



**Short Course on Density Functional Theory
and Applications**
V. Orbital-dependent XC Functionals

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Meta-Generalized Gradient Approximations

Meta-Generalized Gradient XC approximations incorporate gradient corrections but do not use the SGA coefficients, and furthermore use either the KS KE density or the Laplacian of the density. A relatively recent example is TPSS [J. Tao, J.P. Perdew, V.N. Staroverov, and G.E. Scuseria, Phys. Rev. Lett. 91, 146401 (2003)]; an earlier one which was surprisingly unsuccessful is PKZB [J.P. Perdew, S. Kurth, A. Zupan, and P. Blaha, Phys. Rev. Lett. 82, 2544 (1999)]. A summary of TPSS follows.

- **Define the usual GGA inhomogeneity functions**

$$s(\mathbf{r}) := \frac{|\nabla n|}{2(3\pi^2)^{1/3} n^{4/3}}; \quad t(\mathbf{r}) := \left(\frac{\pi}{4}\right)^{1/2} \frac{|\nabla n|}{2(3\pi^2)^{1/6} n^{7/6}}$$

and define the KS KE density and local von Weizsäcker KE density as

$$\tau_{\sigma}(\mathbf{r}) := \frac{1}{2} \sum_i^{occ} n_{i\sigma} |\nabla \phi_{i\sigma}|^2; \quad \tau_{\sigma}^W(\mathbf{r}) := \frac{|\nabla n_{\sigma}|^2}{8n_{\sigma}}$$

and construct an MGGA X enhancement factor that builds on PBE and a C functional that modifies PKZB. Note that PKZB C uses an enhancement factor with respect to PBE C.

Meta-Generalized Gradient Approximations –TPSS summary (cont'd.)

The X functional in TPSS has the form

$$E_x^{MGGA}[n] = \int d\mathbf{r} n(\mathbf{r}) u_x^{HEG}[n] F_x^{MGGA}[n, s, \tau]$$

$$F_x^{MGGA}[n, s, \tau] = 1 + \kappa - \frac{\kappa}{1 + x[n, s, \tau] / \kappa}$$

$$E_x[n_\uparrow, n_\downarrow] = \frac{1}{2} E_x[2n_\uparrow] + \frac{1}{2} E_x[2n_\downarrow]$$

- Note that the last line of the foregoing equation is the exact spin-scaling relation between non-spin-polarized and spin-polarized X functionals. This does not hold for C functionals.

The functional $x[n, s, \tau]$ is complicated and not worth tabulating here; See eq. (22) of Perdew et al. [J. Chem. Phys. 120, 6898 (2004)]. The TPSS correlation functional is

$$E_c^{MGGA}[n_\uparrow, n_\downarrow] = \int d\mathbf{r} n(\mathbf{r}) u_c^{revPKZB}[n_\uparrow, n_\downarrow, s, \tau] \left\{ 1 + d_c u_c^{revPKZB}[n_\uparrow, n_\downarrow, s, \tau] (\tau^W / \tau)^3 \right\}$$

but the revPKZB correlation energy density functional $u_c^{revPKZB}$ is another messy multi-line equation; see eqns (25) – (27) of the foregoing reference.

What is worth displaying is the list of constraints satisfied by TPSS; next slide.

Meta-Generalized Gradient Approximations –TPSS summary (cont'd.)

Comparison of constraints satisfied by functionals

TABLE I. Satisfaction (Yes/No) of selected exact constraints by approximate exchange–correlation functionals.

Constraint	LSDA	PBE	PKZB	TPSS
Global properties				
$E_x < 0$	Y	Y	Y	Y
$E_c \leq 0$	Y	Y	N	Y
$E_c = 0$ if $\int n(\mathbf{r}) d^3r = 1$	N	N	Y	Y
$E_{xc} \geq -D \int n^{4/3}(\mathbf{r}) d^3r^a$	Y	Y	YN ^b	Y
$E_{xc} = E_{xc}^{\text{LSDA}}$, $n_\uparrow, n_\downarrow = \text{const}$	Y	Y	Y	Y
$E_x = -U[n]$ if $\int n(\mathbf{r}) d^3r = 1^c$	N	N	N	YN ^d
Highest order in ∇ for E_x^{GEA} ^e	0	0	2 ^f	4
Highest order in ∇ for E_c^{GEA} ^e	0	2	2	2
Spin and density scaling ^g				
$E_x[n_\uparrow, n_\downarrow] = \frac{1}{2} \sum_{\sigma=\uparrow, \downarrow} E_x[2n_\sigma]^h$	Y	Y	Y	Y
$E_x[n_\lambda] = \lambda E_x[n]^i$	Y	Y	Y	Y
$E_c[n_\lambda] > \lambda E_c[n]$, $\lambda > 1^i$	Y	Y	Y	Y
$\lim_{\lambda \rightarrow \infty} E_c[n_\lambda] > -\infty^j$	N	Y	Y	Y
$\lim_{\lambda \rightarrow 0} \lambda^{-1} E_c[n_\lambda] > -\infty^j$	Y	Y	Y	Y
$\lim_{\lambda \rightarrow \infty} E_x[n_\lambda^x] > -\infty^j$	N	N	N	N
$\lim_{\lambda \rightarrow 0} E_x[n_\lambda^x] > -\infty^j$	Y	Y	Y	Y
$\lim_{\lambda \rightarrow \infty} E_c[n_\lambda^x] > -\infty^j$	N	Y	Y	Y
Asymptotic behavior				
$v_x(\mathbf{r}) \rightarrow -1/r$, $r \rightarrow \infty$	N	N	N	N
$v_x(\mathbf{r})$ finite at the nucleus	Y	N	N	YN ^k
$v_c(\mathbf{r})$ finite at the nucleus	Y	N	YN ^l	YN ^l

^aThe Lieb–Oxford bound (Refs. 17, 35). $1.44 < D < 1.68$ (or < 1.6358 —Ref. 36).

^bY for exchange, N for exchange–correlation.

^cCancellation of spurious electrostatic self-interaction energy in one-electron systems: $U[n] = \frac{1}{2} \int d^3r \int d^3r' n(\mathbf{r})n(\mathbf{r}')/|\mathbf{r}-\mathbf{r}'| d^3r'$.

