



**Short Course on Density Functional Theory  
and Applications**  
**VII. Hybrid, Range-Separated,  
and One-shot Functionals**

**Samuel B. Trickey**

©Sept. 2008

Quantum Theory Project

Dept. of Physics and Dept. of Chemistry

**[trickey@qtp.ufl.edu](mailto:trickey@qtp.ufl.edu)**



## So Is B3LYP the Answer?

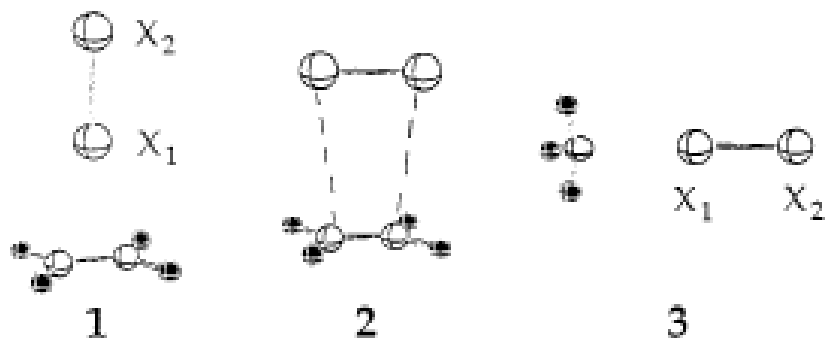
- Given that it has only 3 parameters and performs remarkably well, is B3LYP about as good as as we are going to do?

- Quite some time ago, Ruiz, Salahub, and Vela [J. Phys. Chem. 100, 12265 (1996)] responded in the negative:

“The B3LYP results lie between those of the GGA and MP2.” “[Our results] for the so-called half-and-half potential are in very good agreement with those obtained through second-order Møller-Plesset calculations and with available experimental data. **However, the more widely used three-parameter, B3LYP, functional does not perform well; the hybrid methods are not a panacea.**”

- They studied  $C_2H_4 \dots X_2$  ( $X=F, Cl, Br, \text{ or } I$ ) complexes in three orientations  $\rightarrow$

- See their table, next slide.



## So Is B3LYP the Answer?

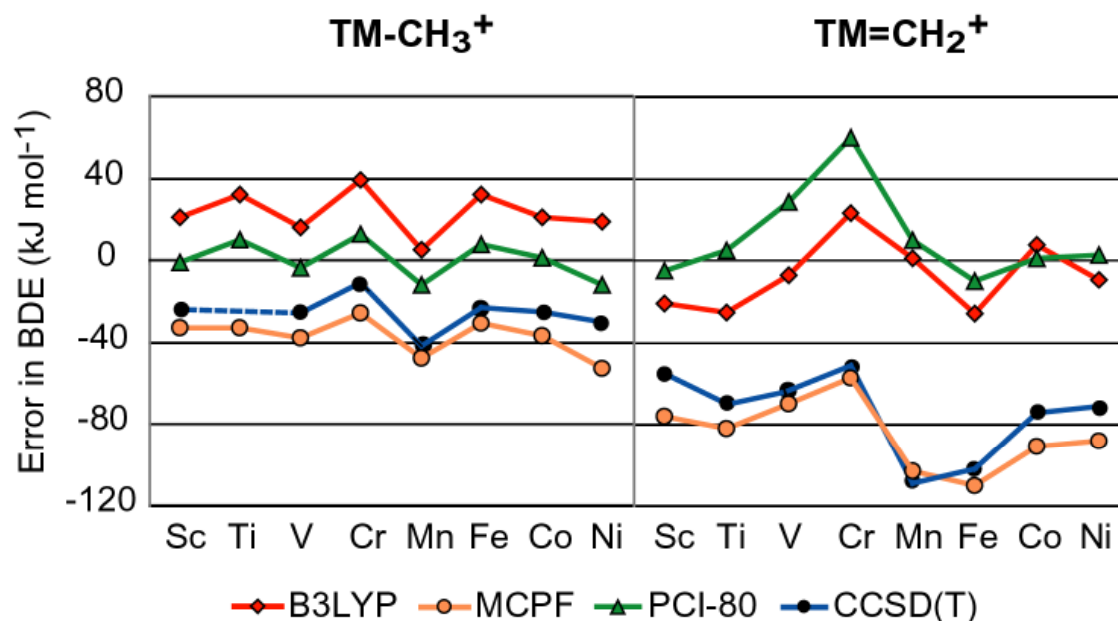
TABLE 1: Optimized Geometrical Parameters, Rotational Constants, Harmonic Cl–Cl Stretching Frequencies, Total and Interaction Energies, and Mulliken Population Analysis for the  $C_2H_4 \cdots Cl_2$  Complex Calculated with Different Methodologies and the Available Experimental Data<sup>g</sup>

