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Deorbitalization strategies for meta-generalized-gradient-approximation exchange-correlation functionals

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We explore the simplification of widely used meta-generalized-gradient approximation (mGGA) exchange-correlation functionals to the Laplacian level of refinement by use of approximate kinetic-energy density functionals (KEDFs). Such deorbitalization is motivated by the prospect of reducing computational cost while recovering a strictly Kohn-Sham local potential framework (rather than the usual generalized Kohn-Sham treatment of mGGAs). A KEDF that has been rather successful in solid simulations proves to be inadequate for deorbitalization, but we produce other forms which, with parametrization to Kohn-Sham results (not experimental data) on a small training set, yield rather good results on standard molecular test sets when used to deorbitalize the meta-GGA made very simple, Tao-Perdew-Staroverov-Scuseria, and strongly constrained and appropriately normed functionals. We also study the difference between high-fidelity and best-performing deorbitalizations and discuss possible implications for use in *ab initio* molecular dynamics simulations of complicated condensed phase systems.

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I. INTRODUCTION

As is well known, the key ingredient for computational use of density-functional theory (DFT) in its Kohn-Sham (KS) form [1] is the exchange-correlation (XC) functional E_{xc}. It is the only term in the DFT variational functional

$$E[n] = T_{\mathrm{s}}[n] + E_{\mathrm{Ne}}[n] + E_{\mathrm{H}}[n] + E_{\mathrm{xc}}[n] + E_{\mathrm{NN}} \tag{1}$$

which requires approximation. Here, as usual, for N_e electrons in the field of fixed nuclei, the ground-state number density is $n(\mathbf{r})$, the KS (noninteracting) kinetic-energy functional is $T_{\mathrm{s}}[n]$, the nuclear-electron interaction energy is $E_{\mathrm{Ne}}[n]$, the Hartree energy (classical electron-electron repulsion) is $E_{\mathrm{H}}[n]$, and the internuclear repulsion energy is E_{NN}.

Minimization, in principle, gives a single Euler equation. Overwhelmingly predominant practice, however, is to render the minimization in terms of the KS orbitals via

$$n(\mathbf{r}) = \sum_{i=1}^{N_e} |\varphi_i(\mathbf{r})|^2, \tag{2}$$

where for simplicity we have assumed unit occupation. The noninteracting kinetic energy is

$$T_{\mathrm{s}}\big[\{\varphi_i\}_{i=1}^{N_e}\big] := \frac{1}{2}\sum_{i=1}^{N_e}\int d\mathbf{r}\,|\nabla\varphi_i(\mathbf{r})|^2 \equiv \int d\mathbf{r}\, t_{\mathrm{s}}^{\mathrm{orb}}(\mathbf{r}) \tag{3}$$

(the positive-definite form in Hartree a.u.). Minimization then gives the ubiquitous KS equation

$$\big\{-\tfrac{1}{2}\nabla^2 + v_{\mathrm{KS}}([n];\mathbf{r})\big\}\varphi_i(\mathbf{r}) = \epsilon_i\varphi_i(\mathbf{r}). \tag{4}$$

Here $v_{\mathrm{KS}} = \delta(E_{\mathrm{Ne}} + E_{\mathrm{H}} + E_{\mathrm{xc}})/\delta n$ is the KS potential.

For more than two decades, pursuit of accuracy combined with broad applicability has led to increasingly complicated inclusion of explicit orbital dependence in approximate XC functionals. Such inclusion occurs first on the meta-generalized-gradient-approximation (mGGA) [2–12] rung of the Perdew-Schmidt ladder of functional types [13]. mGGA functionals of this type use the KS kinetic-energy density $t_{\mathrm{s}}^{\mathrm{orb}}(\mathbf{r})$ to detect one- and two-electron regions. It is relevant to the present work to note that another kind of mGGA depends on $\nabla^2 n$, not $t_{\mathrm{s}}^{\mathrm{orb}}(\mathbf{r})$. For clarity, from here on we denote such functionals as "mGGA-L" and reserve "mGGA" for those that use $t_{\mathrm{s}}^{\mathrm{orb}}(\mathbf{r})$.

It has come to be accepted that the ratio

$$\alpha[n] := \big(t_{\mathrm{s}}^{\mathrm{orb}}[n] - t_W[n]\big)\big/t_{TF}[n] := t_\theta/t_{TF} \tag{5}$$

is the most useful form of kinetic-energy-based region detector [14] in a constraint-based mGGA. Here the Thomas-Fermi [15,16] and von Weizsäcker [17] kinetic-energy (KE) densities are

$$t_{TF} = c_{TF}n^{5/3}(\mathbf{r}), \quad c_{TF} := \tfrac{3}{10}(3\pi^2)^{2/3}, \tag{6}$$

$$t_W = \tfrac{5}{3}t_{TF}s^2, \tag{7}$$

and

$$s := \frac{|\nabla n(\mathbf{r})|}{2(3\pi^2)^{1/3}n^{4/3}(\mathbf{r})}. \tag{8}$$

Other dimensionless ratios that involve the KE density which appear in the mGGA context are

$$z[n] := t_W[n]/t_s^{\mathrm{orb}}[n] \tag{9}$$

and

$$w[n] := \frac{t_{TF}[n]/t_s^{\mathrm{orb}}[n] - 1}{t_{TF}[n]/t_s^{\mathrm{orb}}[n] + 1}. \tag{10}$$

Note that $w[n]$ has become very popular in the development of semiempirical mGGAs [18,19], while $z[n]$ was used in

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such early nonempirical mGGAs as those of Perdew, Kurth, Zupan, and Blaha (PKZB) [2] and Tao, Perdew, Staroverov, and Scuseria (TPSS) [4].