^dY for a one-electron exponential density.

^eThe highest correct order in the gradient expansion approximation (GEA) for slowly-varying densities. The true GEA is known to fourth order in ∇ for exchange (Ref. 37) and to second order for correlation (Ref. 38).

^fTwo of the three fourth-order terms are also reproduced (Ref. 19).

^gUniform scaling of the density: $n_\lambda(\mathbf{r}) = \lambda^3 n(\lambda \mathbf{r})$; non-uniform scaling: $n_\lambda^x(x, y, z) = \lambda n(\lambda x, y, z)$. See Ref. 39 for a review.

^hDerived in Ref. 31.

ⁱDerived in Ref. 40.

^jDerived in Ref. 41.

^kY for one- and spin-compensated two-electron densities.

^lY for one-electron densities.

V.N. Staroverov, G.E. Scuseria, J. Tao, and J.P. Perdew,
Phys. Rev. B **69**, 075102 (2004)

MGGAs - TPSS Validation Study

Statistical summary of the errors of different functionals for various properties of molecules, solids, and surfaces [J. Tao, J.P. Perdew, V.N. Staroverov, and G.E. Scuseria, Phys Rev Lett. 91, 146401 (2003)]

PBE0 – “hybrid” of PBE X and single-determinant X (not yet discussed)

Property (units)	Test set	Mean value of property	Mean absolute errors					Mean error of TPSS
			LSD	PBE	PBE0	FKZB	TPSS	
Atomization energy ΣD_0 (kcal/mol)	G2 (148 mols.)	478	83.8	17.1	5.1	4.4	6.2	5.4
Ionization potential (eV)	G2 (86 species)	10.9	0.22	0.22	0.20	0.29	0.23	-0.11
Electron affinity (eV)	G2 (58 species)	1.4	0.26	0.12	0.17	0.14	0.14	-0.01
Bond length r_e (Å)	96 molecules	1.56	0.013	0.016	0.010	0.027	0.014	0.014
Harmonic frequency ω_e (cm ⁻¹)	82 diatomics	1430	48.9	42.0	43.5	51.7	30.4	-18.7
H-bond dissoc. energy D_0 (kcal/mol)	10 complexes	13.4	5.8	1.0	0.7	2.9	0.6	0.2
H-bond lengths r_e (Å)	11 H-bonds	2.06	0.147	0.043	0.032	0.179	0.021	0.021
H-bond angles (deg)	13 angles	111	4.0	2.6	1.8	3.5	2.0	2.0
Lattice constant (Å)	18 solids	4.47	0.069	0.057	...	0.078	0.040	0.039
Bulk modulus (GPa)	18 solids	116	15.1	7.6	...	7.8	8.2	-0.5
XC surface energy (erg/cm ²)	$r_s = 2, 4, 6$	1245	22	55	39	5	13	-10

Credit: N. Rösch



MGGAs - TPSS & Lattice Parameters of Solids

TABLE III. Equilibrium lattice constants (\AA) of the 18 test solids at 0 K calculated from the SJEOS of Eq. (16). The Murnaghan EOS of Eq. (15) yields identical results within the reported number of decimal places. Experimental a_0 values are from Ref. 68 (Li) and Ref. 69 (Na, K, Al, NaCl, NaF, LiCl, LiF, MgO). The rest are based on room temperature values corrected to the $T=0$ limit using linear thermal expansion coefficients from Ref. 70. The numbers in parentheses refer to experimental values with an estimate of the zero-point anharmonic expansion subtracted out. (The calculated values are precise to within 0.001 \AA for the given basis sets, although basis-set incompleteness limits the accuracy to one less digit.)

Solid	a_0^{LSDA}	a_0^{PBE}	a_0^{PKZB}	a_0^{TPSS}	Expt.
Li	3.383	3.453	3.512	3.475	3.477(3.451)
Na	4.049	4.199	4.305	4.233	4.225(4.210)
K	5.093	5.308	5.494	5.362	5.225(5.212)
Al	4.008	4.063	4.040	4.035	4.032(4.020)
C	3.544	3.583	3.592	3.583	3.567(3.556)
Si	5.426	5.490	5.475	5.477	5.430(5.423)
SiC	4.351	4.401	4.404	4.392	4.358(4.349)
Ge	5.633	5.765	5.729	5.731	5.652(5.646)
GaAs	5.592	5.726	5.698	5.702	5.648(5.643)
NaCl	5.471	5.698	5.801	5.696	5.595(5.580)
NaF	4.505	4.700	4.764	4.706	4.609(4.594)
LiCl	4.968	5.148	5.220	5.113	5.106(5.090)
LiF	3.904	4.062	4.109	4.026	4.010(3.987)
MgO	4.156	4.242	4.265	4.224	4.207(4.197)
Cu	3.530	3.636	3.616	3.593	3.603(3.596)
Rh	3.791	3.871	3.844	3.846	3.798(3.793)
Pd	3.851	3.950	3.928	3.917	3.881(3.877)
Ag	3.997	4.130	4.101	4.076	4.069(4.064)
m.e.	-0.069	0.052	0.078	0.039	...
(\AA)	(-0.058)	(0.063)	(0.089)	(0.050)	...
m.a.e.	0.069	0.057	0.078	0.040	...
(\AA)	(0.058)	(0.064)	(0.089)	(0.050)	...
m.a.r.e.	1.55	1.25	1.65	0.83	...
(%)	(1.31)	(1.40)	(1.92)	(1.07)	...

- TPSS is better than PKZB and gives some improvement relative to PBE.
- The relative success of LSDA illustrates why it is still so popular in condensed matter and materials calculations.

V.N. Staroverov, G.E. Scuseria, J. Tao, and J.P. Perdew, *Phys. Rev. B* **69**, 075102 (2004)

MGGAs – Parameterized vs. Non-empirical

- A great deal of clever work has been done, mostly in the Chemistry community, to parameterize functionals against “training sets” of thermochemical data. How do such functionals compare to “constraint-based (or “non-empirical”) functionals. Here’s a fragment of a table from Y. Zhao and D.G. Truhlar, comparing their parameterized MGGAs M06-L with TPSS [J. Chem. Phys. 125, 194101 (2006)] and two other parameterized MGGAs

TABLE III. Mean errors^a [kcal/mol for ionization potentials (IPs), electron affinities (EAs), proton affinities (PAs), and kcal/mol per bond for atomization energies (AEs)].

