Many density functionals are numerically ill-behaved

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Most computational studies in chemistry and materials science are based on the use of density functional theory. Although the exact density functional is unknown, several density functional approximations (DFAs) offer a good balance of affordable computational cost and semi-quantitative accuracy for applications. The development of DFAs still continues on many fronts, and several new DFAs aiming for improved accuracy are published every year. However, the numerical behavior of these DFAs is an often overlooked problem. In this work, we look at all 592 DFAs for three-dimensional systems available in Libxc 5.2.2 and examine the convergence of the density functional total energy based on tabulated atomic Hartree–Fock wave functions. We show that several recent DFAs, including the celebrated SCAN family of functionals, show impractically slow convergence with typically used numerical quadrature schemes, making these functionals unsuitable both for routine applications or high-precision studies, as thousands of radial quadrature points may be required to achieve sub-$\mu E_h$ accurate total energies for these functionals, while standard quadrature grids like the SG-3 grid only contain $O(100)$ radial quadrature points. These results are both a warning to users to always check the sufficiency of the quadrature grid when adopting novel functionals, as well as a guideline to the theory community to develop better behaved density functionals.

I. INTRODUCTION

Computational studies in chemistry and materials science are typically based on the use of density functional theory (DFT). The reason for the usefulness of this theory is that the complicated quantum mechanical interactions between the electrons can be reduced to consideration of the electron density, only, thus making calculations much simpler and more affordable than those with traditional wave function methods.

Fully numerical methods have recently enabled reliable computations of DFT total energies for moderate sized systems to sub-microhartree accuracy, that is, at the complete basis set (CBS) limit. However, in order for fully numerical calculations to be tractable, the density functional approximations (DFAs) used in the calculations have to be well-behaved. Our (S.L.) recent results on the determination of total atomic energies at the CBS limit with fully numerical methods with meta-GGA functionals along the lines of refs. [13] and [14] suggest that many functionals—including recent ones—are problematic in this aspect.

Determining accurate total energies with fully numerical methods requires being able to run self-consistent field (SCF) calculations in extended basis sets that approach the CBS limit. While the SCF procedure can be carried out using various techniques, such as Roothaan’s method of iterative diagonalization or orbital rotation techniques, for example, regardless of the employed approach, the determination of reliable CBS limit total energies requires the ability to

1. evaluate the total energy accurately for a fixed electron density, as in an individual SCF step,
2. converge the iterative SCF procedure tightly in a given one-particle basis set, yielding an optimized density and total energy in the fixed basis, and
3. smoothly converge the total energy to the CBS limit by running SCF calculations in a systematic sequence of larger and larger one-particle basis sets, eventually reaching a value converged to sub-$\mu E_h$ precision.

The above three criteria can be used to study density functional approximations. It is already known that many functionals fail the latter two requirements. For instance, the local $\tau$ approximation of Ernzerhof and Scuseria, and related functionals, produce diverging potentials which complicates SCF calculations even in small basis sets, thereby breaking criterion 2. Next, many Minnesota functionals are known to exhibit pathologically slow convergence to the CBS limit breaking criterion 3. For instance, unexpectedly large $m E_h$ level basis set truncation errors in standard quadruple-\(\zeta\) Gaussian basis sets in their uncontracted form were recently observed for the M11-L functional already for hydrogen, while the truncation errors for well-behaved functionals were found to be around two orders of magnitude smaller.

We will show in this work that many recent functionals fail already for criterion [1] which precedes any SCF calculation. Using tabulated Hartree–Fock wave functions for atoms, we demonstrate that the total energies obtained with standard sized quadrature grids are unreliable. Although reliable total energies can be obtained in principle by using uncustomarily large quadrature grids, we
show that several functionals like the celebrated SCAN family, require impractically many radial quadrature points (thousands instead of around one hundred) to converge to the level of accuracy expected in routine applications of quantum chemistry, as the default SCF convergence settings in most programs require evaluating total energies to sub-μEh precision. As polyatomic systems like molecules and crystals are made from atoms, the issues found in this work also have ramifications to practical applications of these density functionals, suggesting that more work is needed to develop accurate functionals that satisfy all of the three criteria given above.

The layout of this work is as follows. A brief summary of our approach are discussed in section §IV. A summary is presented in section §V, followed by discussion. Atomic units are used throughout unless specified otherwise.