The explicit orbital dependence of a mGGA introduced by $\alpha[n]$, $z[n]$, and/or $w[n]$ makes the XC contribution to the KS potential $v_{\text{xc}} = \delta E_{\text{xc}}/\delta n$ accessible only via the optimized effective potential (OEP) procedure [20–23]. On account of the computational complexity (hence cost) of the OEP procedure that route rarely is taken in practice. Instead, calculations that use mGGAs typically also use the much less costly generalized Kohn-Sham (gKS) procedure. It has a set of nonlocal potentials $\delta E_{\text{xc}}/\delta \varphi_i$ rather than the local v_{xc}. The two schemes are not equivalent in content [24]. Note also that gKS is not as efficient as an ordinary KS calculation with, for example, a GGA functional. In the context of DFT calculations to drive tens of thousands of *ab initio* molecular dynamics [25–28] steps, the seemingly modest increment in computational cost might be quite significant.

The requirement that either OEP or gKS procedures be used arises from the explicit orbital dependence of the KS KE density in $\alpha[n]$, $z[n]$, or $w[n]$. Thus it is at least plausible that recent progress in so-called orbital-free DFT (OFDFT) might provide an alternative route for transforming the mGGA problem into one with better computational efficiency and with the interpretability of an ordinary KS equation. The strategy is to evaluate $\alpha[n]$, for example, with an *orbital-independent* approximation for $t_{\text{s}}^{\text{orb}}[n]$. As far as we know, that strategy has been studied only a few times previously. The first time was with the Lee-Yang-Parr (LYP) correlation functional [29]. That had mixed success, partly because the Colle-Salvetti C functional [30] that was deorbitalized has the peculiarity of being non-N representable [31] and partly because the Thomas-Fermi (TF) [15,16] KE density functional (KEDF) was used in the deorbitalizing role. The other instance is Perdew and Constantin's deorbitalization [32] of the TPSS [4] mGGA. They used a Laplacian-containing KEDF, showed that the result seemed to mimic the full TPSS mGGA, and gave a small sample of numerical results in support of that assertion. The two other deorbitalization examples of which we are aware [33,34] addressed the nonadditive part of subsystem DFT, hence lack direct bearing on the original deorbitalization strategy.

In the present work we take up various versions of the deorbitalization strategy. We explore a wide variety of KEDFs, present an alternative KEDF parametrization scheme dependent on KS calculations only for a small set of atoms, and provide thorough numerical validation in the context of standard molecular test sets. In Secs. II and III we outline the formulation and constraints, delineate the KEDFs we have considered, and summarize the code environment and techniques implemented. Sections IV–VI give parametrizations and comparative test results, followed by a brief concluding section.

II. FORMULATION, CONSTRAINTS, AND KEDFS

The numerator t_θ in α, Eq. (5), is known in the orbital-free KE literature as the "Pauli term." It has two positivity properties [35,36] that are strict constraints on any t_θ approximation. They are

$$T_\theta[n] = \int d\mathbf{r} t_\theta[n(\mathbf{r})] \geqslant 0 \tag{11}$$

and

$$\frac{\delta T_\theta[n]}{\delta n(\mathbf{r})} \geqslant 0 \, \forall \, \mathbf{r}. \tag{12}$$

An important limitation is obvious. Even if an approximate t_θ meets these constraints that does not ensure that it is a good local approximation. That is, enforcement of (11) and (12) does not guarantee that

$$t_\theta^{\text{approx}}[n] \approx t_s^{\text{orb}}[n] - t_W[n] \tag{13}$$

for arbitrary proper n. Note that $t_\theta^{\text{approx}} = t_s[n] - t_W[n]$ is an approximation to the exact Pauli term, which uses a selected approximate kinetic-energy density functional $t_s[n]$ instead of the exact orbital-dependent kinetic-energy density $t_s^{\text{orb}}[n]$. Nevertheless, progress on functionals t_θ^{approx} that do meet those constraints and do a reasonably good job of reproducing conventional KS binding-energy curves, equations of state, etc., [35,37,38] suggests that one should try those functionals.

To proceed it is useful to have definitions of other reduced density derivatives (RDDs) in addition to the familiar reduced density gradient s defined in Eq. (8):

reduced density Laplacian

$$q := \frac{\nabla^2 n}{4(3\pi^2)^{2/3} n^{5/3}}, \tag{14}$$

reduced density Hessian

$$p := \frac{\nabla n \cdot \nabla\nabla n \cdot \nabla n}{4(3\pi^2)^{2/3} |\nabla n|^2 n^{5/3}}, \tag{15}$$

reduced quadratic density Hessian

$$\tilde{p} := \frac{\nabla n \cdot \nabla\nabla n \nabla\nabla n \cdot \nabla n}{16(3\pi^2)^{4/3} |\nabla n|^2 n^{10/3}}. \tag{16}$$

From the great variety of available single-point KEDFs, initially, we examined several to see if they reproduced $t_\theta[n]$ for densities from very accurate Hartree-Fock (HF) orbitals for the first 18 neutral atoms [39,40]. Those KEDFs tested include the second-order gradient expansion approximation (GEA2)

$$t_{\text{GEA2}}[n] = t_{\text{TF}}[n] + \tfrac{1}{9} t_{\text{W}}[n], \tag{17}$$

the Liu and Parr (LP) homogeneous functional expansion [41], the asymptotic PBE kinetic (APBEK) functional [42], the PBE2 and PBE4 functionals [37], VT84F [38], Perdew and Constantin (PC) mGGA [32], Cancio and Redd (CR) mGGA [43,44], the regularized (by enforcing the von Weizsäcker kinetic-energy density lower bound) version of the Thomas-Fermi plus Laplacian (TFLreg) mGGA [34], and a modified version of VT84F

$$t_{\text{MVT}}[n] = \theta_{\text{MVT}}[n] t_{\text{VT}}[n] + (1 - \theta_{\text{MVT}}[n]) t_{\text{W}}[n]. \tag{18}$$

In it, $t_{\text{VT}}[n]$ is the original VT84F KEDF, and $\theta_{\text{MVT}}[n]$ is an interpolation function

$$\theta_{\text{MVT}} = \text{Erf}[\sqrt{\Theta}] \tag{19}$$

based on the density-overlap-region indicator (DORI) [45]

$$\Theta := 4\left(1 + \frac{\tilde{p}}{s^4} - 2\frac{p}{s^2}\right). \tag{20}$$

Because $\Theta(\mathbf{r}) = 0$ for the hydrogen atom and $\to \infty$ for the homogeneous electron gas (HEG) [46], use of θ_{MVT} with VT84F removes spurious isolated H contributions.