	VWN	BP	PP	PW	HHLYP	MP2	expt
Distances (Å)							
$d(C-H)$	1.095 (1.097)	1.092 (1.094)	1.092 (1.094)	1.079 (1.081)	1.077 (1.077)	1.085 (1.085)	.(1.085) <sup>a</sup>
$d(C-C)$	1.344 (1.326)	1.348 (1.347)	1.347 (1.336)	1.345 (1.329)	1.322 (1.317)	1.341 (1.337)	.(1.339) <sup>a</sup>
$d(Cl-Cl)$	2.130 (2.023)	2.137 (2.053)	2.123 (2.043)	2.157 (2.048)	2.038 (2.021)	2.044 (2.028)	.(1.988) <sup>b</sup>
$d(Cl \cdots plane)$	2.435	2.649	2.730	2.448	3.055	3.003	3.128 <sup>c,d</sup>
Angles (deg)							
C–C–H	121.6 (121.8)	121.6 (121.7)	121.6 (121.8)	121.6 (121.7)	121.7 (121.7)	121.4 (121.4)	.(121.1) <sup>a</sup>
plane (C–C)–H	1.0 (0.0)	0.5 (0.0)	0.8 (0.0)	1.1 (0.0)	0.1 (0.0)	0.1 (0.0)	.(0.0) <sup>a</sup>
Rotational Constants (GHz)							
$A_0$	24.5335	24.4732	24.4988	24.7310	25.3455	24.7689	25.520 <sup>c,d</sup>
$B_0$	1.5409	1.4042	1.4043	1.5148	1.2383	1.2613	1.2244 <sup>c,d</sup>
$C_0$	1.4796	1.3528	1.3530	1.4554	1.1996	1.2202	1.1841 <sup>c,d</sup>
Frequency (cm <sup>-1</sup> )							
Cl–Cl	386 (544)	385 (519)	392 (520)	373 (528)	515 (550)	506 (539)	527 <sup>e</sup> (559) <sup>b</sup>
Total Energy (au)							
	–995.263 931	–999.071 759	–999.435 567	–998.902 834	–998.927 808	–997.584 575	
Interaction Energy (kcal/mol)							
BSSE corrected	–12.6	–5.2	–6.3	–6.8	–2.1	–1.6	–1.7 to 2.7 <sup>f</sup>
BSSE noncorrected	–12.6	–5.2	–6.5	–6.9	–2.5	–2.9	
BSSE	0.0	0.0	0.2	0.1	0.4	1.3	

Ruiz, Salahub, and Vela [J. Phys. Chem. 100, 12265 (1996)]

## So Is B3LYP the Answer?

Errors in transition-metal <sup>TM</sup>-ligand bond dissociation energies (BDE, in kJ mol<sup>-1</sup>) of methyl and carbene complexes of first-row transition metal cations



- BDE by CI methods MCPF, CCSD(T) always too small, sometimes significantly (carbenes!)
- Curves for B3LYP and PCI-80(MP2) quite similar in shape [PCI-80: correlation energy (from MP2 or CCSD) scaled by an empirical factor]
- For M-CH<sub>3</sub><sup>+</sup>, PCI-80 uniformly very good; **B3LYP in general too large**, second best
- For M-CH<sub>2</sub><sup>+</sup>, PCI-80 often somewhat too large; **B3LYP overall best**

Credit: N. Rösch

## Ways Forward? - KLI

There is a relatively fast way to do ExX approximately with fairly high accuracy, the Krieger-Lee-Iafrate (KLI) approximation. Suppose we had a good  $E_c$  functional to go with this approximate ExX. Is that a way forward? Here is a sobering table. “F” under method is KLI ExX.

**Table 12.** Spectroscopic constants of  $N_2$ : Results obtained by combination of the exact exchange with different correlation functionals (LDA [26], PW91-GGA [28], CS [23], SIC-LDA [22], C2 ( $E_c^{(2)}$ ) [18] and ISI [21]) in comparison with HF, MP2, quadratic configuration interaction with single and double excitations (QCISD) [55], complete SIC-LDA, conventional LDA and PW91-GGA, as well as experimental [90] results (all OPM values rely on the KLI approximation, F+CS-data from [91]).

method	$R_e$ [Bohr]	$E_b = D_e + h\omega_e/2$ [eV]	$\omega_e$ [cm <sup>-1</sup> ]
expt.	2.075	9.908	2360
HF	2.037	4.952	2738
MP2	2.135	9.333	2180
QCISD	2.105	8.488	2400
F	2.011	4.972	2736
F+GGA	1.997	7.574	2801
F+CS	1.998	7.818	
F+SIC-LDA	2.003	7.880	2770
F+C2		unbound	
F+ISI	2.235	12.225	1401
SIC-LDA(x+c)	1.876	-49.490	3245
LDA	2.068	11.601	2396
GGA	2.079	10.545	2352