II. THEORY

In DFT, the total energy is expressed as

\[ E[n_\uparrow, n_\downarrow] = T[n_\uparrow, n_\downarrow] + V[n] + E_J[n] + E_{xc}[n_\uparrow, n_\downarrow], \]

where \( n_\uparrow \) and \( n_\downarrow \) are the spin-up and spin-down electron densities and \( n = n_\uparrow + n_\downarrow \) is the electron density, \( T \) is the kinetic energy (typically evaluated in terms of the occupied orbitals as suggested by Kohn and Sham [2]), \( V \) is the nuclear attraction energy, \( E_J \) is the classical Coulomb repulsion of the electrons, and \( E_{xc} \) is the quantum mechanical exchange-correlation energy. Common DFAs express \( E_{xc} \) as

\[ E_{xc}[n] = \int n \epsilon_{xc}(n_\uparrow, n_\downarrow, \gamma_\uparrow \uparrow, \gamma_\downarrow \downarrow, \gamma_\uparrow \downarrow, \gamma_\downarrow \uparrow, \nabla^2 n_\uparrow, \nabla^2 n_\downarrow, \tau_\uparrow, \tau_\downarrow) d^3r, \]

where \( \gamma_{\sigma\sigma'} \) are reduced gradients

\[ \gamma_{\sigma\sigma'} = \nabla n_{\sigma} \cdot \nabla n_{\sigma'}, \]

and \( \tau_\uparrow \) and \( \tau_\downarrow \) are the local kinetic energy densities

\[ \tau_\sigma = \frac{1}{2} \sum_{\text{occupied}} |\nabla \psi_\sigma|^2, \]

and \( \sigma \) and \( \sigma' \) are a spin indices. The \( \epsilon_{xc} \) term in equation (2) is the DFA, which is a (often complicated) mathematical function with known analytical form. DFAs can be classified on Jacob’s ladder [20] based on their ingredients:

- local density approximation (LDA): dependence only on the electron density \( n_\uparrow \) and \( n_\downarrow \)
- meta-LDA approximation [21] dependence on \( n_\uparrow \) and \( n_\downarrow \) as well as the local kinetic energy density \( \tau_\uparrow \) and \( \tau_\downarrow \)
- generalized-gradient approximation (GGA): dependence on \( n_\uparrow \) and \( n_\downarrow \) as well as their gradients \( \nabla n_\uparrow \) and \( \nabla n_\downarrow \) through \( \gamma_{\sigma\sigma'} \)
- meta-GGA approximation: further dependence on the Laplacian \( \nabla^2 n_\uparrow, \nabla^2 n_\downarrow \), and/or \( \tau_\uparrow, \tau_\downarrow \)

In addition to a term of the form of equation (2), many common DFAs also add post-DFT terms such as

- exact exchange in either the full Hartree–Fock (global hybrids, e.g. the B3LYP functional [31] or range-separated form (range-separated hybrids, e.g. the \( \omega B97X \) functional [32])
- non-local correlation (e.g. \( \omega B97X-N \)) or semiempirical dispersion (e.g. the \( \omega B97X-D3 \) functional [33])
- post-Hartree–Fock correlation (double hybrids, e.g. the XYZG3 functional [34])

These additional ingredients will not be discussed further in this work as they are not thought to present major issues with numerical behavior. Instead, the issues with numerical ill behavior arise mainly from equation (2).

For completeness, we note here that local hybrid functionals, which include a position-dependent DFA-type fraction of exact exchange energy density, have also been suggested [35,36]. However, as i) there are fewer local hybrids than functionals that fit in the above classification, ii) local hybrids have not become widely used, and iii) the analysis of numerical ill behavior in local hybrids is not as straightforward to study as that arising from equation (2), we do not consider local hybrid functionals in this work.

Programs that employ atomic orbital basis sets typically evaluate equation (2) using the multicenter quadrature approach developed by Becke [37]. By inserting a resolution of the identity

\[ \sum_A w_A(r) = 1 \]

in terms of atomic weight functions \( w_A(r) \), the integral in equation (2) can be evaluated as a sum of atom-centered integrals

\[ \int f(r) d^3r = \sum_A \int_A f(r) w_A(r) d^3r, \]

The atom-centered integrals are evaluated on a grid obtained as the tensor product of a radial quadrature grid [38,39]

\[ \int_0^\infty r^2 f(r) dr \approx \sum_p w_p f(r_p) \]

and an angular grid

\[ \int f(\Omega) d\Omega \approx \sum_q w_q f(\Omega_q) \]
which is almost invariably a Lebedev grid\textsuperscript{19,63}, although other types of grids have also been suggested\textsuperscript{43,54}. Note that programs that do not employ atomic-orbital basis sets also use quadrature to evaluate equation (2), meaning that any ill behavior found in this work may have ramifications to also such other approaches.

Regardless of the approach used, the quadrature error in equation (2) can be made negligible by using sufficiently many points. Our hypothesis is that the convergence of the quadrature with the number of points is intimately related to the numerical well-behavedness of the DFA. This leads to the question if the calculation converges quickly enough for the DFAs that are currently available to allow the determination of total energies with high precision.