The quality measure [47] we used to determine which functional might yield reasonable approximations to $\alpha[n]$ was

$$\sigma = \frac{\int d\mathbf{r}\,\left|t_\theta^{\mathrm{orb}} - t_\theta^{\mathrm{approx}}\right|}{T_s} = \frac{\int d\mathbf{r}\,\left|t_s^{\mathrm{orb}} - t_s^{\mathrm{approx}}\right|}{T_s}. \tag{21}$$

Numerical integrals were performed by double-exponential radial quadratures [48] with 200 points. This numerical scheme matched, to machine precision, the integrated KE obtained by analytical integration for all 18 atoms.

Table I lists average σ values for the first 18 neutral atoms. Four KEDFs stand out by virtue of having the smallest average σ values ($\sigma < 0.2$) and being well separated from those of the other candidate KEDFs. The four are the PC mGGA [32], Cancio and Redd (CRloc) mGGA [44], the TFLreg mGGA [34], and the modified VT84F plus Laplacian (MVT84F+L). The PC mGGA uses a modified fourth-order gradient expansion (MGE4) with several appealing features. Written in an enhancement function form,

$$T_s[n] = \int d\mathbf{r}\, t_{TF}(\mathbf{r}) F_t(s,q,p), \tag{22}$$

the MGE4 functional is

$$F_t^{\mathrm{MGE4}} = \frac{F_t^{(0)} + F_t^{(2)} + F_t^{(4)}}{\sqrt{1 + \left[F_t^{(4)}/\left(1 + F_t^W\right)\right]^2}}, \tag{23}$$

with

$$F_t^{(0)} = 1, \tag{24}$$

$$F_t^{(2)} = \tfrac{5}{27}s^2 + \tfrac{20}{9}q, \tag{25}$$

$$F_t^{(4)} = \tfrac{8}{81}q^2 - \tfrac{1}{9}s^2 q + \tfrac{8}{243}s^4, \tag{26}$$

$$F_t^W = \tfrac{5}{3}s^2. \tag{27}$$

Perdew and Constantin assumed that when the MGE4 enhancement function F_t^{MGE4} is smaller than the von Weizsäcker one F_t^W, that indicates the need for $F_t^{PC} = F_t^W$. Thus their functional interpolates between F_t^{MGE4} and F_t^W with

$$\theta_{PC}(z) = \begin{cases} 0, & z \leqslant 0, \\ \left[\frac{1+e^{a/(a-z)}}{e^{a/z}+e^{a/(a-z)}}\right]^b, & 0 < z < a, \\ 1, & z \geqslant a. \end{cases} \tag{28}$$

They optimized the parameters a and b by minimizing the mean absolute relative error (MARE) of the integrated kinetic energy of 50 atoms and ions, nine spherical jellium clusters (with the bulk parameter corresponding to Na), and three systems composed of eight jellium spheres calculated in the liquid-drop model. The result was $a = 0.5389$ and $b = 3$. The final form of the PC mGGA enhancement factor is

$$F_t^{PC} = F_t^W + z^{PC}\,\theta_{PC}(z^{PC}), \tag{29}$$

with

$$z^{PC} = F_t^{\mathrm{MGE4}} - F_t^W. \tag{30}$$

TABLE I. Average σ values for the first 18 neutral atoms computed with several kinetic-energy density functionals. "Regularized" denotes conformance with the von Weizsäcker lower bound. Other functionals not referenced in the text also were used, including Tran and Wesolowski (TW02) [49], Lembarki and Chermette (LC94) [50], Ou-Yang and Levy (OL1 and OL2) [51] and Ernzerhof (E00) [52]. Functionals ending in "+L" were built by adding $20/9\ q$ to their original enhancement function.

Functional	Regularized?	σ
PBE2	no	1.576
VT84F	no	1.405
PBE4	no	1.272
LP	no	1.112
APBEK	no	1.028
TW02	no	1.027
LC94	no	1.027
OL2	no	1.017
OL1	no	1.016
GEA2	no	1.013
E00	no	0.996
LP+L	yes	0.827
W	yes	0.473
RDA	yes	0.382
CR	yes	0.271
MVT84F	yes	0.243
TW02+L	yes	0.239
GEA2+L	yes	0.237
MVT84F+L	yes	**0.164**
TFLreg	yes	**0.147**
PC	yes	**0.117**
CRloc	yes	**0.103**

Cancio and Redd [44] noticed some odd behavior of the PC mGGA for regions of small p and negative q, which led them to suggest their CR mGGA [43,44]. [Note that Cancio and Redd's p variable is *not* the same as the one defined in Eq. (15) above. Further their definition has an obvious typographical error; it should have n^2 in its denominator, not n.] The original CR mGGA is based on the second-order gradient expansion including the Laplacian term

$$F_t^{\mathrm{GEA2+}L} = 1 + \tfrac{5}{27}s^2 + \tfrac{20}{9}q \tag{31}$$

and imposition of the von Weizsäcker lower bound via the interpolation function

$$\theta_{CR}(z) = \{1 - \exp[-1/|z|^a][1 - H(z)]\}^{1/a}. \tag{32}$$

Here $H(z)$ is the Heaviside unit step function. The resulting CR mGGA enhancement function is

$$F_t^{CR} = 1 + F_t^W + z^{CR}\theta_{CR}(z^{CR}), \tag{33}$$

with

$$z^{CR} = F_t^{GEA2+L} - F_t^W - 1 \tag{34}$$

and $a = 4$. They also gave an alternative formulation of their functional (CRloc) in which the local gradient expansion

$$F_t^{\mathrm{GEAloc}} = 1 - 0.275s^2 + 2.895q \tag{35}$$

is used in place of F_t^{GEA2+L}. This local expansion is valid only for the nuclear region and is not expected, because of the sign of the s^2 term, to yield accurate integrated KEs by itself. Cancio and Redd discuss this in detail, but it is not an issue for our purposes.