Method	AE109		IP13		EA13		PA8		TMUE ^c
	MSEPB	MUEPB ^a	MSE ^b	MUE	MSE ^b	MUE	MSE ^b	MUE	
				Local					
VSXC	-0.18	0.57	2.31	3.29	0.22	2.80	1.83	1.98	1.10
OLYP	-0.05	0.86	-1.50	2.66	3.23	3.57	2.30	2.30	1.35
M06-L	0.05	0.85	0.76	3.09	2.96	3.84	2.01	2.06	1.39
TPSS	0.63	1.03	1.80	3.11	0.51	2.31	2.67	2.67	1.43

^aMUEPB denotes mean unsigned error (MUE) per bond.

^bMSE denotes mean signed error.

^cTMUE denotes total MUE and it is defined as $TMUE = [MUEPB \times 109 + MUE(IP) \times 13 + MUE(AE) \times 13 + MUE(PA) \times 8] / 143$

^dIn all tables where the last row is “Average,” it is the average of that column for all functionals in the table.

VSXC: T. Van Voorhis and G. E. Scuseria, J. Chem. Phys. 109, 400 (1998) mgga

OLYP: N.C. Handy and A.J. Cohen, Mol. Phys. 99, 403 (2001) mgga

- **But, M06-L has 37 empirical parameters; TPSS has none.** We will come back to the motive and merit of M06-L.



MGGAs - Remarks

- The ratio τ^W/τ which appears in TPSS is a so-called “iso-orbital indicator”. Recall (Lect. II-27) that the von Weizsäcker KE T_w is the exact KE for one-electron and for two-electron singlets. This is the physical basis for the proof (omitted) that $\tau^W/\tau \rightarrow 1$ in any spatial region associated with a single orbital.
- In TPSS τ^W/τ is used to assure that one-electron self-correlation (part of the spurious self-interaction) is removed:

$$E_c[n_{j\alpha}, 0] = E_c[0, n_{j\beta}] = 0$$

$$n_{j\sigma} := |\varphi_{j\sigma}|^2$$

- Notice that MGGAs are explicitly orbital-dependent functionals. Nevertheless, the KS potential for an MGGA is local, $v_{xc}(\mathbf{r})$.

Self-interaction-Corrected Functionals

Recall (Lect.II-8) that the exact exchange energy in DFT is defined with respect to the KS determinant, NOT the Hartree-Fock determinant:

$$\begin{aligned} E_x[n] &= \langle \Phi_{min;n} | \hat{\mathcal{V}}_{ee} | \Phi_{min;n} \rangle - \frac{1}{2} \int d\mathbf{r}_1 d\mathbf{r}_2 g(\mathbf{r}_1, \mathbf{r}_2) n(\mathbf{r}_1) n(\mathbf{r}_2) \\ &= -\frac{1}{2} \sum_{\sigma} \int d\mathbf{r}_1 d\mathbf{r}_2 g(\mathbf{r}_1, \mathbf{r}_2) \gamma_{KS;n}(x_1 | x_2) \gamma_{KS;n}(x_2 | x_1) \end{aligned}$$

- Exact exchange (“ExX” in the jargon) has the desirable property of cancelling spurious self-interaction correctly.
- But compared to the X functionals we have been examining, this has an unpleasant explicit dependence on the KS orbitals. We will come back to that.
- But first, is there a simpler way out of the self-interaction problem?

Self-interaction-Corrected Functionals (cont'd)

Consider some specific XC model (e.g. LSDA, GGA) and the partial density associated with a single KS orbital, α -spin for convenience.

Self-interaction cancellation should go as

$$n_{j\alpha}(\mathbf{r}) := |\varphi_{j\alpha}(\mathbf{r})|^2$$

$$E_{ee}[n_{j\alpha}] + E_{xc}[n_{j\alpha}, 0] = 0$$

So define the self-interaction corrected functional as

[J.P. Perdew and A. Zunger, Phys. Rev. B 23, 5048 (1981)]

$$E_{xc}^{SIC,approx}[n_\alpha, n_\beta] := E_{xc}^{approx}[n_\alpha, n_\beta] - \sum_{j,\sigma}^{occ} \Delta_{j\sigma}$$

$$\Delta_{j\alpha} := E_{ee}[n_{j\alpha}] + E_{xc}^{approx}[n_{j\alpha}, 0]$$

$$\Delta_{j\beta} := E_{ee}[n_{j\beta}] + E_{xc}^{approx}[0, n_{j\beta}]$$

Remarks

- This scheme also can be defined for fractionally occupied orbitals (omitted here for simplicity).
- There is a major problem with this approach (next slide).

Self-interaction-Corrected Functionals (cont'd)

- The SIC scheme is not invariant under unitary transformation of the occupied KS orbitals. But the KS expressions themselves are invariant. The problem is in singling out the individual orbital partial densities in nonlinear expressions. Suppose a unitary transformation U . Compare what happens with the KS KE density τ that appears in TPSS and the SIC correction $\Delta_{j\alpha}$

$$U^\dagger U = \mathbf{1}$$

$$\begin{aligned}\tau_\sigma[U\varphi](\mathbf{r}) &= \frac{1}{2} \sum_j \left\{ \left| \nabla \sum_s^{occ} U_{sj}^* \varphi_{s\sigma} \right| \left| \nabla \sum_t^{occ} U_{jt} \varphi_{t\sigma} \right| \right\} \\ &= \frac{1}{2} \sum_{s,t}^{occ} \sum_j^{occ} U_{sj}^* U_{jt} |\nabla \varphi_{s\sigma}| |\nabla \varphi_{t\sigma}| = \frac{1}{2} \sum_t |\nabla \varphi_{t\sigma}|^2 = \tau_\sigma[\varphi](\mathbf{r})\end{aligned}$$

$$n_{j\alpha}[U\varphi](\mathbf{r}) = \left| \sum_s^{occ} U_{sj}^* \varphi_{s\alpha} \right| \left| \sum_t^{occ} U_{jt} \varphi_{t\alpha} \right| \neq |\varphi_{j\alpha}(\mathbf{r})|^2$$

$$\Rightarrow \Delta_{j\alpha}[U\varphi] \neq \Delta_{j\alpha}[\varphi]$$

Implication: The size of SIC contributions is basis-set dependent. The practical computational consequences have been (a) to work in a highly localized (by some criterion) basis, and (b) to use SIC relatively little.