**NONE of the ExX +  $E_c$  combinations does better than GGA!  
Finding an  $E_c$  to go with ExX is not easy.**

## Ways Forward? Local Hybrid Functionals

Hybrid functionals mix exact (single-determinant) exchange,  $E_{xKS}$ , with approximate  $E_x$  and  $E_c$  contributions in fixed proportions:

$$E_{xcHybrid} = \lambda E_{xKS} + (1-\lambda) E_{x,approx} + E_{c,approx}$$

Why not do the mixing *locally*, i.e., pointwise? Here is the Jaramillo et al. version of the idea [J. Chem. Phys. **118**, 1068 (2003)]

$$E_{xcLocHybrid} = \int d\mathbf{r} n(\mathbf{r}) \left\{ \lambda(\mathbf{r}) u_{xKS}(\mathbf{r}) + \left[ (1-\lambda(\mathbf{r})) u_{x,approx}(\mathbf{r}) \right] + u_{c,approx}(\mathbf{r}) \right\}$$

$$\lambda(\mathbf{r}) := 1 - \frac{\tau^W(\mathbf{r})}{\tau(\mathbf{r})}; \quad \tau^W(\mathbf{r}) := \frac{|\nabla n(\mathbf{r})|^2}{8n(\mathbf{r})}$$

Recall (Lect. V-3, 8, II-27):  $\tau^W/\tau$  is a so-called “iso-orbital indicator”.

Results – next slide.

## Ways Forward? Local Hybrid Functionals (cont'd.)

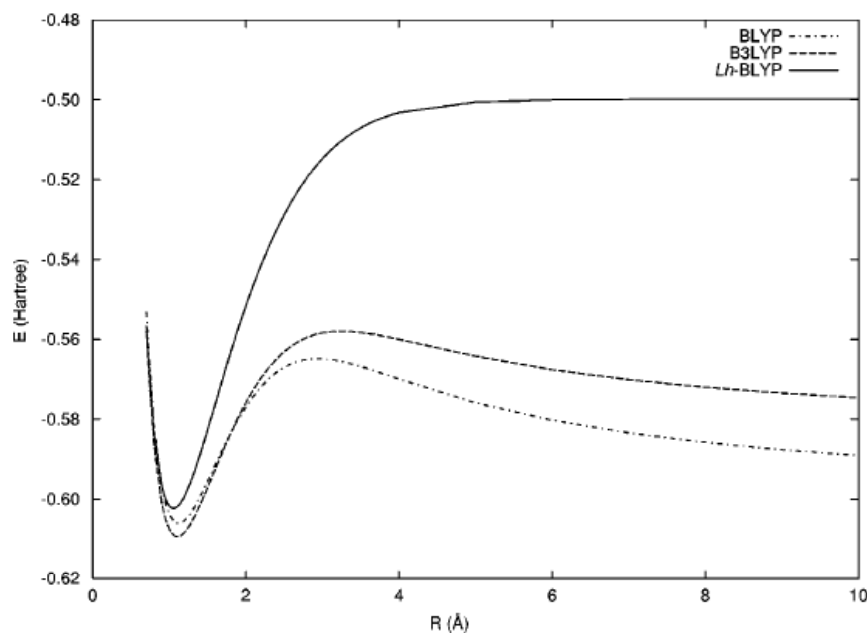


TABLE IV. Statistical data for atomization energies (kcal/mol) of the sma G2 set (55 molecules). All calculations are carried out using post-HF densities.

	BLYP	B3LYP	<i>Lh</i> -BLYP	<i>Lh</i> -PBEPKZB
MAE <sup>a</sup>	3.9	4.1	19.6	13.0
RMS <sup>b</sup>	5.2	5.6	23.8	17.7
Max (-) dev.	-16.7	-19.5	-59.3	-51.7
Max (+) dev.	6.4	7.5	7.5	7.8

<sup>a</sup>Mean absolute error.

<sup>b</sup>Root mean square deviation.

## Dissociation of $H_2^+$ for BLYP, B3LYP, and *lh*-BLYP XC. 6-311G++(3df,3pd) basis. [J. Chem. Phys. **118**, 1068 (2003)]

TABLE III. Reaction energy barrier (kcal/mol) for the linear hydrogen abstraction  $H_2 + H \rightarrow H + H_2$ .

Functional	Energy barrier <sup>a</sup>
HF <sup>b</sup>	17.9
BLYP <sup>b</sup>	2.9
B3LYP	6.0
<i>Lh</i> -BLYP	10.4
<i>Lh</i> -PBEPKZB	8.9
CCSD(T) <sup>b</sup>	9.9
Exp. <sup>b</sup>	9.7

<sup>a</sup>Zero-point energy correction for this reaction is estimated at  $\sim 1$  kcal/mol (Ref. 29), and should be subtracted from the data tabulated here before comparing to experiment.

