

Practical Density Functionals Beyond the Zero-Sum Game

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Abstract

Density functional theory (DFT), the world's most widely-used electronic structure approximation, is facing a crisis. Standard strategies for density functional approximations (DFAs), no matter whether employing exact constraints or empirical parameterization, cannot avoid a "zero-sum game" between overdelocalization (fractional charge error, FC) and underestimation of covalent bonding (fractional spin error, FS). We present a new strategy, combining practical "Rung 3.5" ingredients with insights from hyper-generalized-gradient approximations (hyper-GGAs) that reduce both FS and FC errors. Prototype DFAs built using this strategy qualitatively improve over 40 years of standard DFAs, while maintaining low computational cost and practical evaluation of properties. Numerical results ranging from transition metal thermochemistry to excited-state geometries highlight this strategy's potential and areas for improvement.

DFT is experiencing a crisis of confidence.¹ Faced with a bewildering array of approximations (DFAs, Figure 1), users stick to² DFAs that are over 20 years old.³⁻⁵ Vigorous debates over developers "straying from the path",⁶⁻⁸ and spiraling efforts to build in ever more expensive *ab initio* corrections, highlight this crisis.

Figure 1 shows *why* users (including the authors⁹) use older DFAs. Kohn-Sham DFT¹⁰ combines molecular orbital (Hartree-Fock) theory with a DFA for many-body electron-electron correlation. (Without such correlations, the dissociated ground-state singlet H₂ energy includes contributions from high-energy ionic configurations $H^+ \dots H^-$ and $H^- \dots H^+$ where both electrons occupy the same atom.) Essentially all standard DFAs, whether designed around exact conditions¹¹ or empirical fits,¹² replace some or all of the exact Hartree-Fock exchange with a semilocal *approximation* for exchange! This apparently foolish decision, to "contaminate" an exact quantity with an approximate one, fortuitously captures some of the correlation effects that localize dissociated H₂'s electrons to different atoms.¹³ Approximating correlation with exchange reduces this "fractional spin error" (each H atom in dissociated H₂ has on average 1/2 \uparrow and 1/2 \downarrow electrons, see Refs.^{14,15} for illuminating perspectives), making DFT usefully accurate for covalent bonds¹³ and metals.¹⁶ (Symmetry