Self-interaction-Corrected Functionals (cont'd)

A central field atom has an intrinsically localized basis, so testing SIC on such atoms is an obvious choice. Here is an expanded version of the table (Lect. IV-3) of atomic I values calculated from HOMO energies and total energy differences (all in eV) [adapted from SBT, Phys. Rev. Lett. **56**, 881 (1986); HF values from C. Froese Fischer, *The Hartree-Fock method for Atoms*, SIC values from Perdew and Zunger, Phys. Rev. B **23**, 5048 (1981)]

Atom	$-\epsilon_{HOMO}^{LSDA}$	ΔE^{LSDA}	$-\epsilon_{HOMO}^{LSDA-SIC}$	$-\epsilon_{HOMO}^{HF}$	Expt.
H	7.6	13.3	13.6	13.6	13.595
He	15.6	24.2	25.8	25.0	24.6
Li	3.4	5.7	5.4	5.3	5.4
N	6.5	12.3	14.9	15.4	14.54
Ne	13.3	22.7	22.9	23.1	21.6
Na	3.3	5.6	5.1	5.0	5.14
P	6.5	10.7	10.0	10.7	10.55
Ar	10.6	16.1	15.8	16.1	15.76
Cr	4.2	7.7	6.7	6.5	6.67

The physics is right: even in LSDA, the SIC HOMO eigenvalue comes close to fulfilling the Ionization potential theorem. SIC-LSDA also gets the electron affinity of F^- about right: 3.6 eV vs. 3.4 eV from experiment.

Self-interaction-Corrected Functionals (cont'd)

- Here → are some data from an early SIC calculation on rare gas crystals. The basis set is LMTO (linearized muffin-tin orbitals) and the “atomic sphere approximation” was used. The LDA is PZ. [Z. Szotek, W. Temmerman, and H. Winter, *Sol. State Commun.* **74**, 1031 (1990)] Notice that LDA overbinding is NOT corrected systematically.
- SIC nonetheless is used today for workable calculations on systems in which spurious self-interaction is a prohibitive barrier to computational study [Example: T C Schulthess *et al*, *J. Phys.: Condens. Matter* **19**, 165207 (2007)]

The lattice constant (a_e , bohr), bulk modulus (B_0 , GPa), static lattice binding energy (E_0 , eV/atom), and band gap (e_g eV) for fcc rare gases.

Quantity	Ne	Ar	Kr	Xe
a_e LDA	6.953	9.262	10.172	11.372
a_e SIC	7.178	9.917	10.969	12.256
a_e Expt	8.428	10.050	10.658	11.584
B_0 LDA	25.7	14.5	11.9	9.5
B_0 SIC	16.4	7.1	5.1	4.5
B_0 Expt	1.1	2.7	3.5	3.6
E_0 LDA	0.325	0.375	0.314	0.095
E_0 SIC	0.082	0.146	0.067	-0.172
E_0 Expt	0.020	0.080	0.116	0.170
e_g LDA	11.5	8.2	6.8	5.8
e_g SIC	21.5	13.3	11.0	9.1
e_g Expt	21.4	14.2	11.6	9.3

- There is also considerable evidence that while LDA-SIC is better than LDA for molecules, GGA-SIC is not systematically better than GGA – and can be worse! [O.A. Vydrov and G.E. Scuseria, *J. Chem. Phys.* **121**, 8187 (2004)] For extensive review of SIC see Sect. III-B, S. Kümmel and L. Kronik, *Rev. Mod. Phys.* **80**, 3 (2008).

LDA + U

- Some physical situations seem to break unitary invariance among occupied orbitals: one subgroup of electrons of a certain dominant symmetry will be quite distinct from all the others. A narrow d-band in the midst of a manifold of ordinary metallic s- and p- bands is an example. Narrow band means high localization, means big problems with spurious self-repulsion in LDA or GGA.
- Such “strongly correlated systems” are semi-quantitatively described by a Hubbard Hamiltonian

$$\hat{\mathcal{H}}_{Hubbard} = \sum_{I,K;m,m';\sigma} t_{IK}^{mm'} c_{Im\sigma}^\dagger c_{Km'\sigma} + \frac{U-J}{2} \sum_{I;m\neq m'} (\hat{n}_{Im\uparrow} \hat{n}_{Im'\uparrow} + \hat{n}_{Im\downarrow} \hat{n}_{Im'\downarrow}) + \frac{U}{2} \sum_{I;m,m'} \hat{n}_{Im\uparrow} \hat{n}_{Im'\downarrow}$$

In an oddly non-chemical way, this is a very atomic-like picture.

I, K label sites; m, m' label one-electron states.

The $c_{Im\sigma}^\dagger, c_{Im\sigma}$ add or remove an electron at site I , state m , spin σ .

The n operators are number operators.

The t matrix element is the energy to hop from I to K .

U, J are the on-site Coulomb repulsion and exchange energies resp.

If U/t is big enough, the electrons will stay put because of the hopping energy cost.

LDA + U (cont'd.)

• There are many variants of LDA+U. The concept is the same. Treat the localized electrons via a Hubbard model, and subtract their contribution – in the mean – from the DFT energy in order to eliminate double counting. Here's one version.

- A. Keep only the potential energy terms in the Hubbard Hamiltonian.
- B. Treat the number operators in mean-field approximation, analogous with KS.