## Ways Forward? Range-separated Hybrids

Rather than mix exact (single-determinant) exchange,  $E_{xKS}$ , with approximate  $E_x$  on a local basis, what about separating the Coulomb potential into a short- and long-ranged part and treating them separately to get a hybrid? [A. Savin et al., *Internat. J. Quantum Chem.* **56**, 327 (1995); *Chem. Phys. Lett.* **275**, 151 (1997)] **Motivation:** approximate  $E_{xc}$  functionals are local or “semi-local”, so use them at short range and use exact  $E_{xKS}$  at long range.

Here is the range-separated Coulomb interaction:

$$g(r_{ij}) = \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \equiv \frac{1}{r_{ij}} = \frac{\gamma(r_{ij})}{r_{ij}} + \frac{1 - \gamma(r_{ij})}{r_{ij}} := g_{LR}(r_{ij}) + g_{SR}(r_{ij})$$

$$\hat{\mathcal{V}}_{ee,LR} = \frac{1}{2} \sum_{i \neq j} g_{LR}(r_{ij}); \quad \hat{\mathcal{V}}_{ee,SR} = \frac{1}{2} \sum_{i \neq j} g_{SR}(r_{ij})$$

$$\gamma(r_{ij}) = \text{erf}(\mu r_{ij}); \quad \text{erf}(x) := \frac{2}{\sqrt{\pi}} \int_0^x dx' e^{-x'^2}$$

## Ways Forward? Range-separated Hybrids (cont'd.)

And here is the range-separated universal functional and its minimum:

$$\begin{aligned}
 F_{RS}[n] &:= \min_{\psi \mapsto n} \langle \psi | \hat{\mathcal{T}} + \hat{\mathcal{V}}_{ee,LR} + \hat{\mathcal{V}}_{ee,SR} | \psi \rangle \\
 &= \min_{\psi \mapsto n} \langle \psi | \hat{\mathcal{T}} + \hat{\mathcal{V}}_{ee,LR} | \psi \rangle + \left\{ \min_{\psi \mapsto n} \langle \psi | \hat{\mathcal{T}} + \hat{\mathcal{V}}_{ee} | \psi \rangle - \min_{\psi \mapsto n} \langle \psi | \hat{\mathcal{T}} + \hat{\mathcal{V}}_{ee,LR} | \psi \rangle \right\} \\
 E_0 &= F_{RS}[n_0] + E_{ext}[n_0] = \min_{\psi} \langle \psi | \hat{\mathcal{T}} + \hat{\mathcal{V}}_{ee,LR} + \hat{\mathcal{V}}_{ee,SR} | \psi \rangle + E_{ext}[n_0] \\
 &= \min_{\psi} \langle \psi | \hat{\mathcal{T}} + \hat{\mathcal{V}}_{ee,LR} | \psi \rangle + \min_n \left\{ \underbrace{\min_{\psi \mapsto n} \langle \psi | \hat{\mathcal{T}} + \hat{\mathcal{V}}_{ee} | \psi \rangle}_{\text{Usual } E_{v_{\text{cxt}}} \text{ functional}} - \underbrace{\min_{\psi \mapsto n} \langle \psi | \hat{\mathcal{T}} + \hat{\mathcal{V}}_{ee,LR} | \psi \rangle}_{\text{LR version of } E_{v_{\text{cxt}}}} \right\} + E_{ext}[n_0]
 \end{aligned}$$

$$F_{RS}[n] = \min_{\psi \mapsto n} \langle \psi | \hat{\mathcal{T}} + \hat{\mathcal{V}}_{ee,LR} | \psi \rangle + F_{SR}[n]$$

## Ways Forward? Range-separated Hybrids (cont'd.)

One version of a “range-separated hybrid LDA”, makes the following approximations [Gerber et al., J. Chem. Phys. 127, 054101 (2007)]

$$F_{RS}[\Phi; n] = \langle \Phi | \hat{\mathcal{T}} + \hat{\mathcal{V}}_{ee,LR} | \Phi \rangle + F_{SR}[n]$$

$$\Phi(1, \dots, N_e) = \frac{1}{\sqrt{N_e!}} \det | \varphi_1 \dots \varphi_{N_e} |$$

$$u_{xLDA}^{SR,\mu}(\mathbf{r}) = -\frac{3}{\pi} \left( \frac{3}{2} \right)^{1/3} \left\{ \frac{3}{8} - A(\mathbf{r}) \left[ \sqrt{\pi} \operatorname{erf}(1/2A(\mathbf{r})) \right. \right. \\ \left. \left. + (2A(\mathbf{r}) - 4A^3(\mathbf{r})) \exp(-1/(4A^2(\mathbf{r}))) - 3A(\mathbf{r}) + 4A^3(\mathbf{r}) \right] \right\}$$

$$A(\mathbf{r}) = \frac{\mu}{2(3\pi^2)^{1/3} n^{1/3}(\mathbf{r})}$$

The SR xLDA comes from short-ranged HEG work of Toulouse, Savin, and Fladd [Internat. J. Quantum Chem. 100, 1047 (2004)]. In the calculations shown on the next slide, Gerber et al. used VWN for  $E_c$ .