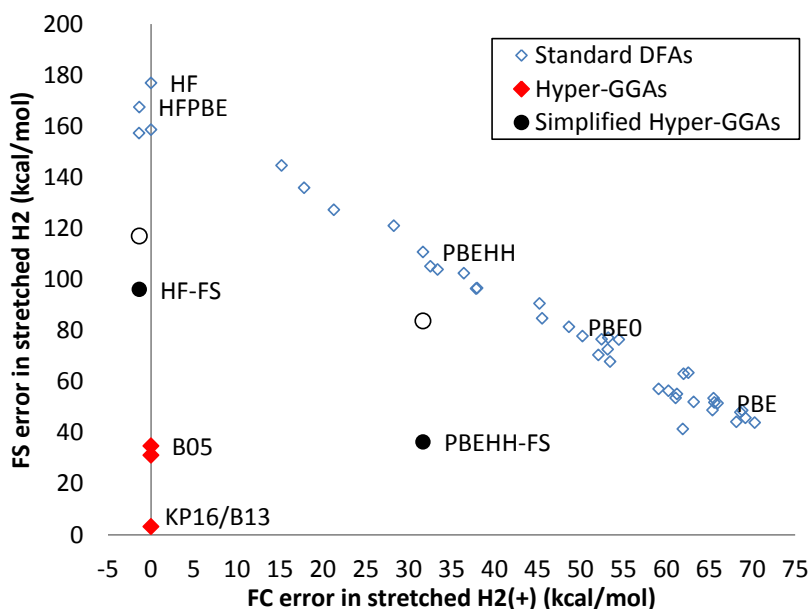


Figure 1: FC vs. FS errors. Open symbols are 40 years of standard DFAs: APFD, B3LYP, B971, B972, B97D, BHHLYP, BLYP, BMK, BRxBRc, CAMB3LYP, HCTH147, HCTH407, HCTH93, Slater exchange, HF, HF plus LDA/PBE/TPSS correlation, HISS, HSE, LCwPBE, LDA, M06, M062X, M06HF, M06L, M08HX, M11, MN12-SX, MN12L, MN15, MN15L, N12-SX, O3LYP, PBE, PW6B95, PW91, SOGGA11X, TPSS, VSXC, wB97XD, X3LYP, $X\alpha$. Filled diamonds are hyper-GGAs. Filled (open) circles are simplified hyper-GGAs with the single empirical parameter $b = 0.05$ (thermochemically optimal b).

breaking also reduces FS error but is not a panacea.¹⁷⁾ Unfortunately, because exact exchange exactly cancels the Hartree self-interaction, introducing approximations *lets each electron interact with itself!* This creates a litany of over-delocalization errors in atomic cores,¹⁸ Rydberg states,¹⁹ paramagnetic defects,^{20,21} insulators,²² charge-transfer excitations,²³ conical intersections,^{24,25} many transition states,²⁶ and "fractionally charged" (FC) atoms as in dissociated H_2^+ . Figure 1 shows how 40 years of standard DFAs, whether designed around exact constraints^{11,27} or empirical fits,¹² all suffer from the same zero-sum tradeoff between FS and FC error. (This is a stark contrast to the "paths of accuracy" visible in Ref.,⁷ and a fundamental limitation of standard "approximate but computationally tractable forms for the approximations" in Ref.⁸) Despite recent progress in other areas,²⁷⁻²⁹ standard DFAs' crude hack of approximating correlation as exchange is both at the heart of DFT's widespread adoption, and at the heart of why users regard new DFAs as little better than the old ones.

Figure 1 also highlights DFT developers' 15-year project to address this crisis: using a *new ingredient* to do by design what approximate exchange does accidentally.³⁰⁻⁴⁰ The hyper-generalized-gradient approximations (hyper-GGAs) in Figure 1 use the exact exchange energy density³⁰ to build better approximations for correlation.

$$e_{X\sigma}(\vec{r}) = -\frac{1}{2} \int d^3\vec{r}' \frac{|\gamma_{\sigma}(\vec{r}, \vec{r}')|^2}{|\vec{r} - \vec{r}'|}. \quad (1)$$

(Here $\gamma_{\sigma}(\vec{r}, \vec{r}') = \sum_{i\sigma} \psi_{i\sigma}(\vec{r})\psi_{i\sigma}^*(\vec{r}')$ is the σ -spin one-particle density matrix of the noninteracting Kohn-Sham reference system, made from occupied MOs $\{\psi_{i\sigma}(\vec{r})\}$.) Becke's seminal real-space nondynamical correlation functional B05,^{32,33} the KP16/B13 refinement,^{34,35} and PSTS³¹ all qualitatively improve over standard DFAs, within a practical occupied-orbital-only framework.¹ Several recent Letters to this Journal explicitly address aspects of this important problem.^{24,25,41,42}

Unfortunately, hyper-GGAs are today almost exclusively used by hyper-GGA developers. Evaluating Eq. 1 is more computationally expensive than evaluating integrated exact

exchange. Analytically differentiating it is even more expensive,⁴³ and such derivatives (with respect to nuclear position, applied electromagnetic fields, etc.) are essential for practical predictions of properties such as bond lengths, IR/Raman spectra, NMR spectra, excited state geometries and fluorescence.⁴⁴ The efficiency of evaluating Eq. 1 and its derivatives has improved recently, starting from approximate schemes based on the resolution of identity^{36,37} to more recent exact seminumerical schemes.³⁸⁻⁴⁰ The latter offer efficiency and precision advantageous for large systems,^{39,40} but require additional coding and implementation effort. Similar issues mean that "strong correlation" DFAs recently discussed in this Journal present only H₂ and hydrogen chain energies.^{41,42} Substantial development efforts are needed before hyper-GGAs and other advanced DFAs are available for routine application to real chemistry.