III. COMPUTATIONAL DETAILS

A. Radial quadrature

Our main focus is the study of the numerical well-behavedness of equation (2) based on tabulated atomic Hartree–Fock wave functions. In the case of a single atom, the Becke weighting yields an unit weight. The electron density arising from the Hartree–Fock wave function is assumed to be spherically symmetric, $n_x(r) = n_x(r)$, and the integral in equation (2) thus reduces to a radial one

$$E_{xc}[n] = 4\pi \int_0^\infty r^2 n_x(n_\uparrow, n_\downarrow, \ldots) dr. \quad (9)$$

We evaluate this integral by $N$-point quadrature

$$E_{xc}(N) = 4\pi \sum_{i=1}^N w_i r_i^2 n_x(n_\uparrow, n_\downarrow, \ldots). \quad (10)$$

Several kinds of radial quadratures are considered. Each type of quadrature is expressed as a coordinate transformation $r = r(x)$ from a primitive quadrature coordinate $x$. The primitive quadrature can be over $x \in [-1, 1]$ or $x \in [0, 1]$, depending on the rule.

Note that most rules were originally developed in combination with atomic size adjustments, $r = r(x) \rightarrow r = R r(x)$, where $R$ is an element specific parameter, as in the original scheme of Becke\textsuperscript{40}. The atomic scaling changes the radii linearly $r_i \rightarrow R r_i$ and the weights cubically $w_i \rightarrow R^3 w_i$. As the quadratures anyway approach exactness with $N \rightarrow \infty$ quadrature points, for simplicity we do not consider size adjustments in this work and set $R = 1$.

The following radial schemes will be considered:

1. The M4 grid of Treutler and Ahlrichs\textsuperscript{44}, again with the atomic scaling parameter set to $\xi = 1$

$$r = \frac{1}{\ln 2} \ln \frac{2}{1 - x} \quad \text{with} \quad x \in [-1, 1]. \quad (12)$$

2. The M4 grid of Treutler and Ahlrichs\textsuperscript{44}, with the atomic scaling parameter set to $\xi = 1$

$$r = \frac{1}{\ln 2} \left(1 + x\right)^\alpha \ln \frac{2}{1 - x} \quad \text{with} \quad x \in [-1, 1] \text{ and where } \alpha = 0.6 \text{ is the optimized value of Treutler and Ahlrichs\textsuperscript{43}}, \text{ the case } \alpha = 0 \text{ reduces to the M3 quadrature of equation (11).}$$

3. The scheme of Murray, Handy, and Laming\textsuperscript{43} is given by

$$r = \left(\frac{x}{1 - x}\right)^2 \quad \text{with} \quad x \in [0, 1]; \text{ this transform was originally introduced by Handy and Boys\textsuperscript{55}}. \text{ This scheme is commonly referred to as Euler–Maclaurin quadrature.}$$

4. The Mura and Knowles\textsuperscript{45} scheme

$$r = -\log(1 - x^m) \quad \text{with} \quad x \in [0, 1] \text{ and } m = 3 \text{ which is the recommended value for molecular systems.}$$

These schemes were chosen to be representative of quantum chemistry programs in general: by default, scheme 1 is used in ERKALE\textsuperscript{56} and ORCA\textsuperscript{27} scheme 2 is used in TURBOMOLE\textsuperscript{55}, Psi4\textsuperscript{50} and PySCF\textsuperscript{60}, scheme 3 is used in Gaussian\textsuperscript{61} and Q-Chem\textsuperscript{62} and scheme 4 is used in Molpro\textsuperscript{53} and NWChem\textsuperscript{54} for example. Other types of radial grids have also been proposed\textsuperscript{46,47,65–71}, but the four schemes above suffice for the present purposes.

Gauss–Chebyshev quadrature over $x$ was used in the pioneering work by Becke\textsuperscript{40}, who preferred this quadrature over others thanks to its quadrature points and weights being given by simple analytical formulas. Gauss–Chebyshev quadrature was likewise used by Treutler and Ahlrichs\textsuperscript{44}. However, equations for the quadrature rules were not provided in refs. 40 and 44. In contrast, the scheme of Murray, Handy, and Laming\textsuperscript{43} relies on the special properties\textsuperscript{55} of equation (13) in combination with the Euler–Maclaurin quadrature formula to obtain a simple quadrature rule that coincides with the trapezoidal rule\textsuperscript{55}.

In this work, the primitive $N$-node quadratures in $x$ are generated with closed-form Gauss–Chebyshev quadrature formulas of the second kind given by Pérez-Jordá, Becke, and San-Fabián\textsuperscript{22}, see their equations (31)–(33) [N.B. this is not the rule used for radial quadrature in ref. \textsuperscript{72}], unless specified otherwise. The weights are derived from Gauss–Chebyshev quadrature formulas, $\int_{-1}^1 f(x) \sqrt{1 - x^2} dx = \sum_{i=1}^N w_i f(x_i)$ with $x_i = \cos(\pi i/(N+1))$ and $w_i = \pi \sin^2(\pi i/(N+1))/(N+1)$ with a change of variables that converts the rule to the form with a unit weight function, $\int_{-1}^1 f(x) dx = \sum_{i=1}^N w_i f(x_i)\textsuperscript{22}$.
The quadrature for \( x \in [0, 1] \) for schemes 3 and 4 is obtained by the change of variables \( x \to x' = (1 + x)/2 \).