## Ways Forward? Range-separated Hybrids (cont'd.)

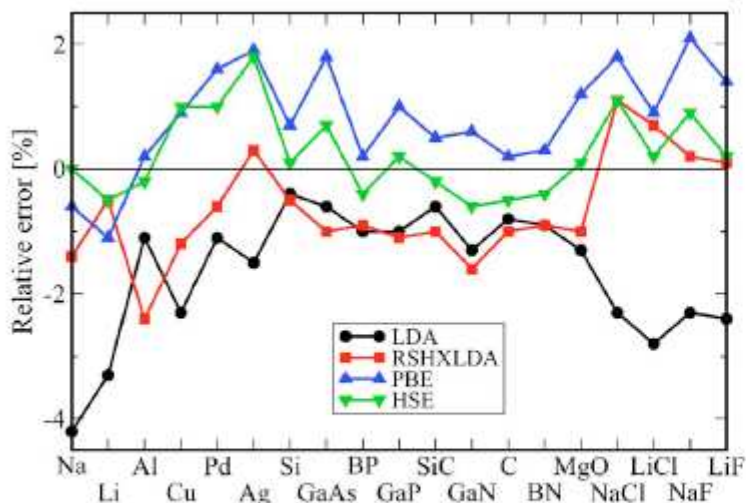


FIG. 1. (Color online) Relative errors in the LDA (black), PBE (blue), HSE (green), and RSHXLDA ( $\mu=0.75 \text{ \AA}^{-1}$ ) (red) lattice parameters with respect to experiment. HSE= Heyd, Scuseria, Ernzerhof hybrid

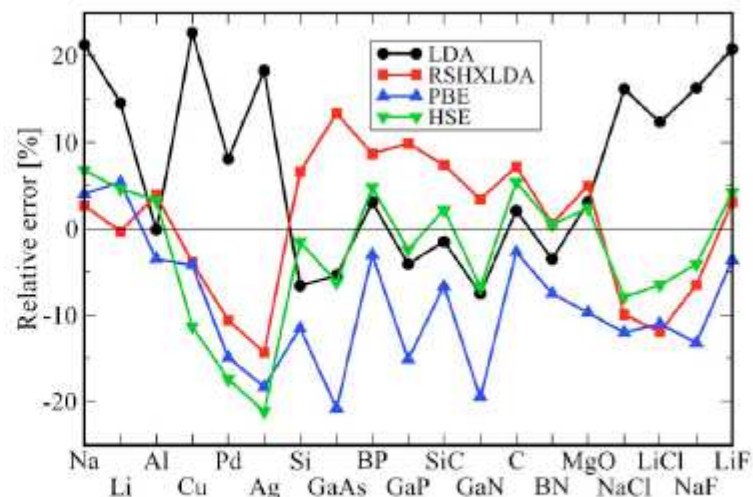


FIG. 2. (Color online) Relative errors in the LDA (black), PBE (blue), HSE (green), and RSHXLDA ( $\mu=0.75 \text{ \AA}^{-1}$ ) (red) bulk moduli with respect to experiment.

**Remark – though this is good work based on a very clever idea, it isn't obvious that the results are a major improvement on ordinary hybrids.**

[Gerber et al., J. Chem. Phys. **127**, 054101 (2007)]

## Ways Forward? Range-separated Hybrids (cont'd.)

TABLE III. Lattice parameters  $a_0$  (Å), spin magnetic moments  $M_s$  ( $\mu_B$ ), and band gaps  $\Delta$  (eV) for the transition metal monoxides MnO, FeO, CoO, and NiO, obtained from LDA and RSHXLDA ( $\mu=0.5 \text{ \AA}^{-1}$ ) calculations B3LYP results were obtained by the CRYSTAL code; LDA and PBE0 values, as well as experimental reference data, were taken from Ref. 70 (and references therein).

	LDA <sup>a</sup>	PBE0 <sup>a</sup>	B3LYP	LDA <sup>b</sup>	RSHXLDA	Expt.
MnO (Ref. 68)						
$a_0$	4.32	4.51	4.50	4.31	4.36	4.45
$M_s$	4.19	4.40	4.73	4.14	4.39	4.58
$\Delta$	0.8	1.3	3.92	0.4	7.1	3.9
FeO (Ref. 26)						
$a_0$	4.18	4.40	4.37	4.17	4.24	4.33
$M_s$	3.35	3.55		3.26	3.48	3.32, 4.2
$\Delta$	0.0	1.2	3.70	0.0	6.2	2.4
CoO (Ref. 68)						
$a_0$	4.11	4.32	4.32	4.10	4.16	4.25
$M_s$	2.36	2.66	2.69	2.23	2.50	3.35, 4.0
$\Delta$	0.0	2.1	3.63	0.0	6.2	2.5
NiO (Ref. 69)						
$a_0$	4.07	4.24	4.23	4.06	4.09	4.17
$M_s$	1.21	1.78	1.67	1.06	1.47	1.64
$\Delta$	0.4	2.9	4.1	0.4	7.0	4.0