Table 1: ME per electron (kcal/mol) in atom H-Ar total energies E_{tot} , RMS deviation (pm) in MGBL20 bond lengths BL, RMS and max error (kcal/mol) in MGAE109 atomization energies, RMS in ccCA-TM/11 3d transition metal complex ΔH_f^o (kcal/mol), RMS in (N)HTBH38/08 reaction energies ΔE and barriers Barr, error in H₂+H transition state transferred atom spin polarization Z (10^{-2} e), error in ethylene rotational barrier Rot (eV).

Method	E_{tot}	MGAE		ccCA-TM/11		HT		NHT		Z	Rot	
		BL	RMS	Max	RMS	Max	ΔE	Barr	ΔE			Barr
HF-PBE	-2.0	4.34	38.3	89 ^a	139.5	749 ^e	4.1	7.8	8.4	10.2	-6.7	-0.41
HF-FS	25.8	6.02	24.2	59 ^b	132.9	828 ^f	3.8	11.0	10.5	16.9	-1.1	-0.26
PBEHH	-8.4	2.31	14.0	35 ^c	68.5	433 ^e	1.7	1.8	4.6	4.2	-2.8	-0.11
PBEHH-FS	2.8	2.79	13.0	34 ^b	66.3	373 ^e	2.2	2.8	5.3	5.5	0.2	-0.04
PBE	-14.2	1.22	18.0	47 ^d	39.1	179 ^f	1.8	10.4	6.4	13.1	1.6	0.18
PBE0	-11.4	1.24	6.2	22 ^c	23.0	34 ^e	1.1	4.8	4.5	6.8	-0.6	0.04

^aCF₃CN, ^bSpiro-C₅H₈, ^cSiF₄, ^dC₅H₅N, ^eCr₃O₉, ^fV₄O₁₀.

We propose that a practical strategy out of DFT's crisis is to find *more new ingredients* that capture the physics of Eq. 1 at reduced cost, and to use these to implement the insights of hyper-GGAs.³¹⁻³⁵ We present the first major steps down this road, two prototype DFAs combining exact exchange (HF-FS) or a standard⁴⁵ global hybrid (PBEHH-FS) with a simple, size-consistent, and analytically differentiable "Rung 3.5"⁴⁶ correlation functional

correcting FS error.

$$E_C^{FS} = \sum_{\sigma} \int d^3\vec{r} f(\vec{r}) (F[\zeta] - 1) (e_{X\sigma}^{PBE}(\vec{r}) - \tilde{e}_{X\sigma}(\vec{r})), \quad (2)$$

$$\tilde{e}_{X\sigma}(\vec{r}) = (aN_{d\sigma}(\vec{r}))^{2/3} e_{X\sigma}^{PBE}(\vec{r}), \quad (3)$$

$$N_{d\sigma}(\vec{r}) = \rho_{\sigma}^{-1}(\vec{r}) \left| \int d^3\vec{r}' \gamma_{\sigma}(\vec{r}, \vec{r}') \phi_{\vec{r};d}^{1s}(\vec{r}') \right|^2, \quad (4)$$