For comparison, we also examine trapezoidal quadrature for schemes 3 and 4. Scheme 4 was originally described with such a rule, and Gill and Chien\(^{55}\) describe scheme 4 to likewise use trapezoidal quadrature. Trapezoidal nodes and weights for \( x \in [0, 1] \) given by \( x_i = i/(N + 1) \) and \( w_i = 1/(N + 1) \) were used with \( i \in [1, N] \) the corresponding rule for \( x \in [-1, 1] \) is \( x_i = 1 - 2i/(N + 1) \) with \( w_i = 2/(N + 1) \).

We examine the numerical well-behavedness of DFAs by studying the convergence of the energy given by equation (9) with the number of quadrature points within each radial scheme. As was already mentioned in section III, the motivation for this approach is that it is widely used in DFT calculations for molecular and solid state systems, and any results from this work therefore immediately generalize into a larger context. For example, electronic structure calculations are often started from either atomic densities\(^{74,75}\) or atomic potentials\(^{76}\); the use of tabulated Hartree–Fock densities corresponds to the former approach and quadrature errors in the total energy seen for gas-phase atoms will also be observable for the superposition of atomic densities in polyatomic calculations.

Equation (10) should show robust convergence for well-behaved DFAs. This means that it should be possible to bound the quadrature error to be smaller than a preset threshold \( \epsilon \) as

\[
|E_{xc}(N) - E_{xc}^{\text{ref}}| \leq \epsilon
\]  

for all \( N \geq N' \) given some suitable choice of \( N' \) (which depends on the chosen value for \( \epsilon \), with the reference value \( E_{xc}^{\text{ref}} \) in equation (13) being given by the exact value of the integral that should be obtainable at the limit

\[
E_{xc}^{\text{ref}} = \lim_{N \to \infty} E_{xc}(N).
\]  

It is easy to see from equation (15) that the difference

\[
\delta(N_1, N_2) = |E_{xc}(N_1) - E_{xc}(N_2)|
\]  

should also be bounded by an arbitrarily small value for sufficiently large \( N_1 \) and \( N_2 \), that is, whenever \( N_1, N_2 \geq N' \). However, we will demonstrate later in this work that the measure \( \delta \) is not small for many recent DFAs.

### B. Atomic wave functions

The best known example of tabulated Hartree–Fock wave functions is the seminal work of Clementi and Roetti\(^{27}\). However, the Clementi–Roetti wave functions are inconvenient, because the tables are not in machine readable format and thus require error-prone parsing. Moreover, the Clementi–Roetti wave functions have limited accuracy—they are given at fixed precision with five decimals—and are deficient for heavy atoms: Koga, Tatewaki, and Thakkar\(^{75}\) reported reoptimized wave functions with energies improved by as much as 53 \( mE_h \) (for Cd), while Koga et al.\(^{79}\) found few-\( mE_h \) improvements over Clementi and Roetti for all cations and anions with \( Z \geq 37 \) as well as a staggering \( 1.8 \) \( E_h \) decrease for \( Tc^- \).

Better-quality wave functions have been since published. Koga et al.\(^{80}\) reported wave functions for light elements with \( mE_h \) truncation errors over numerical Hartree–Fock (NHF) calculations, while Koga et al.\(^{81}\) reported wave functions for heavy elements with \( mE_h \) level truncation errors compared to NHF. Although the Hartree–Fock wave functions of Koga et al.\(^{80}\) and Koga et al.\(^{81}\) are also reported at fixed precision, the tabulation including 7 decimals, the wave functions are sufficient for the purposes of this work.

The wave functions of Koga et al.\(^{80}\) and Koga et al.\(^{81}\) are available\(^{82}\) in a simple and easy-to-use Python package called AtomicOrbitals.\(^{83}\) AtomicOrbitals allows for easy access to the atomic density data that can be stored to disk and read into custom implementations of novel DFAs. As part of this work, AtomicOrbitals was interfaced to Libxc, and the quadrature approaches discussed in section IIIA were implemented therein.

### IV. RESULTS

In our experience, lithium and nitrogen are often especially hard cases for many functionals, as the electron density ranges from essentially full spin restriction at the nucleus to full spin polarization far away, where the electron density is dominated by the slowest decaying orbital which is only partially occupied. An analysis of the 592 functionals for three-dimensional systems in Libxc 5.2.2 was performed for the lithium, nitrogen, neon, sodium, phosphorus, and argon atoms with the tabulated Hartree–Fock wave functions of Koga et al.\(^{80}\) These atoms all have either closed-shell or half-closed "S ground states, meaning that their ground state naturally has a spherically symmetric electron density.