PBE0= PBE-based hybrid

[Gerber et al., J. Chem. Phys. **127**, 054101 (2007)]



## *Ways Forward? Range-separated Hybrids (cont'd.)*

**From the Abstract of Gerber et al. [J. Chem. Phys. 127, 054101 (2007)]**

**“The RSHX functional, which has the main feature of providing a correct asymptotic behavior of the exchange potential, has a tendency to improve the description of structural parameters with respect to local and generalized gradient approximations. The band gaps are too strongly opened by the presence of the long-range Hartree-Fock exchange in all but wide-gap systems. In the difficult case of transition metal oxides, the gap is overestimated, while magnetic moments and lattice constants are slightly underestimated.”**

**Note: “Hartree-Fock exchange” is again a misnomer, even though they work with an orbital-dependent (non-local) potential.**

## Adiabatic Connection

Now comes one of the more powerful concepts for understanding functionals and constructing them. The objective is a smooth transformation from the *non-interacting* KS system to the *fully interacting* physical system. (This is distinct from the *smooth mixing* that is in range-separated and local hybrid functionals.)

The first ingredient is the Hellmann-Feynman theorem. Suppose the Hamiltonian depends smoothly on a parameter  $\lambda$ . Then, the ground state is

$$\hat{H}_\lambda \Psi_{\lambda,0} = E_{\lambda,0} \Psi_{\lambda,0}; \quad \langle \Psi_{\lambda,0} | \Psi_{\lambda,0} \rangle = 1 \quad \text{Differentiate w/r to the parameter}$$

$$\begin{aligned} \frac{\partial E_{\lambda,0}}{\partial \lambda} &= \left\langle \frac{\partial \Psi_{\lambda,0}}{\partial \lambda} \middle| \hat{H}_\lambda \middle| \Psi_{\lambda,0} \right\rangle + \langle \Psi_{\lambda,0} | \frac{\partial \hat{H}_\lambda}{\partial \lambda} | \Psi_{\lambda,0} \rangle + \langle \Psi_{\lambda,0} | \hat{H}_\lambda | \frac{\partial \Psi_{\lambda,0}}{\partial \lambda} \rangle \\ &= E_{\lambda,0} \frac{\partial}{\partial \lambda} \langle \Psi_{\lambda,0} | \Psi_{\lambda,0} \rangle + \langle \Psi_{\lambda,0} | \frac{\partial \hat{H}_\lambda}{\partial \lambda} | \Psi_{\lambda,0} \rangle = \langle \Psi_{\lambda,0} | \frac{\partial \hat{H}_\lambda}{\partial \lambda} | \Psi_{\lambda,0} \rangle \end{aligned}$$

The second ingredient is the Pauli coupling constant trick. Given the Hamiltonian

$$\hat{H}_\lambda = \hat{H}_0 + \lambda \hat{H}_1$$

it follows from the Hellmann-Feynman theorem that

$$E_{\lambda=1} - E_{\lambda=0} = \int_0^1 d\lambda \langle \psi_\lambda | \hat{H}_1 | \psi_\lambda \rangle$$

## Adiabatic Connection (cont'd.)

Go back to Levy-Lieb constrained search but for a one-parameter Hamiltonian as in the Pauli trick. Then the universal functional is

$$F_\lambda[n] = \min_{\psi_\lambda \mapsto n} \langle \psi_\lambda | \hat{T} + \lambda V_{ee} | \psi_\lambda \rangle$$

$$\lambda = 0: \quad F_0[n] = \min_{\Phi \mapsto n} \langle \Phi | \hat{T} | \Phi \rangle \equiv \langle \Phi_{min,n} | \hat{T} | \Phi_{min,n} \rangle \equiv T_s[n]$$

$$\lambda = 1: \quad F_1[n] = \min_{\psi_{\lambda=1} \mapsto n} \langle \psi_{\lambda=1} | \hat{T} + V_{ee} | \psi_{\lambda=1} \rangle \equiv \langle \psi_{min,n} | \hat{T} + V_{ee} | \psi_{min,n} \rangle$$

Therefore  $F_1[n] - F_0[n] = E_{xc}[n] + E_{ee}[n]$

By invoking a Lagrange multiplier potential  $v_\lambda(\mathbf{r})$  which keeps the density UNchanged across the whole range  $0 \leq \lambda \leq 1$ , and using the Hellmann-Feynman theorem and Pauli trick, one can prove the adiabatic connection

$$E_{xc}[n] = \int_0^1 d\lambda \langle \psi_{\lambda,min}[n] | \hat{V}_{ee} | \psi_{\lambda,min}[n] \rangle - E_{ee}[n]$$

Notice that (a)  $v$ -representability is back in the picture, both non-interacting and interacting and (b) we don't have to know the potential  $v_\lambda(\mathbf{r})$ .