The TFLreg mGGA is based on the TFL enhancement function

$$F_t^{\mathrm{TFL}} = 1 + \tfrac{20}{9} q \tag{36}$$

augmented by imposition of the von Weizsäcker lower bound

$$F_t^{\mathrm{TFLreg}} = \max\left(F_t^{\mathrm{TFL}}, F_t^{vW}\right). \tag{37}$$

The MVT84F plus Laplacian functional is an extension of Eq. (18),

$$t_{\mathrm{MVT+L}} = \theta_{\mathrm{MVT}}\left(t_{\mathrm{VT}} + \tfrac{1}{6}\nabla^2 n\right) + (1-\theta_{\mathrm{MVT}})t_{\mathrm{W}}. \tag{38}$$

Despite its good performance, we did not pursue it because of difficulties in integrating the DORI function with standard numerical techniques used in many DFT codes. Those difficulties arise from the high-order spatial derivatives introduced by DORI and are exacerbated by the use of Gaussian basis sets.

That leaves three candidate KEDFs. Additional numerical estimates of the deorbitalization performance of those candidates were obtained from several additional error indicators. A global error indicator useful for all orbital-dependent mGGAs,

$$\Delta_\alpha = \sum_i^M \frac{1}{N_i} \int d\mathbf{r} n_i \left|\alpha_i^{\mathrm{orb}} - \alpha_i^{\mathrm{approx}}\right| \tag{39}$$

$$= \sum_i^M \frac{1}{N_i} \int d\mathbf{r} n_i \frac{\left|t_s^{\mathrm{orb}}[n_i] - t_s^{\mathrm{approx}}[n_i]\right|}{t_{TF}[n_i]}, \tag{40}$$

was suggested in Ref. [34]. Here M is the number of systems tested, N_i is the number of electrons in the ith system, and α is as in Eq. (5). Unfortunately, both σ and Δ_α tend to emphasize errors in a particular region and not over the whole space. σ has a strong bias to the core region where t_s is at its maximum, whereas Δ_α tends to favor the tail region where $\alpha \to \infty$. A more balanced indicator can be obtained by restricting the radial integration in Eq. (5) to a small sphere around the nuclei, yielding

$$\Delta_\alpha^{\mathrm{near}} = \sum_i^M \frac{4\pi}{N_i^{\mathrm{near}}} \int_0^4 dr\, r^2 n_i \left|\alpha_i^{\mathrm{orb}} - \alpha_i^{\mathrm{approx}}\right|, \tag{41}$$

where N_i^{near} denotes the fraction of electrons inside a sphere with a radius of 4 bohrs. The sphere radius was chosen to be sufficiently large to enclose all standard C, N, and O single bonds [53] and at the same time be sufficiently small to avoid divergence of α. Moreover, this choice of radius also encompasses many more bonds occurring in molecules and solids, hence should be sufficient for adequate transferability.

Post–self-consistent field (post-SCF) Δ_α and $\Delta_\alpha^{\mathrm{near}}$ values were obtained for the 18-neutral-atom test set. Table II shows Δ_α and $\Delta_\alpha^{\mathrm{near}}$ values for the PC, CR, and TFLreg mGGA functionals. On the assumption that those two error estimates are good indicators, those results point to the TFLreg functional as the potentially best performer in deorbitalizing a mGGA exchange-correlation functional, at least for those mGGAs in which orbital dependence arises solely from α.

TABLE II. Error indicator Δ_α values for various mGGA kinetic-energy density-functional approximations.

	Δ_α	$\Delta_\alpha^{\mathrm{near}}$
PC	0.470565	0.232595
CRloc	0.437642	0.185015
TFLreg	0.243281	0.152519

III. REPARAMETRIZATION OF KEDF

Unfortunately, some functionals with low Δ_α values may yield poor thermochemistry outcomes. (We discuss this below in the context of Tables V–VII.) To compensate for possible misassessment by Δ_α and/or $\Delta_\alpha^{\mathrm{near}}$, we reoptimized the parameters in all three functionals to minimize $\Delta_\alpha + \Delta_\alpha^{\mathrm{near}}$. Reoptimization was done post-SCF, again for the first 18 neutral atoms. The reoptimized functionals are named PCopt, CRopt, and TFLopt. For the PCopt functional, the parameters to be optimized were those of the $\theta_{PC}(z^{PC})$ interpolation function. For CRopt and TFLopt, the parameters to be optimized were the coefficients of the second-order gradient expansion, yielding

$$z^{\mathrm{CRopt}} = as^2 + bq - F_t^W \tag{42}$$

and

$$F_t^{\mathrm{TFLopt}} = \max\left(1 + as^2 + bq, F_t^{vW}\right), \tag{43}$$

respectively.

In addition, a new interpolation function

$$\theta_{\mathrm{TANH}}(z) = \{\tanh(|z|^{-8})[1 - H(z)] + H(z)\}^{1/8} \tag{44}$$

was used to define the new functional called TANH as

$$F_t^{\mathrm{TANH}} = 1 + F_t^W + z^{\mathrm{CRopt}}\theta_{\mathrm{TANH}}(z^{\mathrm{CRopt}}). \tag{45}$$

The motivation is that this form imitates closely the TFLopt functional without having the discontinuous derivative introduced by the max function in Eq. (43).

Parameter optimization used *Mathematica's* NMINIMIZE built-in procedure [54] with the Nelder-Mead method [55].

Table III shows $\Delta_\alpha + \Delta_\alpha^{\mathrm{near}}$ for each of the newly reparametrized functionals as well as the originals. The PC, PCopt, and CRloc functionals clearly are the worst performers.

TABLE III. Error indicator $\Delta_\alpha + \Delta_\alpha^{\mathrm{near}}$ values for the reoptimized mGGA$\{a,b\}$ kinetic-energy density-functional approximations.

	a	b	$\Delta_\alpha + \Delta_\alpha^{\mathrm{near}}$
PC	0.538900	3.000000	0.712057
PCopt	1.784720	0.258304	0.649567
CRloc	−0.275000	2.895000	0.631376
TFLreg	0.000000	2.222222	0.398936
CRopt	−0.295491	2.615740	0.383805
TANH	−0.216872	2.528000	0.365022
TFLopt	−0.203519	2.513880	0.361805

TABLE IV. Post-SCF noninteracting kinetic energy from various kinetic-energy density-functional approximations.