We will base our analysis on the difference (equation (17)) of the \( N \)-point quadrature formula from the 2501-point quadrature formula

\[
|\Delta E(N) = \delta(N, 2501) = |E_{xc}(N) - E_{xc}(2501)|.
\]  

As discussed in section IIIA this measure can be expected to be reasonable for well-behaved density functionals.

This analysis, performed by visual examination of plots of \( \Delta \), revealed many interesting results. Due to the large number of examined functionals, figures are shown in the main text only for the key points of our discussion. We will also mostly limit the discussion to functionals with numerical ill behavior greater than 1 \( nE_h \), as energy differences smaller than this are not thought to cause concern even for high-precision applications. The full set of figures is available in the Supporting Information (SI).
Our first and main finding is that “well-behaved” DFAs exhibit fast convergence. For example, the LDA\textsuperscript{83,84,85}, the Perdew–Burke–Ernzerhof\textsuperscript{86,87,88,89} (PBE) GGA, the Tao–Perdew–Scuseria–Staroverov\textsuperscript{85,89} (TPSS) meta-GGA, as well as the recent TASK\textsuperscript{90} meta-GGA exchange functionals converge rapidly, only requiring a few radial quadrature points to converge equation (9) to better than $10^{-14}E_h$ (which is essentially machine precision) for the fixed densities. This is illustrated by the TPSS exchange functional in figure 1.

The results can be contrasted with those of “ill-behaved” functionals, which we will discuss in the following. However, we will first simplify the analysis to a single radial scheme.

A. Radial quadratures

As was already argued in section II, the four radial schemes discussed in section II A are in general found to yield results of similar quality when Chebyshev quadrature is used: well-behaved functionals are found to converge to a similar level of precision with a similar number of quadrature points, while any pathological behavior is similarly reproducible with any of the studied radial grids.

Trapezoidal quadrature was also studied for schemes 3 and 4. While trapezoidal quadrature was found to be competitive for scheme 3 for the case of low numbers of grid points and modest error thresholds with Chebyshev quadrature, Chebyshev quadrature becomes noticeably more accurate than trapezoidal quadrature for large numbers of radial grid points for many well-behaved DFAs. However, there are also many DFAs for which the opposite conclusion applies. Striking examples include the CCDF\textsuperscript{91} (GGA_C_CCDF) and GAPloc\textsuperscript{92} (GGA_C_GAPLOC) GGA correlation functionals, which will be further discussed in section IVC for which scheme 3 requires roughly three times more quadrature points to reach machine precision with Chebyshev quadrature than with trapezoidal quadrature.

In contrast to the description of the Mura–Knowles scheme (scheme 1) in Gill and Chien\textsuperscript{15}, trapezoidal quadrature was found to yield extremely poor accuracy for the Mura–Knowles scheme and this combination will therefore not be considered further in this work.

Overall, the Ahlrichs radial grids (schemes 1 and 2) appear to afford the best convergence, followed by the Mura–Knowles scheme with Chebyshev quadrature. The performance of the Euler–Maclaurin scheme (scheme 3) with either trapezoidal or Chebyshev weights is found to be less systematic than that of the Ahlrichs grids or the Mura–Knowles grid. Based on these findings, the figures presented herein (including the already-shown figure 1) use scheme 1 exclusively; that is, the Ahlrichs M5 grid, in combination with Chebyshev quadrature. Plots for all studied DFAs with all studied radial grids can be found in the SI.

Having established the computational methodology, we will proceed to discuss functionals that show signs of numerical ill behavior. However, this requires first answering the question posed in section II of what constitutes “quick enough” convergence, as this is the criterion used in this work to determine numerical ill behavior in density functionals. In fact, quite a bit of work has been dedicated to answering this question in the literature (as well as in determining the defaults of various quantum chemistry programs) in the case of well-behaved functionals.

For example, the standard grids (SG) originally developed by Gill, Johnson, and Pople\textsuperscript{93} contain up to 26 radial points per atom for SG-0\textsuperscript{94} for SG-1\textsuperscript{95} 50 for SG-2\textsuperscript{95} and 99 for SG-3\textsuperscript{95} SG-1 is well known to yield sufficiently converged energies for LDAs and most GGAs; SG-2 is recommended for tougher GGAs and most meta-GGAs, while SG-3 is recommended for Minnesota functionals.\textsuperscript{95} Although the used number of radial grid points may depend on the atom, many other quantum chemistry programs also use around 100 radial quadrature points in their default grids.

Such quadratures clearly are sufficient for reaching $\mu E_h$ level accuracy with well-behaved density functionals exemplified in figure 1. The maximal quadrature errors for TPSS exchange shown in figure 1 are $1.527 \times 10^{-4}E_h$ for 50 radial points (similarly to SG-1), $3.496 \times 10^{-6}E_h$ for 75 radial points (similarly to SG-2, which would be the recommended default grid for TPSS exchange), and $5.188 \times 10^{-9}E_h$ for 100 radial points (1 more than in SG-3). However, we will demonstrate that many functionals require way more radial quadrature points to achieve sub-$\mu E_h$ converged total energies.

