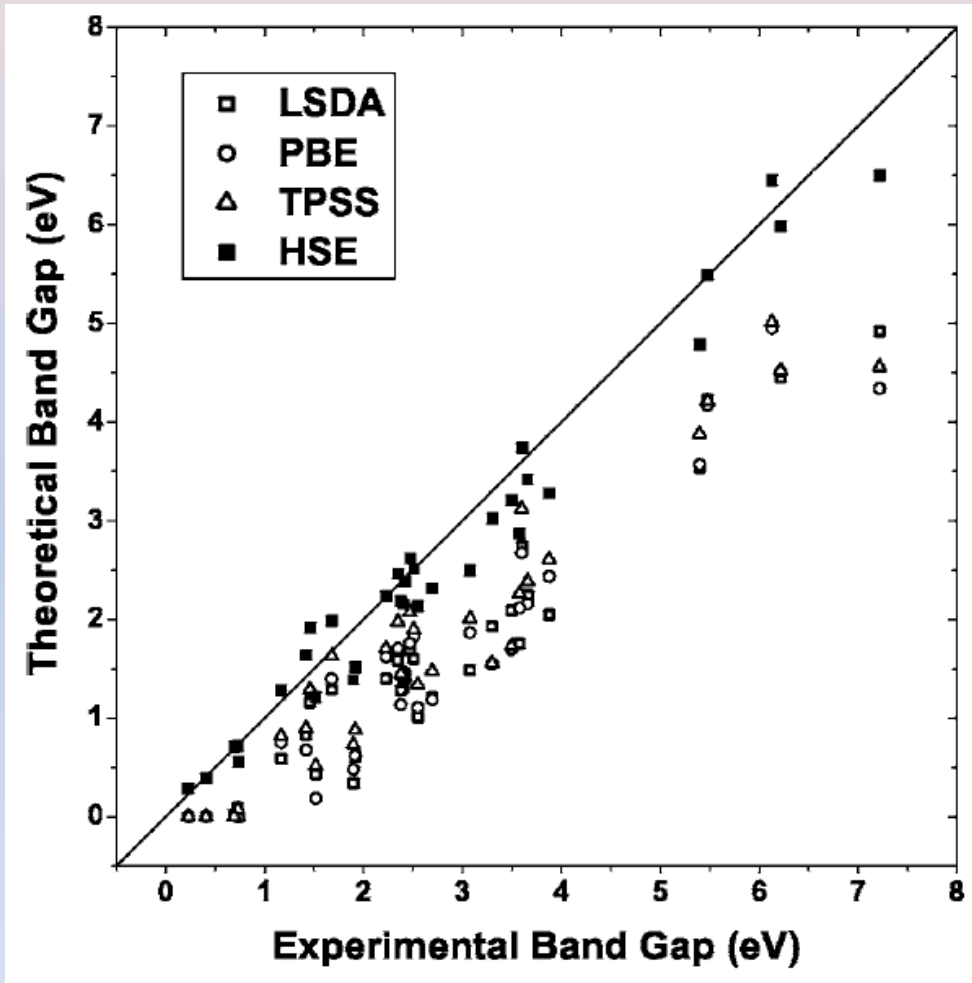
40 Semiconductors

TABLE VI. Lattice constant error statistics for the SC/40 test set (Å).

Solid	LSDA	PBE	TPSS	HSE
ME ^a	-0.046	0.076	0.063	0.035
MAE ^b	0.047	0.076	0.063	0.037
rms ^c	0.058	0.084	0.071	0.044
Max (+) ^d	0.017	0.158	0.143	0.100
Max (-) ^e	0.139	-0.014

Heyd, Peralta, Scuseria, and Martin, *J. Chem. Phys.* **123**, 174101 (2005)

Band gaps



Heyd, Peralta, Scuseria, and Martin, *J. Chem. Phys.* **123**, 174101 (2005)

Recent developments

- Local hybrids

$$E_{xc} = \int d^3 r [\alpha(\mathbf{r})\epsilon_x^{\text{exact}}(\mathbf{r}) + (1 - \alpha(\mathbf{r}))\epsilon_x^{\text{GGA}}(\mathbf{r})] + E_c^{\text{GGA}}$$

- Double hybrids

$$E_{xc} = \alpha E_x^{\text{exact}} + (1 - \alpha) E_x^{\text{GGA}} + \beta E_c^{\text{PT2}} + (1 - \beta) E_c^{\text{GGA}}$$



Second-order (non-local) correlation energy