	He	Ne	Ar	Kr	Xe
PC	2.99305	129.3158	530.6552	2761.1804	7249.7497
PCopt	2.99491	123.5084	494.3828	2538.1368	6625.5351
CRloc	3.03627	126.7640	511.8635	2659.1147	6988.2001
CRopt	3.02671	125.9625	508.7109	2645.2305	6955.5975
TANH	2.90845	123.3855	503.7825	2633.6734	6938.1354
TFLreg	3.00568	128.6246	524.2290	2724.8688	7155.7830
TFLopt	2.88039	123.1157	503.5572	2634.4597	6941.5470
KS	2.86168	128.5471	526.8175	2752.0549	7232.1390

However, even though PCopt has the second-worst error indicator, it is not ignorable. The reason is that it retains almost all the asymptotic behavior of the original PC functional and, as a consequence, of α^{approx} as well. The only limiting behavior modified by the reparametrization is that F_t approaches $0.906485 + F_t^{\text{W}}$ instead of $1.0 + F_t^{\text{W}}$ when $|q| \to \infty$ (this is a direct consequence of a being larger than 1). Moreover, when Δ_α and $\Delta_\alpha^{\text{near}}$ are minimized independently, the optimized parameters for PCopt are almost identical for each case, suggesting balanced performance among core, valence, and tail density regions. This is not true for any of the other KEDFs.

At this point, it is important to reiterate that good performance for the chosen error indicators may not translate into correspondingly good performance in the total noninteracting KE. The converse also is true. Bad performers with respect to those error indicators may have beneficial error cancellation when integrated, thereby yielding a very good total noninteracting KE estimate. Post-SCF noninteracting kinetic energies listed in Table IV illustrate the point.

Also it is interesting to note that all KEDFs listed in Table IV enforce the von Weizsäcker bound; however, F_t^{W} is not exact at the nuclei of elements with occupied p orbitals [56]. Excluding PC and PCopt, which behave (approximately) as $1 + F_t^{\text{W}}$ at the nuclei, it is possible that the bad performance in the total noninteracting KE is due to the missing p-shell contribution, which can amount to 12% of the KE in the $Z \to \infty$ limit.

IV. MVS EXCHANGE FUNCTIONAL

We consider deorbitalizations of specific mGGAs, beginning with the mGGA "made very simple" (MVS) exchange functional [10].

The exchange energy can be written as

$$E_{\text{x}}[n] = \int n\, \varepsilon_{\text{x}}^{\text{unif}}\, F_{\text{x}}(s,\alpha)\, d\mathbf{r}, \tag{46}$$

where $\varepsilon_{\text{x}}^{\text{unif}} := -(3/4)(3n/\pi)^{1/3}$ is the uniform-electron-gas exchange energy per particle and $F_{\text{x}}(s,z,\alpha,\dots)$ is known as the enhancement factor. The MVS exchange enhancement factor $F_{\text{x}}^{\text{MVS}}(s,\alpha)$ disentangles the $\alpha[n]$ and s dependencies and respects several constraints, including the second-order gradient expansion for the slowly varying density with coefficient $\mu = 10/81$ and the asymptotic expansion of the exchange energy of neutral atoms. Explicitly,

$$F_{\text{x}}^{\text{MVS}}(s,\alpha) = \frac{1 + 0.174\, f_{\text{x}}(\alpha)}{(1 + 0.0233\, s^4)^{1/8}}, \tag{47}$$

where the function $f_{\text{x}}(\alpha)$ is given by

$$f_{\text{x}}(\alpha) = \frac{1-\alpha}{[(1 - 1.6665\,\alpha^2)^2 + 0.7438\,\alpha^4]^{1/4}}. \tag{48}$$

The MVS mGGA exchange is paired with the modified PBE GGA correlation used for the revised TPSS (revTPSS) functional [9].

Deorbitalized versions of the MVS mGGA exchange functional [10] were implemented in DEMON2K [57] and in NWCHEM [58]. The results quoted here are from NWCHEM; DEMON2K results are consistent. The NWCHEM calculations used the def2-TZVPP basis set [59] and extrafine grid settings. Details of the testing which led to the use of that grid are in Sec. VI. Heats of formation were computed according to the established procedure from Curtiss *et al.* [60] for the 223 molecules of the G3X/99 test set [61]. The T96-R set [62,63] was used to obtain the optimized bond lengths statistics, and the T82-F set [62,63] was used for the harmonic vibrational frequencies.

Table V presents the results for the two variants of each of the three deorbitalization candidates presented above. The PCopt and CRopt results are a striking example of an unexpected finding. The PCopt error results are reasonably close to the original MVS values, while the CRopt error magnitudes are substantially superior.

The difference illustrates two quite distinct deorbitalization objectives regarding a given mGGA XC functional. One is *faithful* deorbitalization, the other is *best-performance* deorbitalization. The faithful deorbitalization objective is to produce test-set results that are as nearly indistinguishable as possible from those of the original mGGA. The best performance objective is the deorbitalization that reduces the error magnitudes (on the original test sets) as much as feasible below the original mGGA results. Additional stipulations are that the number of fitting parameters in the deorbitalization should not be greatly in excess of the number in the original mGGA and that the fitting not be to the test sets themselves.

Perhaps it is no surprise that the most faithful MVS deorbitalization follows from the PCopt KEDF since that KEDF does not alter the gradient expansion of $\alpha[n]$ for slowly varying densities. That expansion was explicitly taken into account in the development of MVS. The very bad performance of TFLreg and TFLopt may be the consequence of several factors. First, imposition of the von Weizsäcker bound through the max function can introduce discontinuities in the potential, which in turn can lead to badly behaved densities. Second, TFLreg and TFLopt describe α very well inside the core region of the first 18 atoms but have the largest deviations, among the KEDFs tested, for the valence region of C.