The following discussion will thereby focus on functionals that do not behave as the functionals exemplified by figure 1; ones that either require hundreds more grid
points to converge to machine precision, and ones that fail to converge to machine precision even with unreasonably many (2500) radial quadrature points.

B. Ill-behaved LDAs

The 1957 functional by Gell-Mann and Brueckner (Libxc identifier LDA_C_RPA), \( \epsilon_c = a \log r_s + b + cr_s \log r_s + dr_s \), where \( r_s \) is the Wigner–Seitz radius of the electron density, appears grid sensitive. The Ahlrichs M4 grid (scheme 2) affords quick and robust convergence, whereas the Ahlrichs M3 grid (scheme 1) shows long tails. The Mura–Knowles scheme yields poor results for this functional.

The 1972 correlation functional by Gordon and Kim (LDA_C_GK72) has a piecewise definition, which is likely the cause for the poor convergence behavior shown in the SI; the quadrature error saturates to \( |\Delta E| = O(10^{-4} E_h) \).

The third 1980 functional by Vosko, Wilk, and Nusair (LDA_C_VWN_3; defined in their equation 4.7) contains a ratio that is tentatively the reason for the observed odd behavior, which is characterized by sharp features and rapid oscillations with long-range order. Quadrature errors up to \( |\Delta E| = O(10^{-6} E_h) \) are observed for the N and P atoms for this functional.

Importantly, the functional form recommended by Vosko, Wilk, and Nusair, usually known as VWN (available in Libxc as LDA_C_VWN, and sometimes also known as VWN5) is well-behaved. Other VWN variants are well-behaved as well. Importantly, this includes the version which is used in the B3LYP functional [1] that is based on random phase approximation data (LDA_C_VWN_RPA) instead of the more accurate quantum Monte Carlo data used in VWN5; unfortunately, this version is called VWN in the Gaussian program [2].

The 1981 correlation functional by Perdew and Zunger (LDA_C_PZ) is widely available in various electronic structure programs. The functional has a piecewise definition with a cusp, leading to sketchy convergence with numerical noise in the order \( |\Delta E| = O(10^{-6} E_h) \) persisting even with thousands of grid points.

The 1994 correlation functional by Ortiz and Ballone (LDA_C OB_PZ) shares the form of the PZ functional, likewise leading to an apparent lack of convergence, while the parametrization of Ortiz and Ballone of the Perdew–Wang functional (LDA_C OB_PW) is well-behaved.

The 1996 correlation functional by Liu and Parr (LDA_C LP96) has a simple form

\[
\epsilon_{xc}(n) = C_1 + C_2 n^{-1/3} + C_3 n^{-2/3},
\]

yet the convergence is very slow, and sharp features in the plot are observed for the Li and Na atoms. Also this functional appears to plateau to a quadrature error around \( |\Delta E| = O(10^{-6} E_h) \). The kinetic energy functional defined in the same paper (LDA_K LP96) employs the same functional form, and similarly shows poor convergence.

The 2009 correlation functional of Proynov and Kong (LDA_C PK09) is found to be ill-behaved. However, the ill behavior may be caused by differences in the thresholding of the various denominators appearing in the functional’s equations that appear to be used in the authors’ reference implementation, but have not been described in ref. [103].

C. Ill-behaved GGAs

The 1969 exchange functional by Herman, Van Dyke, and Ortenburger (GGA_X_HERMAN) has a simple functional form—the enhancement factor is \( F_s(x) = 1 + cx^2 \)—yet there is noticeable noise in the energy; the quadrature error plateaus quickly to \( |\Delta E| = O(10^{-5} E_h) \). This is not surprising, as the enhancement factor diverges in the asymptotic limit as \( x \to \infty \).

The 1976 kinetic energy functional by Meyer, Wang, and Young (GGA_K MEYER) is likewise ill-behaved. The functional form includes a logarithm of a quantity that has a denominator that can diverge; thus the stability of the quadrature observed—plateauning to \( |\Delta E| = O(10^{-5} E_h) \)—is surprisingly good.

The 1981 correlation functional by Langreth and Methfessel (GGA_C LM) was one of the first GGA functionals, and its convergence leaves something to be desired: the quadrature error plateaus to \( |\Delta E| = O(10^{-7} E_h) \).

The 1986 correlation functional by Perdew and Zunger (GGA_C_P86) was one of the first successful GGA functionals. It is based on the PZ LDA, and inherits its poor convergence behavior, plateauing to \( |\Delta E| = O(10^{-6} E_h) \). Interestingly, this functional has been also used in some fully numerical studies. A variant based on VWN (that is, VWN5) correlation is available in several programs, and this variant (GGA_C_P86VWN) is numerically well-behaved.