That gives

$$\hat{n}_{Im\sigma} \hat{n}_{Im'\sigma'} \approx \bar{n}_{Im\sigma} \hat{n}_{Im'\sigma'} + \bar{n}_{Im'\sigma'} \hat{n}_{Im\sigma} - \bar{n}_{Im\sigma} \bar{n}_{Im'\sigma'}$$

$$\Rightarrow \mathcal{E}^{HubbMF} = \frac{U-J}{2} \sum_{I\sigma} \left[\bar{n}_{I\sigma}^2 - \sum_m \bar{n}_{Im\sigma}^2 \right] + \frac{U}{2} \sum_I \bar{n}_{I\uparrow} \bar{n}_{I\downarrow}$$

$$\text{with } n_{I\sigma} := \sum_m n_{Im\sigma}$$

- C. To handle double counting, remove $\mathcal{E}^{DC} = \frac{U-J}{2} \sum_{I\sigma} \bar{n}_{I\sigma} (\bar{n}_{I\sigma} - 1) + \frac{U}{2} \sum_I \bar{n}_{I\uparrow} \bar{n}_{I\downarrow}$

D. Then the LDA+U energy functional is

$$\mathcal{E}_{LDA+U} = E_{v_{ext}}^{LDA} + \mathcal{E}^{HubbMF} - \mathcal{E}^{DC}$$

$$= E_{v_{ext}}^{LDA} + \frac{U-J}{2} \sum_{Im\sigma} (n_{Im\sigma} - \bar{n}_{I\sigma}^2)$$

LDA + U (cont'd.)

E. Variation of this functional gives a set of effective, orbital-dependent KS equations:

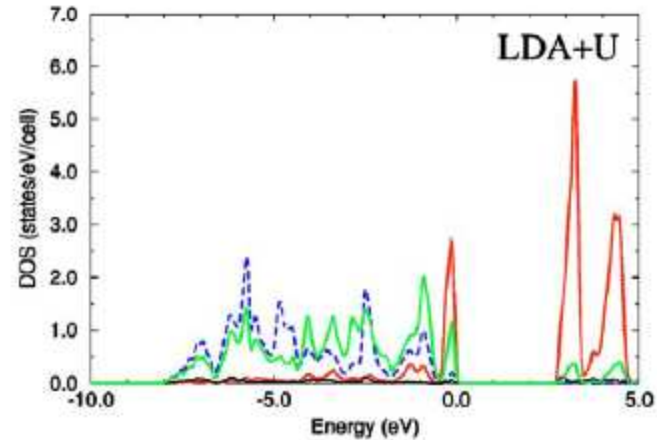
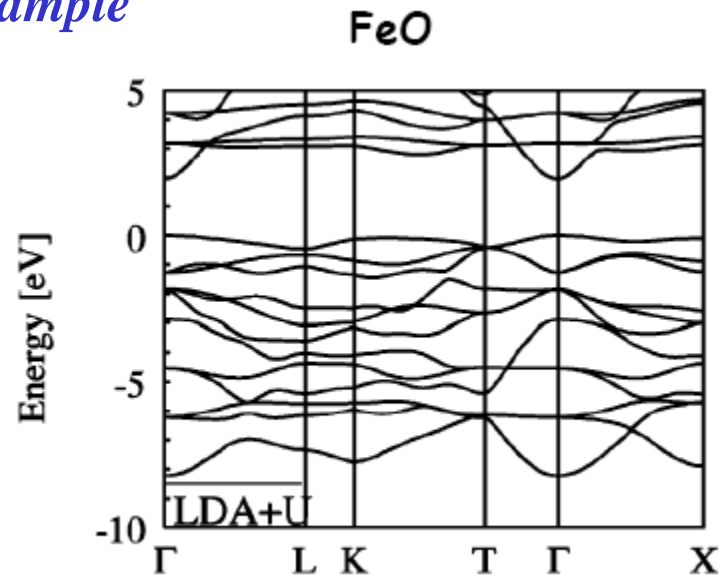
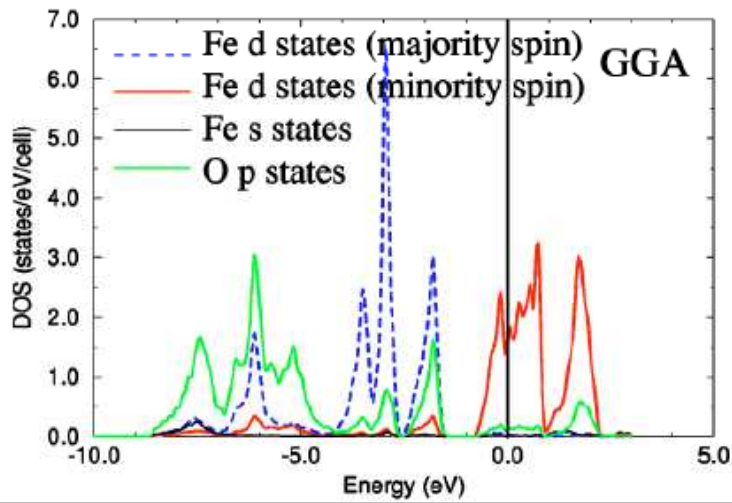
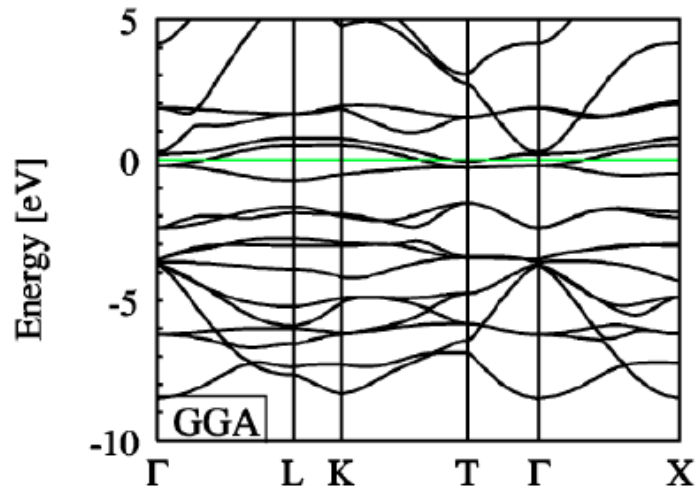
$$v_{Im\sigma} = v_{KS,\sigma} + (U - J) \left(\frac{1}{2} - \bar{n}_{Im\sigma} \right)$$

F. For a fully occupied level, the added term shifts the potential down by $(U-J)/2$, whereas an empty level is shifted up by the same amount. This is why LDA+U is often interpreted as being a form of self-interaction correction.

G. Determination of the values of U, J can be done from experiment, from fitting to wave-function-based calculations on tractable systems, or from some form of internally consistent averaging (by evaluating so-called Slater F integrals).