$$f(\vec{r}) = \left(1 + b(s^2 + (d/r_s)^4 + (r_s/d)^4) \right)^{-1} \quad (5)$$

The key "Rung 3.5" quantity Eq. 4 determines the extent to which the orbitals, density matrix γ , and exchange hole are localized within distance d about point \vec{r} . Technical details are below. Figure 1 shows that both DFAs qualitatively improve over 40 years of standard approximations. Choosing the single empirical parameter (compare to five in PSTS³¹) $b = 0.05$ highlights the tremendous advances possible, while thermochemically optimal $b = 0.15$ (HF-FS) and $b = 0.5$ (PBEHH-FS) provide more general improvements (Table 1). FS correction improves the underlying DFAs' main-group and 3d transition metal thermochemistry, maintains reasonable treatments of bond lengths and radical reaction barriers, and reduces the density-driven error⁴⁷ in H₂+H transition state polarization Z (CCSD reference -9.3×10^{-2} e, Ref.,⁴⁸ negative error denotes over-polarization) and the error in symmetry-broken singlet calculations on the ethylene rotational barrier Rot (experimental value 2.59 eV, Ref.⁴⁹) Figure SI-1 confirms that HF-FC and PBEHH-FC are identical to the underlying DFAs for H₂⁺ and improve the entire H₂ dissociation potential energy surface. Table 1 is one of very few applications of hyper-GGAs to "real" chemistry: recent strong correlation DFAs reported in this journal, which were applied only to model systems like H₂ and hydrogen chains,^{41,42} are the rule rather than the exception.

As discussed above, hyper-GGAs are rarely used in practical spectra simulations, due to the difficulty of differentiating Eq. 1.⁴³ Table 2 reports adiabatic linear response time-dependent (TD-) DFT calculations⁵⁰ on the absorption energy of He atom and a lithium fluoride F-center (color center),²⁰ and the geometry and adiabatic transition energy T_e of the

Table 2: First bright state excitation energy of He atom and lithium fluoride F-center defect F-cen (eV); and optimized C=O bond length (Angstrom), out-of-plane angle ϕ (degrees), and adiabatic transition energy T_e (eV) of formaldehyde $1^1A''$ excited state.

Method	He	F-cen	R(C=O)	ϕ	T_e
Ref	21.2	5.08	1.25	22	3.49
HF-PBE	25.19	5.43	1.234	32.4	3.29
HF-FS	23.74	5.37	1.226	26.1	3.22
PBEHH	23.65	5.05	1.266	20.1	3.86
PBEHH-FS	22.92	5.00	1.264	19.9	3.72
PBE0	22.89	4.94	1.285	21.8	3.63
PBE	22.13	4.33	1.308	23.7	3.40

formaldehyde $1^1A''$ excited state.^{44,51} FS corrections ameliorate the overestimated HF-PBE helium and F-center excitations, and do not greatly affect the formaldehyde excited-state properties.

Table 3: Wall times (minutes) for a single SCF cycle on extended alanine₂₅ peptide, 6-311+G(2d,p) basis set. "PBE" is the total time for a PBE calculation, "HF exchange" is the extra time for HF-PBE vs. PBE, and "FS correlation" is the extra time for HF-FS vs. HF-PBE.

PBE calculation	47
HF exchange	+136
FS correlation	+70
FS, $d = a_0$	+41
FS, $d = a_0/2$	+24

The computational cost of standard hyper-GGAs is *at least* that of global hybrids, due to the extra cost of evaluating Eq. 1. Table 3 shows that FS correlation can have a computational cost even **below** that of exact exchange in a relatively large peptide. Decreasing d accelerates evaluation by reducing the range of the integrand in Eq. 4.

These results are a major step towards practical DFAs beyond the zero-sum game. However, the journey is not complete. Eq. 2 does not outperform standard DFAs for 3d transition metal thermochemistry or hydrogen-transfer reaction barriers, even when contaminated with 50% semilocal exchange. (The B13 hyper-GGA does not outperform GGAs for "spin-

depolarized" or "fully symmetrized" atoms³⁴ and the KP16/B13 hyper-GGA does not outperform B3LYP for atomization energies.³⁵) The remaining task is to incorporate Eq. 4 into more sophisticated replacements for Eq. 2, designed around exact conditions¹¹ or empirical fits.¹² However, we believe that this practical, analytically differentiable, occupied-orbital-only¹ approach represents the best hope for addressing the crisis in DFT.