The 1993 exchange functional by Lacks and Gordon (GGA_X_LG93) has a complicated form with a high-order polynomial, a root and a well-behaved denominator. As a result, the functional requires several hundred quadrature points to converge to machine precision.

The 1997 correlation functional by Filatov and Thiel (GGA_C FT97) is characterized by slow convergence. Over 1000 quadrature points are required to reduce the quadrature error to the plateaued value \( |\Delta E| = O(10^{-11} E_h) \).

The range separated \( \omega \)PBEh functional by Ernzerhof and Perdew (PBEh), Heyd, Scuseria, and Ernzerhof (HSE), and Heyd and Scuseria, Heyd, Scuseria, and Ernzerhof (HSE) is characterized by a surprising amount of numerical noise, quickly plateauing to an error around \( |\Delta E| = O(10^{-5} E_h) \). This behavior is
also carried out into the range separated hybrids that are based on the ωPBEh functional, such as the HSE03\textsuperscript{113} and HSE06\textsuperscript{114} functionals.

The 1999 exchange functional by Gilbert and Gill\textsuperscript{115} (GGA\textsubscript{X}GG99) appears to yield energies that are susceptible to numerical noise, as the quadrature error plateaus to $|\Delta E| = O(10^{-6}E_h)$. The 1999 one-parameter progressive correlation functional by Tsuneda, Suzumura, and Hirao\textsuperscript{119,120} based on the PW91 exchange functional\textsuperscript{121,122} (GGA\textsubscript{C}OP_PW91) is extremely ill-behaved, plateauing to $|\Delta E| = O(1 E_h)$ for Li and Na. The variants based on other exchange functionals are better behaved.

The 2008 range-separated exchange functional by Henderson, Janesko, and Scuseria\textsuperscript{123} based on the 1988 exchange functional of Becke\textsuperscript{124} (GGA\textsubscript{X}HJS\textsubscript{B88}) appears noisy, plateauing to $|\Delta E| = O(10^{-6}E_h)$. Also the later version introduced in 2009 by Weintraub, Henderson, and Scuseria\textsuperscript{125} (GGA\textsubscript{X}HJS\textsubscript{B88}_V2) does not appear to be smooth, although it plateaus to a smaller quadrature error of $|\Delta E| = O(10^{-6}E_h)$. The functionals of Henderson, Janesko, and Scuseria\textsuperscript{125} based on other exchange functionals (GGA\textsubscript{X}HJS\textsubscript{PBE}, GGA\textsubscript{X}HJS\textsubscript{PBE\_SOL}, and GGA\textsubscript{X}HJS\textsubscript{B97X}) appear to be smoother, but still require several hundred grid points to converge to machine precision.

The 2011 exchange functional by Haas et al.\textsuperscript{126} (GGA\textsubscript{X}HTBS) is a limited-range spline interpolation between the GGA exchange functionals of Hammer, Hansen, and Nørskov\textsuperscript{127} (GGA\textsubscript{X}RPBE) and Wu and Cohen\textsuperscript{128} (GGA\textsubscript{X}WC). Although the quadratures for the latter two converge rapidly, the limited-range spline interpolation makes the HTBS enhancement function less smooth and quadrature errors around $|\Delta E| = O(10^{-10}E_h)$ persist even with over 1000 radial quadrature points. (The recent CASE21 machine learned GGA by Sparrow et al.\textsuperscript{123}, HYB\textsubscript{GGA\_XC\_CASE21}, shows similar convergence.)

The 2012 exchange functional by Wellendorff et al.\textsuperscript{130} (GGA\textsubscript{X\_BEEFVDW}) functional is somewhat grid sensitive, and plateaus to a level of numerical noise of $|\Delta E| = O(10^{-10}E_h)$.

The 2014 correlation functional by Fabiano et al.\textsuperscript{129} (MGGA\textsubscript{C\_GAPLOC}) exhibits remarkably slow convergence for a GGA functional, requiring around 600 radial points for Ar to reach machine precision. The 2019 correlation functional by Mbar, Kunkel, and Reuter\textsuperscript{127} (GGA\textsubscript{C\_CCDF}) also exhibits a similar issue, requiring some 800 radial points for Ar to reach machine precision.

![Figure 2. Quadrature error (equation (18)) for the TPSS meta-GGA correlation functional as a function of the number of radial points.](image)

D. Ill-behaved meta-GGAS

The 1994 correlation functional by Becke\textsuperscript{131} (MGGA\textsubscript{C\_B94}) appears well-behaved but requires hundreds of radial quadrature points for reliable convergence; around 600 are needed to converge N to machine precision. The 1998 exchange-correlation functional by Becke\textsuperscript{132} (MGGA\textsubscript{C\_B98}) has a similar behavior, likewise requiring around 700 radial quadrature points to reach machine precision.