## Ways Forward? Adiabatic Connection Functionals

The adiabatic connection can be rewritten simply to a suggestive form

$$E_{xc}[n] = \int_0^1 d\lambda \left[ \langle \psi_{\lambda, \min}[n] | \hat{V}_{ee} | \psi_{\lambda, \min}[n] \rangle - E_{ee}[n] \right] := \int_0^1 d\lambda W[\lambda, n]$$

Some facts are known  
about the  $W$  functional:

$$W[0, n] = E_{xKS}[n]$$

$$W'_0 \equiv \left. \frac{\partial W}{\partial \lambda} \right|_0 = E_{c,2}^{GL}[n], \quad \text{2nd-order Goerling-Levy C}$$

$$\frac{\partial W}{\partial \lambda} < 0 \quad \forall \lambda$$

A scheme for calibrating  
approximate interpolation  
 $\lambda=0 \rightarrow \lambda=1$  based on  
approximate  $E_{xc}$  also is  
known.

$$W[\lambda, n] = \frac{\partial}{\partial \lambda} E_{xc}[n_{1/\lambda}(\mathbf{r})]$$
$$\approx E_{x, \text{approx}}[n] + 2\lambda E_{c, \text{approx}}[n_{1/\lambda}(\mathbf{r})] + \lambda^2 \frac{\partial}{\partial \lambda} E_{c, \text{approx}}[n_{1/\lambda}(\mathbf{r})]$$

$$n_{1/\lambda}(\mathbf{r}) = \lambda^{-3} n(\mathbf{r} / \lambda)$$

[Cohen, Mori-Sánchez, and  
Yang, J. Chem. Phys. **127**,  
034101 (2007)]



## Ways Forward? Adiabatic Connection Functionals (cont'd.)

The Mori-Sánchez, Cohen, and Yang [J. Chem. Phys. 124, 091102 (2006)] model adiabatic-connection path is

$$W[\lambda, n] = a[n, \{\varphi\}] + \frac{\lambda b[n, \{\varphi\}]}{1 + \lambda c[n, \{\varphi\}]}$$

$$E_{xc}[n, \{\varphi\}] = a + \frac{b}{c} - \frac{b \ln(1+c)}{c^2}$$

The choice of BLYP as the interpolating functional, for example, gives

$$E_{xc}[n, \{\varphi\}] = E_{xKS} + W_0' \frac{c - \ln(1+c)}{c^2}$$

$$c = \frac{-E_{xKS} - \lambda W_0' + W_{\lambda_p}^{BLYP}}{\lambda_p (E_{xKS} - W_{\lambda_p}^{BLYP})}$$

A selected summary of results [Cohen, Mori-Sánchez, and Yang, J. Chem. Phys. 127, 034101 (2007)] follows. The original paper has many very large tables.

## Ways Forward? Adiabatic Connection Functionals (cont'd.)

TABLE II. Performance of several different models constructed from the adiabatic connection. All these models use  $W_0=HF$ ,  $W'_0=4W_0^{TPSS}$  and  $W_{\lambda_p}^{BLYP}$ . The performance over the 407 set and the HTBH set (MAE in kcal/mol) is compared to standard functionals.

Functional	407	Barrier	
LDA	50.98	17.60	
BLYP	7.68	8.07	
OLYP	6.86	6.32	
PBE	11.11	9.69	
PBE0	6.00	4.04	
B3LYP	6.91	4.40	
BP86	18.43	8.68	
B3P86	17.38	4.40	
Model	407	Barrier	$\lambda_p$
Two parameter models using $W_0$ and $W_{\lambda_p}^{BLYP}$			
$a+b\lambda$	6.09	6.61	(0.55)
$\frac{a}{1+b\lambda}$	6.12	6.58	(0.56)
$a \exp(-b\lambda)$	6.09	6.84	(0.56)
Three parameter models using $W_0$ , $W'_0$ and $W_{\lambda_p}^{BLYP}$			
$a+b\lambda+c\lambda^2$	6.60	1.78	(0.68)
$a+\frac{b\lambda}{1+c\lambda}$	4.60	2.08	(0.64)
$a+b \exp(-c\lambda)$	4.36	2.12	(0.59)
$a+b \log(1+c\lambda)$	5.30	1.68	(0.69)
$a+b \tanh(-c\lambda)$	4.23	2.84	(0.53)
$a+b\lambda \exp(-c\lambda)$	5.49	2.17	(0.59)

TABLE IV. Comparison of errors (kcal/mol) of different functionals for ionization potentials and electron affinities of the G3 set.