H. In actual practice, the formulation has to treat the rotational symmetry of the orbitals more carefully than shown above.

LDA + U – Crystalline FeO as an Example



U =
4.29 eV

M. Cococcioni Ph. D. Thesis (2002); M. Cococcioni and S. de Gironcoli, Phys. Rev. **71**, 035105 (2005)

Exact Exchange and Optimized Effective Potential

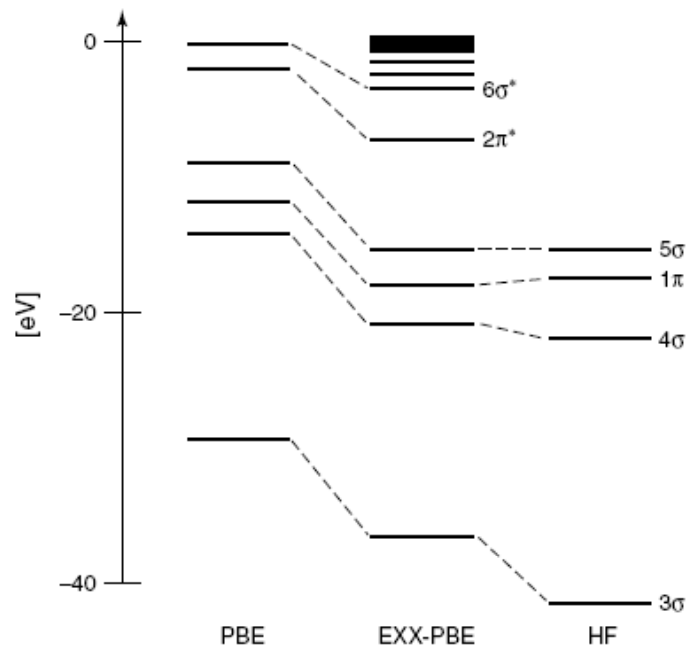


Figure 4. Eigenvalue spectrum of the CO molecule [Reproduced by permission of APS Journals from A. Görling (1999) *Phys. Rev. Lett.*, 83, 5459.]⁽⁹⁵⁾

But why fool around with these schemes? Why not just implement exact exchange (ExX)? In principle, it should yield a multiplicative potential, instead of the orbital-dependent potentials of SIC and LDA+U. And, it should make a big difference in the KS eigenvalues.

As confirmation, before sketching the method, here are results for ExX combined with PBE correlation for the CO molecule. Notice that the results reflect both a better potential for occupied KS states than PBE and a better potential for virtuals (empty levels) than HF.

Exact Exchange and Optimized Effective Potential

We know the KS-DFT exchange expression exactly (Lect. II-8):

$$E_{xKS} [\varphi[n]] = -\frac{1}{2} \sum_{ij}^{occ} \delta_{\sigma_i \sigma_j} \int d\mathbf{r}_1 d\mathbf{r}_2 g(\mathbf{r}_1, \mathbf{r}_2) \varphi_i^*(\mathbf{r}_1) \varphi_j(\mathbf{r}_1) \varphi_j^*(\mathbf{r}_2) \varphi_i(\mathbf{r}_2)$$

The issue is to get $v_{xc}[n] = \frac{\delta E_{xKS,c}}{\delta n}$ as a multiplicative potential. Outline is as follows (exchange only)

$$\int d\mathbf{r}' \frac{\delta E_{xKS}}{\delta n(\mathbf{r}')} \frac{\delta n(\mathbf{r}')}{\delta v_{KS}(\mathbf{r})} = \sum_i^{occ} \int d\mathbf{r}' \frac{\delta E_{xKS}}{\delta \varphi_i(\mathbf{r}')} \frac{\delta \varphi_i(\mathbf{r}')}{\delta v_{KS}(\mathbf{r})} := \Lambda_x(\mathbf{r})$$

$$\frac{\delta E_{xKS}}{\delta n(\mathbf{r}')} = v_x(\mathbf{r}'); \quad \frac{\delta n(\mathbf{r}')}{\delta v_{KS}(\mathbf{r})} = \chi_{KS}(\mathbf{r}', \mathbf{r}) = \sum_j^{occ} \sum_a^{virt} \frac{\varphi_j^*(\mathbf{r}) \varphi_a(\mathbf{r}) \varphi_a^*(\mathbf{r}') \varphi_j(\mathbf{r}')}{\epsilon_j - \epsilon_a} + c.c.$$

$$\Rightarrow \int d\mathbf{r}' \chi_{KS}(\mathbf{r}', \mathbf{r}) v_x(\mathbf{r}') = \Lambda_x(\mathbf{r})$$

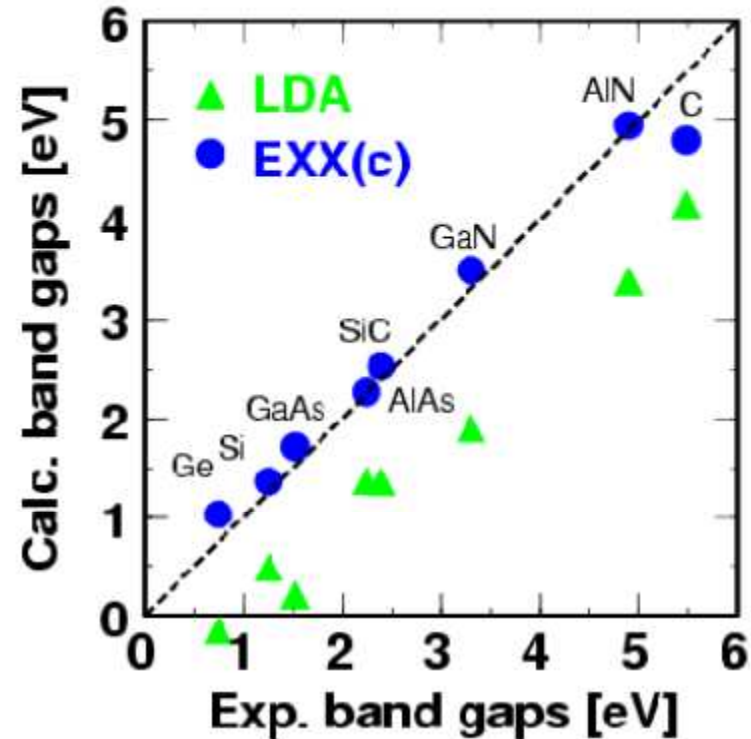
$$\frac{\delta \varphi_i(\mathbf{r}')}{\delta v_{KS}(\mathbf{r})} = \sum_{j(\neq i)} \varphi_j^*(\mathbf{r}') \frac{\varphi_j(\mathbf{r}) \varphi_s(\mathbf{r})}{\epsilon_j - \epsilon_s} \quad \text{from 1st order P.T.}$$

And we can do $\frac{\delta E_{xKS}}{\delta \varphi_j}$ from the explicit E_x directly.