As already noted, the best-performance deorbitalization was unanticipated. The finding regarding MVS is unequivocal, however. On these test sets at least, MVS is improved by conversion to a Laplacian-level functional, mGGA-L, rather than the conventional mGGA form in which it was developed. On the test sets considered, MVS-L delivers performance quite

TABLE V. Performance of the deorbitalized versions of the MVS exchange-correlation functional. Heat of formation errors are in kcal/mol, bond length errors are in angstroms, and frequency errors are in cm^{-1}.

	Error	PC	PCopt	TFLreg	TFLopt	CRloc	CRopt	MVS
Heats of formation	ME	24.00	−15.37	18.27	19.18	2.71	2.89	−17.33
	MAE	25.53	15.94	19.09	19.91	7.53	6.20	18.34
Bonds	ME	0.0069	−0.0025	0.0092	0.0072	0.0025	0.0049	−0.0016
	MAE	0.0137	0.0127	0.0139	0.0139	0.0121	0.0130	0.0139
Frequencies	ME	2.9	39.3	9.6	20.0	25.3	28.7	46.2
	MAE	29.4	46.0	34.7	37.7	37.0	42.6	52.0

similar to the highly sophisticated strongly constrained and appropriately normed (SCAN) mGGA functional.

V. TPSS EXCHANGE-CORRELATION FUNCTIONAL

Of the three mGGAs considered for deorbitalization, the TPSS exchange-correlation functional [4] is the most challenging case. It has orbital dependence in both exchange and correlation terms. Moreover, the TPSS exchange enhancement factor $F_{\rm x}^{\rm TPSS}(s,z,\alpha)$ has the additional complication of being dependent on two orbital-dependent dimensionless ratios, $z[n]$ and $\alpha[n]$. Such complication does not occur in either MVS (compare above) or SCAN (compare below) enhancement factors. The TPSS exchange enhancement factor is given by

$$F_{\rm x}^{\rm TPSS}(s,z,\alpha) = 1 + \kappa - \frac{\kappa^2}{\kappa + x(s,z,\alpha)}, \tag{49}$$

where

$$x = \left\{ \left[\mu_{\rm GE} + c\frac{z^2}{(1+z^2)^2} \right] s^2 + \frac{146}{2025}\tilde{q}_b^2 - \frac{73}{405}\tilde{q}_b\sqrt{\frac{1}{2}\left(\frac{3}{5}z\right)^2 + \frac{1}{2}s^4} + \frac{\mu_{\rm GE}^2}{\kappa}s^4 + 2\sqrt{e}\mu_{\rm GE}\left(\frac{3}{5}z\right)^2 + e\mu_{\rm PBE}s^6 \right\} \Big/ (1+\sqrt{e}s^2)^2 \tag{50}$$

and

$$\tilde{q}_b = \frac{\frac{9}{20}(\alpha - 1)}{[1 + b\alpha(\alpha-1)]^{1/2}} + \frac{2}{3}s^2. \tag{51}$$

The constants $\kappa = 0.804$, $\mu_{\rm GE} = 10/81$, $\mu_{\rm PBE} = 0.21951$, $b = 0.40$, $c = 1.59096$, and $e = 1.537$ were fixed by imposition of several conditions.

TPSS correlation has slightly simpler orbital dependence in that it depends only on the dimensionless ratio z. It can be written as

$$E_c[n] = \int n\,\epsilon_c^{\rm TPSS}\,d\mathbf{r}, \tag{52}$$

where

$$\epsilon_c^{\rm TPSS} = \epsilon_c^{\rm revPKZB}\left[1 + 2.8z^3\epsilon_c^{\rm revPKZB}\right]. \tag{53}$$

The revised PKZB correlation energy $\epsilon_c^{\rm revPKZB}$ is an mGGA itself, which is given by

$$\epsilon_c^{\rm revPKZB} = \epsilon_c^{\rm PBE}[1 + C(\zeta,\xi)z^2] - [1 + C(\zeta,\xi)]z^2\sum_\sigma \frac{n_\sigma}{n}\tilde{\epsilon}_c^\sigma, \tag{54}$$

with

$$C(\zeta,\xi) = \frac{0.53 + 0.87\zeta^2 + 0.50\zeta^4 + 2.26\zeta^6}{\{1 + \xi^2[(1+\zeta)^{-4/3} + (1-\zeta)^{-4/3}]/2\}^4}, \tag{55}$$

$$\zeta = \frac{n_\uparrow - n_\downarrow}{n}, \quad \xi = \frac{\nabla\zeta}{2(3\pi^2 n)^{1/3}}, \tag{56}$$

and

$$\tilde{\epsilon}_c^\sigma = \max\left[\epsilon_c^{\rm PBE}(n_\uparrow,n_\downarrow,\nabla n_\uparrow,\nabla n_\downarrow),\epsilon_c^{\rm PBE}(n_\sigma,0,\nabla n_\sigma,0)\right]. \tag{57}$$

Here $\epsilon_c^{\rm PBE}$ is the PBE (GGA) correlation energy per particle [64].

Table VI presents the results for the deorbitalized TPSS variants. It did not prove possible to achieve a best-performance case with any of the KEDF candidates we examined. The most nearly faithful case was obtained through the TFLreg KEDF. That KEDF provides the most balanced behavior for describing both $z[n]$ and $\alpha[n]$. Even that deorbitalization is not entirely successful in that all of its MAE values are worse than those from the original TPSS. Nevertheless, TPSS-L (with TFLreg) may be good enough to be useful in the simulation context.

TABLE VI. The same as in Table V for the deorbitalized versions of the TPSS exchange-correlation functional.

	Error	PC	PCopt	TFLreg	TFLopt	CRloc	CRopt	TPSS
Heats of formation	ME	10.13	13.51	1.14	7.45	12.65	9.15	−4.37
	MAE	12.29	15.61	6.24	10.86	15.05	11.89	5.28
Bonds	ME	0.0212	0.0215	0.0209	0.0214	0.0224	0.0217	0.0134
	MAE	0.0215	0.0217	0.0209	0.0217	0.0224	0.0218	0.0156
Frequencies	ME	−42.7	−44.5	−42.5	−44.2	−46.5	−45.2	−18.3
	MAE	49.6	50.2	47.5	49.5	51.4	50.0	31.2

TABLE VII. The same as in Table V for the deorbitalized versions of the SCAN exchange-correlation functional.