	BLYP	TPSS	B3LYP	MCY1	MCY2
IP ME	-3.59	-2.74	-0.96	1.49	1.71
IP MAE	6.25	5.18	4.58	3.54	3.76
EA ME	-0.52	-0.79	-0.20	-0.50	-0.90
EA MAE	3.03	3.12	2.89	2.44	2.82

**Remark – we are back to the no free lunch theorem. These are intricate functionals that require extensive work to generate and program, yet give comparatively modest improvement over simple hybrids.**

[Cohen, Mori-Sánchez, and Yang, *J. Chem. Phys.* **127**, 034101 (2007)]

## Ways Forward? Back to the GGA?!?

**Armiento and Mattsson**  
[Phys. Rev. B 72, 085108 (2005)]  
produced a GGA that behaves properly for two model systems, the HEG and the jellium surface and, in effect, interpolates between them by measuring the local inhomogeneity. The resulting functional has a structure that looks a lot like PBE but is different in content. Results are impressive [J. Chem. Phys. 128, 084714 (2008)]  
Consideration of better ways to constrain (hence parameterize) GGAs is an area of active research.

TABLE II. Lattice constants  $a_0$  (Å), ME, MAE, RMSE, and mean absolute relative error (MARE), obtained with the AM05, LDA, PBE, BLYP, and RPBE functionals, using VASP. The experimental (Exp) results are the same as used in Refs. 10 and 61.

Solid	Exp	AM05	LDA	PBE	BLYP	RPBE
Li	3.477	3.455	3.359	3.433	3.421	3.476
Na	4.225	4.212	4.052	4.201	4.210	4.295
Al	4.032	4.004	3.984	4.041	4.116	4.064
BN	3.616	3.605	3.583	3.627	3.647	3.646
BP	4.538	4.516	4.491	4.548	4.592	4.573
C	3.567	3.551	3.534	3.573	3.598	3.590
Si	5.430	5.431	5.403	5.467	5.532	5.499
SiC	4.358	4.350	4.330	4.377	4.411	4.398
$\beta$ -GaN	4.520	4.492	4.460	4.548	4.611	4.511
GaP	5.451	5.441	5.394	5.509	5.607	5.556
GaAs	5.648	5.672	5.611	5.755	5.871	5.812
LiF	4.010	4.039	3.908	4.065	4.084	4.146
LiCl	5.106	5.119	4.962	5.150	5.232	5.254
NaF	4.609	4.686	4.508	4.708	4.716	4.824
NaCl	5.595	5.686	5.466	5.702	5.763	5.847
MgO	4.207	4.232	4.168	4.259	4.281	4.302
Cu	3.603	3.565	3.523	3.637	3.711	3.682
Rh	3.798	3.773	3.757	3.833	3.905	3.857
Pd	3.881	3.872	3.844	3.946	4.034	3.984
Ag	4.069	4.054	4.002	4.150	4.262	4.215
ME	...	0.001	-0.070	0.039	0.093	0.090
MAE	...	0.025	0.070	0.046	0.100	0.091
RMSE	...	0.033	0.082	0.056	0.114	0.113
MARE	...	0.6%	1.6%	1.0%	2.2%	2.0%

## *A Digression: One-shot Functionals*

Irrespective of the choice of  $E_{xc}$  approximation, it often is desirable to get an estimate of the DFT energy for multiple nuclear configurations  $\{\mathbf{R}\}$  of some system, without, doing the full scf calculation. The Harris approximate, non-iterative functional is the best known of several “one-shot” ways to do this. [J. Harris, Phys. Rev. B 31, 1770 (1985)] Suppose that one has a reasonably good approximate density,  $n_A$ . Then

$$h_{KS}[n_A(\mathbf{r})]\phi_k^{(1)} = \left\{ -\left(\frac{1}{2}\right)\nabla^2 + v_{ext}[n_A(\mathbf{r})] + v_{ee}[n_A(\mathbf{r})] + v_{xc}[n_A(\mathbf{r})] \right\} \phi_k^{(1)} = \varepsilon_k^{(1)} \phi_k^{(1)}$$
$$E_{Harris}[n_A(\mathbf{r})] = \sum_k \varepsilon_k^{(1)} - \frac{1}{2} \iint d\mathbf{r} d\mathbf{r}' \frac{n_A(\mathbf{r})n_A(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{xc}[n_A(\mathbf{r})] - \int d\mathbf{r} V_{xc}[n_A(\mathbf{r})]$$

The rough physical reasoning is that the KS equation was derived from variational stability. Therefore, a non-self-consistent solution of it should lead to an error reduction which is embodied in the resulting eigenvalues  $\varepsilon_i^{(1)}$ . The other terms handle over-counting.

## *Ways Forward – Some Commentary*

- It is probably fair to say that a majority of the DFT functional development community believes explicitly orbital-dependent functionals, beyond the level of MGGAs, are a necessity.
- However, the evolution of increasingly sophisticated hybrids seems to be reaching a state of diminishing returns.
- A minority points to M06-L and AM05 as examples to argue that orbital-dependence beyond the level of MGGAs is, in fact, not necessary. The agenda, therefore, of this minority, is to find MGGA and similar functionals with hybrid-level performance.
- The use of full ExX is still hampered by the lack of really good approximate  $E_c$  functionals to accompany  $E_{xKS}$