Credit: A. Görling

Exact Exchange and Optimized Effective Potential (cont'd.)

- ExX has some successes. Here→ are band gaps for various semi-conductors for ExX + GGA E_c .
- Numerically there are stability problems when done in a Gaussian-type basis. As a result, there is controversy to the effect that OEP degenerates to the HF solution. An example of this failure is *J. Chem. Phys.* **126**, 141103 (2006).
- It cannot be a real problem, because OEP builds a determinant of orbitals that are eigenstates of a local potential, whereas HF orbitals minimize the determinantal expectation value of the original many-electron Hamiltonian. [*J. Chem. Phys.* **127**, 054102 (2007)]



Credit: A. Görling

What E_c should be used with E_{xKS} ?
Return to this question in Lecture VII.

Hybrid Functionals

A.Becke [J. Chem. Phys. 98, 1372 (1993)] introduced the notion of a hybrid functional on the basis of a linear approximation to the integral in the Adiabatic Connection (Lecture VII) for E_{xc} . The argument itself turns out to be wrong but the idea continues. It led to what is called “Becke Half and Half” XC

$$E_{xcBHH} = \frac{1}{2} E_{xKS} + \frac{1}{2} E_{x,approx} + \frac{1}{2} E_{c,approx}$$

Though this may seem a strange idea, the motivation for hybrids is get some self-interaction correction and at the same time get some beneficial balance (cancellation) between the approximate X and C contributions.

A formal rationale for the hybrid procedure comes from Görling and Levy [J. Chem. Phys. 106, 2675 (1997)]. Instead of a KS minimization (Lect. II-4) of the KE alone

$$T_S [n] := \min_{\Phi \rightarrow n} \langle \Phi | \hat{\mathcal{T}} | \Phi \rangle \equiv \langle \Phi_{min;n} | \hat{\mathcal{T}} | \Phi_{min;n} \rangle$$

minimize with a scaled-down electron-electron interaction

$$T_S [n] + \beta E_{coul} [n] := \min_{\Phi \rightarrow n} \langle \Phi | \hat{\mathcal{T}} + \beta \hat{\mathcal{V}}_{ee} | \Phi \rangle \equiv \langle \Phi_{min;n} | \hat{\mathcal{T}} + \beta \hat{\mathcal{V}}_{ee} | \Phi_{min;n} \rangle$$

$$E_{xc,h} = \beta E_{xKS} + (1 - \beta) E_{x,approx} + E_{c,h}$$

The “h” on $E_{c,h}$ is a reminder that a suitably matched C functional must be used.



Hybrid Functionals (cont'd.)

In practice, hybrid functionals have become a playground of empiricism. But some of the work has been quite thoughtful. For example, by parametrization to thermochemistry, Becke [J. Chem. Phys. **98**, 5468 (1993)] introduced

$$E_{xc} = (1 - a_0)E_{xcLSDA} + a_0E_{xKS} + a_x\Delta E_{xB88} + a_c\Delta E_{cPW91}$$

$$\Delta E_{xB88} = E_{xB88} - E_{xLSDA}$$

$$\Delta E_{cPW91} = E_{cPW91} - E_{cLSDA}$$

$$a_0 = 0.20 \quad a_x = 0.72 \quad a_c = 0.81$$

- This is “Becke-3” or “B3”. *NOTE* that the parameters were determined for a *specific* choice of approximate E_x and E_c in conjunction with E_{xKS} .
- Notice that the resulting one-electron equations are H-F like: they have a non-local exchange term. In principle this could be handled by OEP but it usually isn't.
- Results against the “G1 training set” were
 - ✓ average absolute error in dissociation energies: 2.4 kcal/mol
 - ✓ average absolute ionization energy error: 0.14 eV

Hybrid Functionals (cont'd.)

Frank empiricism: Stephens et al. [J. Chem. Phys. 98, 11623 (1994)] chose to use the B3 form and parameters but to use the LYP E_c rather than the PW91 E_c for which the parameters were fitted. This meant they had to approximate the ΔE_c , for which purpose they used VWN C. The resulting hodgepodge is B3LYP, much beloved of computational chemists and bio-chemists

$$E_{xcB3LYP} = (1 - a_0)E_{xcLSDA} + a_0E_{xKS} + a_x\Delta E_{xB88} + a_cE_{cLYP} + (1 - a_c)E_{cVWN}$$

$$\Delta E_{xB88} = E_{xB88} - E_{xLSDA}$$

$$a_0 = 0.20 \quad a_x = 0.72 \quad a_c = 0.81$$

- Notice that B3LYP is a completely *ad hoc* combination. There is no theoretical justification for making this combination.
- Moreover, LYP is a parameterization of a model 2-rdm (Colle and Salvetti) that is known to violate N-representability.
- There is no justification for using this model except sheer pragmatism. By some magic, it gets remarkably close to the proper functional.

Hybrid Functionals (cont'd.)

Frank empiricism: A frontal-assault kind of parameterization is due to Zhao and Truhlar [Theoret. Chem. Acc. 120, 215 (2008)]. Their M06-2X functional is a hybrid-meta-GGA, of the form

$$E_{M06} = a_x E_{xKS} + (1 - a_x) E_{xMGGA} + a_c E_{cMGGA}$$
$$a_x = 0.54$$

The MGGA E_x and E_c are their own construction, based to a considerable extent on LDA and PBE. The result is a family of functionals. The parameter set for M06-2X contains 32 constants in addition to a_x .

There are so many functionals now that “you can’t follow the players without a program”. Here’s a table from Zhao and Truhlar just to illustrate, not really inform! “UEG” checks whether the functional goes to the homog gas limit, ScorF checks if it is self-correlation-free.