	Error	PC	PCopt	TFLreg	TFLopt	CRloc	CRopt	SCAN
Heats of formation	ME	17.57	2.11	56.91	63.60	14.82	7.75	−3.62
	MAE	19.99	5.67	57.23	63.97	16.70	14.81	5.12
Bonds	ME	0.0158	0.0073	0.0198	0.0190	0.0140	0.0168	0.0035
	MAE	0.0189	0.0105	0.0220	0.0221	0.0155	0.0181	0.0089
Frequencies	ME	−38.5	−11.7	−47.8	−43.2	−27.7	−29.8	15.3
	MAE	49.3	28.7	54.5	51.2	38.5	38.6	31.9

VI. SCAN EXCHANGE-CORRELATION FUNCTIONAL

The SCAN exchange-correlation functional is said to provide the best overall performance among all nonempirical mGGAs developed so far. Its orbital dependence comes from $\alpha[n]$ alone for both exchange and correlation, making it a good deorbitalization candidate.

The SCAN exchange enhancement factor is given by

$$F_{\mathrm{x}}^{\mathrm{SCAN}}(s,\alpha) = \{h_x^1(s,\alpha) + f_x(\alpha)[1.174 - h_x^1(s,\alpha)]\}g_x(s), \tag{58}$$

with

$$g_x(s) = 1 - e^{-a_1/\sqrt{s}} \tag{59}$$

and

$$f_x(\alpha) = e^{-c_{1x}\alpha/(1-\alpha)}\theta(1-\alpha) - d_x e^{c_{2x}/(1-\alpha)}\theta(\alpha - 1). \tag{60}$$

The remaining function $h_x^1(s,\alpha)$ is an approximate resummation of the fourth-order gradient expansion for exchange:

$$h_x^1(s,\alpha) = 1 + \frac{k_1 x}{k_1 + x}, \tag{61}$$

where

$$x = \mu_{\mathrm{GE}}s^2\left[1 + \frac{b_4 s^2}{\mu_{\mathrm{GE}}}e^{-b_4 s^2/\mu_{\mathrm{GE}}}\right] + [b_1 s^2 + b_2(1-\alpha)e^{-b_3(1-\alpha)^2}]^2. \tag{62}$$

The constants $a_1 = 4.9479$, $\mu_{\mathrm{GE}} = 10/81$, $b_2 = \sqrt{5913/405000}$, $b_1 = (511/13500)/(2b_1)$, $b_3 = 0.5$, $b_4 = \mu_{\mathrm{GE}}^2/k_1 - 1606/18225 - b_1^2$, $c_{1x} = 0.667$, $c_{2x} = 0.8$, $d_x = 1.24$, and $k_1 = 0.065$ were determined by imposition of known constraints or norms.

The correlation part of SCAN depends on $\alpha[n]$ only through

$$f_c(\alpha) = e^{-c_{1c}\alpha/(1-\alpha)}\theta(1-\alpha) - d_c e^{c_{2c}/(1-\alpha)}\theta(\alpha - 1), \tag{63}$$

where $c_{1c} = 0.64$, $d_c = 0.7$, and $c_{2c} = 1.5$. The interpolation function f_c interpolates between two revised PBE correlation energies per particle, ϵ_c^0 and ϵ_c^1, valid for $\alpha = 0$ and $\alpha = 1$, respectively:

$$E_c^{\mathrm{SCAN}} = \int d\mathbf{r}\, n[\epsilon_c^1 + f_c(\alpha)(\epsilon_c^0 - \epsilon_c^1)]. \tag{64}$$

Results from the deorbitalization of SCAN are shown in Table VII. One sees that the faithful case is essentially achieved by the PCopt functional, with performance very similar to that of the original SCAN for thermochemistry and bond lengths and slightly better performance for harmonic vibrational frequencies than the orbital-dependent SCAN. No example of a best-performance deorbitalization occurred within the range of candidate KEDFs. The faithful deorbitalization is remarkable nevertheless: SCAN-L with PCopt is just about as good as SCAN on these standard test sets.

A subtlety is involved in the computational implementations of SCAN that we have studied. The exchange contribution is computed using the spin-scaling relation, $E_x[n_\uparrow,n_\downarrow] = \frac{1}{2}(E_x[2n_\uparrow] + E_x[2n_\downarrow])$, which means that

$$\alpha_\sigma = \frac{2t_s^\sigma - t_W[2n_\sigma]}{t_{TF}[2n_\sigma]}. \tag{65}$$

However, α in the correlation contribution is computed as (see the Supplemental Material of Ref. [11])

$$\alpha = \frac{t_s - t_W[n]}{\frac{1}{2}[(1+\zeta)^{5/3} + (1-\zeta)^{5/3}]t_{TF}[n]} = \frac{\frac{1}{2}\sum_\sigma 2t_s^\sigma - t_W[n]}{\frac{1}{2}\sum_\sigma t_{TF}[2n_\sigma]}. \tag{66}$$

Note that in the latter case, α uses the spin-scaling relation except for the von Weizsäcker piece (this mismatch was confirmed by reproducing Table SIV from the Supplemental Material of Ref. [11]). As a consequence, a deorbitalization

TABLE VIII. Grid size sensitivity for SCAN and SCAN-L (PCopt).

		SCAN			SCAN-L		
	Error	Medium	Fine	Extrafine	Medium	Fine	Extrafine
Heats of formation	ME	−4.04	−3.61	−3.62	1.45	2.14	2.11
	MAE	5.76	5.13	5.12	5.90	5.71	5.67
Bonds	ME	0.0035	0.0036	0.0035	0.0074	0.0072	0.0073
	MAE	0.0089	0.0090	0.0089	0.0108	0.0106	0.0105
Frequencies	ME	25.1	15.2	15.3	−9.3	−3.0	−11.7
	MAE	42.9	33.5	31.9	41.3	33.4	28.7

TABLE IX. Basis-set sensitivity for SCAN and SCAN-L (PCopt). Double (SVP), triple (TZVPP), quadruple (QZVPP), and complete-basis-set extrapolation (CBS) error values are shown.