Technical details. We follow Becke's use of Eq. 1 to estimate the fraction of the exact exchange hole $h_{X\sigma}(\vec{r}, \vec{r}') = -\rho_{\sigma}^{-1}(\vec{r})|\gamma_{\sigma}(\vec{r}, \vec{r}')|^2$ localized around point \vec{r} . Delocalization of both $h_{X\uparrow}$ and $h_{X\downarrow}$ indicates potential FS error.^{32,33} Eq. 3 approximates Eq. 1 by renormalizing the PBE³ exchange hole from -1 to $-aN_{d\sigma}$. Rung 3.5 quantity $N_{d\sigma}(\vec{r})$ (Eq. 4) measures the degree to which γ itself is localized distance d about \vec{r} , using test function $\phi_{\vec{r};d}^{1s}(\vec{r}') = \left(\frac{2}{\pi d^2}\right)^{3/4} e^{-|\vec{r}-\vec{r}'|^2/d^2}$, an atomic-like state centered at point \vec{r} and decaying over distance d . (DFT+U uses analogous projections onto atomic-like states centered at nuclei.⁵²) $|N_{d\sigma}(\vec{r})|^2 \leq 1$. $d = 2.21$ bohr averages the overlap distances (d maximizing system-averaged $N_d(\vec{r})$, Ref.⁵³) of "appropriate norms"³¹ H and He atom. $a = 1.57$ ensures $\int d^3\vec{r}' \tilde{e}_{X\uparrow}(\vec{r})$ is exact in H atom. The integrand of Eq. 4 is negligible outside volume $V \propto d^3$ about \vec{r} , regardless of the delocaliation of γ , providing asymptotic linear scaling analogous to screened hybrid DFAs.^{54,55} Evaluating Eq. 4 and its analytic derivatives is straightforward in standard atom-centered (AO) basis sets $\{\chi_{\mu}(\vec{r})\}$: the integral becomes $\sum_{\mu\nu} P_{\mu\nu}^{\sigma} \chi_{\mu}(\vec{r}) A_{\nu,d}(\vec{r})$. $P_{\mu\nu}^{\sigma}$ is the AO-basis density matrix. Overlap integral $A_{\nu,d}(\vec{r}) = \int d^3\vec{r}' \chi_{\nu}(\vec{r}') \phi_{\vec{r};d}^{1s}(\vec{r}')$ may be evaluated analytically.⁵⁶ $F[\zeta] = \left[(1+\zeta)^{4/3} + (1-\zeta)^{4/3} - 2 \right] / (2^{4/3} - 2)$,⁵⁷ $\zeta = (\rho_{\uparrow}(\vec{r}) - \rho_{\downarrow}(\vec{r})) / \rho(\vec{r})$ detects closed-shell regions in Eq. 5 Because $N_{d\sigma}(\vec{r})$ only provides useful information where $r_s = (4\pi\rho(\vec{r})/3)^{1/3}$ is close to distance d and reduced gradient $s = |\nabla\rho(\vec{r})|/(2k_F\rho)$ (Figure SI-2), $k_F = (3\pi^2\rho)^{1/3}$ is not too large, we choose Eq. 5 to go to zero outside such regions. This ensures $E_C^{FC} \rightarrow 0$ in high- and low-density regions, respectively an exact constraint and a reasonable choice. HF-FS (PBEHH-FS) combine Eq. 2 plus the PBE dynamical correlation functional with exact exchange ("half-and-half"⁴⁵ PBE global hybrid). Most calculations use the development version of the Gaussian suite of programs.⁵⁸ B05, PSTS, and KP16/B13

are calculated self-consistently as dissociated atoms using an in-house program at Kong's group.

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Supporting Information Available

Details of calculations and test sets, H_2 and H_2^+ total energies and potential energy surfaces, $N_d(\vec{r})$ in representative systems. This material is available free of charge via the Internet at <http://pubs.acs.org/>.

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