Table 3 Tested density functionals

Method	Year	Ref(s)	Exchange				Correlation			
			$\rho_b, \nabla \rho_b$	X	$\tau_\sigma?$	UEG?	$\rho_b, \nabla \rho_b$	$\tau_\sigma?$	SCorF?	UEG?
BLYP	1988	[91,92]	B88	0	No	Yes	LYP	No	Yes	No
B3LYP	1994	[91-94]	B88	20	No	Yes	LYP	No	Yes	No
PBE	1996	[87]	PBE	0	No	Yes	PBE	No	No	Yes
B98	1998	[95]	B98	21.98	No	No	B98	No	No	No
VSXC ^a	1998	[21]	VSXC	0	Yes	No	VSXC	Yes	Yes	No
PBEh ^b	1999	[96]	PBE	25	No	Yes	PBE	No	No	Yes
HFLYP	2002	[97]	None	100	No	Yes	LYP	No	Yes	No
TPSSh	2003	[3]	TPSS	10	Yes	Yes	TPSS	Yes	Yes	Yes
BMK	2004	[5]	BMK	42	Yes	No	BMK	No	No	No
B97-3	2005	[11]	B97-3	26.93	No	No	B97-3	No	No	No
M05	2005	[12]	M05	28	Yes	Yes	M05	Yes	Yes	Yes
M05-2X	2005	[14]	M05-2X	56	Yes	Yes	M05-2X	Yes	Yes	Yes
M06-L	2006	[16]	M06-L	0	Yes	Yes	M06-L	Yes	Yes	Yes
M06-HF	2006	[19]	M06-HF	100	Yes	Yes	M6-HF	Yes	Yes	Yes
M06	2007	Present work	M06	27	Yes	Yes	M06	Yes	Yes	Yes
M06-2X	2007	Present work	M06-2X	54	Yes	Yes	M06-2X	Yes	Yes	Yes

^a Also called VS98

^b Also called PBE1PBE and PBE0



Hybrid Functionals (cont'd.)

Table 4 Mean errors (kcal/mol for ionization potentials (IP), electron affinities (EA), and proton affinities (PA) and kcal/mol per bond for atomization energies (AE))

Method	AE109		IP13		EA13		PA8		SD143
	MSEPB	MUEPB	MSE	MUE	MSE	MUE	MSE	MUE	MUE
M06-2X	-0.18	0.40	1.06	2.54	1.30	2.07	-0.19	1.75	0.82
M05-2X	-0.02	0.48	1.69	3.54	0.53	2.03	-0.25	1.23	0.94
BMK	-0.04	0.47	2.74	4.21	0.28	1.56	-0.49	1.07	0.94
M06	0.15	0.56	-0.08	3.27	1.19	1.82	1.01	1.80	0.99
B98	-0.50	0.64	1.99	3.21	0.30	1.84	1.44	1.44	1.03
M05	-0.01	0.53	-0.41	2.87	2.81	2.96	1.20	2.16	1.06
B97-3	-0.37	0.59	1.56	3.51	0.82	2.07	2.46	2.46	1.10
VSXC	-0.18	0.57	2.31	3.29	0.22	2.80	1.83	1.98	1.10
M06-HF	-0.24	0.64	0.64	3.76	0.60	2.35	0.11	2.21	1.17
PBEh	0.11	0.91	2.44	3.23	1.50	2.76	1.12	1.19	1.30
B3LYP	-0.69	0.91	3.58	4.72	-1.51	2.29	0.18	1.02	1.39
M06-L	0.05	0.85	0.76	3.09	2.96	3.84	2.01	2.06	1.39
TPSSH	-0.12	0.98	1.96	3.17	1.40	2.81	2.78	2.78	1.45
BLYP	-0.47	1.49	-0.41	4.87	-0.11	2.63	-0.69	1.53	1.90
PBE	2.80	3.03	2.11	3.58	-1.20	2.22	0.04	1.35	2.91
HFLYP	-7.85	7.98	1.24	5.09	8.84	9.51	2.41	3.27	7.59
HF	-30.83	30.83	-17.32	17.92	26.96	26.96	2.75	3.19	27.76
Average (DFT) ^a	-0.47	1.32	1.45	3.62	1.24	2.85	0.93	1.83	1.69
Average (all) ^a	-2.26	3.05	0.34	4.46	2.76	4.27	1.04	1.91	3.23

The MG3S basis set and QCISD/MG3 geometries are employed for the AE109, IP13, and EA13 databases; the 6-311+G(2df,2p) basis set and MP2(full)/6-31G(2df,p) geometries are employed for the PA8 database

MUEPB denotes mean unsigned error (MUE) per bond. MSE denotes mean signed error. The MUE for SD143 is defined as: $MUE = [MUEPB \times 109 + MUE(IP) \times 13 + MUE(AE) \times 13 + MUE(PA) \times 8] / 143$

^a In all tables where the last two rows are averages, "Average(DFT)" is the average of that column for all density functionals in the table, and "Average(all)" is the average of that column over all entries in the table (DFT and HF)

[Zhao and Truhlar, Theoret. Chem. Acc. 120, 215 (2008)]



More Intricate XC Approximations – Some Insights

- **Meta-GGAs are some improvement on GGAs, but not as much as one might have hoped.**
- **SIC and LDA+U have important physical realism, but they violate quantum mechanical basics either by singling out a particular localization or by singling out a particular subset of electrons.**
- **Exact exchange has the problematic task – which we’ve not yet examined – of achieving an appropriate C functional. It also has a major extra self-consistent step (inside the KS SCF loop) to construct the OEP.**
Hybrid functionals, peculiarly enough, handle “static correlation” by effectively including it in the GGA exchange [O.V. Gritsenko, P. R. T. Schipper, and E. J. Baerends, *J. Chem. Phys.* **107**, 5007 (1997)].
- **Hybrid functionals, especially empirical ones, demonstrate that the nearly exact functional is achievable. In that limited sense, they represent great progress.**
- **B3LYP, though it is witchcraft, is remarkable given that it has only three parameters.**
- **M06-L illustrates that it is possible to come close to a parameterized hybrid without using any ExX.**