		SCAN				SCAN-L			
	Error	SVP	TZVPP	QZVPP	CBS	SVP	TZVPP	QZVPP	CBS
Heats of formation	ME	−7.06	−3.62	−4.09	−4.15	−6.44	2.11	2.63	2.71
	MAE	11.48	5.12	5.32	5.35	10.67	5.67	5.67	5.68
Bonds	ME	0.0129	0.0035	0.0018		0.0150	0.0073	0.0057	
	MAE	0.0189	0.0089	0.0081		0.0193	0.0105	0.0095	
Frequencies	ME	21.9	15.3	16.5		00.0	−11.7	−9.6	
	MAE	41.7	31.9	32.3		34.0	28.7	30.8	

with higher fidelity might be obtained if the KEDF were to be optimized separately for exchange and correlation.

Exploration of SCAN-L (PCopt) illustrates issues of behaviors with respect to changes in the numerical integration grid or basis-set size, which we encountered repeatedly. Tables VIII and IX compare the results from the original SCAN and the SCAN-L (PCopt) functional for grid and basis-set changes, respectively.

The results in Table VIII were obtained with the def2-TZVPP basis set for three levels of grid quality predefined in NWCHEM. Use of the default grid quality, *medium*, led to SCF convergence issues that rendered the medium option clearly inappropriate for both original SCAN and SCAN-L. The *fine*-quality grid produces well-converged results for all test sets in the case of original SCAN. It also does well for the thermochemistry and bond-length sets with SCAN-L but does not work for the vibrational frequencies set. The same behavior was observed for the deorbitalized versions of MVS and TPSS: the *extrafine* grid quality was needed in order to ensure converged vibrational frequencies with the Laplacian-dependent functionals.

On the other hand, SCAN and SCAN-L both have the same behavior with respect to increasing the basis-set cardinality. They yield oscillatory behavior in the heats of formation and vibrational frequency errors along with a steady shortening of bond-length errors when changing from double- to triple- to quadruple-zeta basis sets. Also shown in Table IX are extrapolations to the complete-basis-set limit obtained with a linear extrapolation of the SCF energy [65,66]. Those extrapolations indicate that the def2-TZVPP results are about 0.5 kcal/mol from the basis-set limit for both original SCAN and SCAN-L.

VII. CONCLUSIONS

We have shown that it is possible to reduce the complexity yet retain the quality of some mGGAs by deorbitalization. To remove the orbital dependence, a kinetic-energy density functional which reproduces as closely as possible the relevant orbital-dependent dimensionless variable must be selected. We recommend the PC, CRloc, and TFLreg KEDFs, along with their respective reparametrizations, as the ones most likely to succeed.

We emphasize that none of the parametrization is to experimental data or to data from outside the domain of DFT. Rather, it is parametrization of approximate KEDFs to deliver (post-SCF) values of the noninteracting KE of the first 18 atoms as close possible to the KE values obtained from the (post-SCF) orbitals on those atoms.

We have delineated the difference between faithful and best-performing deorbitalizations. In the faithful case, the result is a Laplacian-level functional that recovers essentially the same properties for finite systems as from the original. Because the Laplacian-level functional obviates the use of generalized-KS equations, in principle it is computationally more efficient than calculation with the original mGGA. Moreover, the deorbitalized functional also gives an approximate rendition of the local potential that the OEP would give for the original functional. We have not explored exploitation of this last fact.

The best-performance deorbitalization was unexpected. When it can be achieved, the resulting Laplacian-level functional actually combines better numerical results with a less complicated, less computationally demanding functional than the original mGGA. This outcome is an illustration that the putative relationship between the rung of the Perdew-Schmidt Jacob's ladder of functional complexity and performance is not as direct and unambiguous as seems to be widely believed. The computational complexity advantage gained by best-performance deorbitalization is the same as for the faithful case.

Functionals with orbital dependences from two dimensionless ratios, such as TPSS, pose serious challenges to the deorbitalization scheme presented here. Because of that TPSS complexity, other deorbitalization approaches might yield better results than those obtained here. For example, it would be possible to reparametrize the KEDFs to minimize an error indicator based on $z[n]$ or reparametrize using error measures based on both $\alpha[n]$ and $z[n]$ concurrently. Different deorbitalization KEDFs might be used for exchange and correlation. These routes were not explored since one of the objectives of this initial study was to keep the deorbitalization strategy as simple as possible.

On the other hand, MVS and SCAN, which depend only on $\alpha[n]$, are demonstrably very good candidates for deorbitalization. In particular, SCAN-L, the PCopt deorbitalized SCAN, seems to be the most accurate XC functional presently available for use in either true KS (not generalized KS) calculations or orbital-free DFT calculations.

Although the proposed deorbitalized functionals are Laplacian dependent, their computational stability is comparable to that of standard mGGA functionals. Roughly the same number of self-consistent field cycles, as well as geometry optimization steps, were needed to converge the standard and de-deorbitalized versions of three functionals tested. The one exception to this general comparability is the requirement of extrafine grids.

The main drawback of the Laplacian-dependent functionals for molecular calculations as we have done them so far comes from computing the Laplacian of the density, as well as the matrix elements from the exchange-correlation potential. These cause a noticeable performance impact. That impact arises from the need for higher-order derivatives of the basis functions. Our tests were implemented without concern for calculational efficiency, that is to say, in the simplest way possible. Thus we used extant coding where possible. In NWCHEM, for example, this means that we compute the nonredundant part of the Hessian matrix for each basis function, instead of only the three relevant second-order derivatives. If deorbitalization were to be accepted as part of the computational strategy, this impact could be ameliorated substantially by writing optimized code which computes only the relevant derivatives (trace of the Hessian).

We note that corresponding performance degradation is not expected to occur in periodic system computations because the Laplacian terms can be computed with no significant cost in Fourier space. We are refining and testing the present deorbitalization schemes on such systems at this writing.

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