The 1995 exchange functional by Jemmer and Knowles\textsuperscript{133} (MGGA\textsubscript{X\_JK}) is the poster child of numerically unstable functionals. This meta-GGA contains a denominator that can vanish, leading to a significant grid dependence in the functional. The functional was characterized non-self-consistently in ref.\textsuperscript{133} and yields gigantic quadrature errors $|\Delta E| \geq O(1 E_h)$ in our study.

The 1998 exchange functional by Filatov and Thiel\textsuperscript{134} (MGGA\textsubscript{X\_FT98}) is pronouncedly ill-behaved, exhibiting quadrature errors around $|\Delta E| = O(10^{-5}E_h)$ even with thousands of grid points.

The 1998 correlation functional by Rey and Savin\textsuperscript{135}, Kurth, Perdew, and Blaha\textsuperscript{136}, Krieger, Chen, and Kurth\textsuperscript{137}, Toulouse, Savin, and Adamo\textsuperscript{138} (MGGA\textsubscript{C\_KCIK}) appears to be susceptible to numerical noise, quickly plateauing to $|\Delta E| = O(10^{-6}E_h)$.

The 2003 correlation functional by Tao et al.\textsuperscript{139} (MGGA\textsubscript{C\_TPSS}) plateaus to an error $|\Delta E| = O(10^{-8}E_h)$ for alkali atoms, as shown in figure 2. Similar results are also observed for related functionals, including the functional of Constantin, Fabiano, and Sala\textsuperscript{140} (MGGA\textsubscript{C\_TPSSLOC}); the revised correlation functional by Perdew et al.\textsuperscript{141} (MGGA\textsubscript{C\_REVTPSS}); the correlation functional by Tao and Mo\textsuperscript{142} (MGGA\textsubscript{C\_TM}); and the correlation functional of Jana, Sharma, and Samal\textsuperscript{143} (MGGA\textsubscript{C\_REVTM}).

The 2006 exchange-correlation functional of Cancio and Chao\textsuperscript{144} (MGGA\textsubscript{XC\_CC06}) is numerically unstable like the Jemmer and Knowles\textsuperscript{133} functional, as it too has a denominator that can vanish. This is the likely cause for the observed lack of convergence and residual...
quadrature errors that can reach $|\Delta E| \geq O(1 \cdot E_h)$ even with thousands of radial grid points.

Given several hundred grid points, the 1989 exchange functional of Becke and Roussel\textsuperscript{145} (MGGA\textsubscript{X}\_BR89) plateaus to a quadrature error $|\Delta E| < O(10^{-10}E_h)$. However, the 2008 refit by Proynov, Gan, and Kong\textsuperscript{146} (MGGA\textsubscript{X}\_BR89\_EXPLICIT) appears to increase numerical noise by three orders of magnitude; resulting in a plateauing to $|\Delta E| = O(10^{-7}E_h)$.

The 2017 exchange functionals of Loos\textsuperscript{147} (MGGA\textsubscript{X}\_GX and MGGA\textsubscript{X}\_PBE\_GX) appear to be extremely ill-behaved, slowly plateauing to $|\Delta E| \approx O(10^{-12}E_h)$ for Ar. Both functionals include a step function in the definition, which may be the origin of the poor convergence.

The 2019 exchange functional of Patra et al.\textsuperscript{148} (MGGA\textsubscript{X}\_MGGAC) requires several hundred radial grid points to achieve converged total energies. Around 500 radial points are required for the N atom to reach the plateau at $|\Delta E| = O(10^{-12}E_h)$. Slightly fewer quadrature points are necessary for the 2021 exchange functional by Patra, Jana, and Samal\textsuperscript{149} (MGGA\textsubscript{X}\_REGTM), which reaches machine precision for all studied atoms with fewer than 500 radial points. However, the 2021 correlation functional (MGGA\textsubscript{C}\_RREGTM) by Jana et al.\textsuperscript{150} shows pathologically slow convergence to the grid limit, with an error of the order $|\Delta E| = O(10^{-8}E_h)$ with 1000 radial quadrature points, $|\Delta E| = O(10^{-10}E_h)$ with 2000 quadrature points.

The 2019 exchange functionals of Patra et al.\textsuperscript{141} (MGGA\textsubscript{X}\_MBRXC\_BG and MGGA\textsubscript{X}\_MBRXH\_BG) quickly stagnate to $|\Delta E| = O(10^{-7}E_h)$ precision. The 2021 machine learned density functional of Brown et al.\textsuperscript{152} (MGGA\textsubscript{X}\_MCML) requires hundreds of radial grid points for accurate energies. Around 600 radial points are necessary to converge all atoms to machine precision.

E. Kinetic meta-GGAs

The dependence on the Laplacian of the density in kinetic energy meta-GGAs makes the functionals less well behaved. This is demonstrated by the 1973 gradient expansions of Hodge\textsuperscript{153} to the second (MGGA\textsubscript{K}\_GGA2) and fourth (MGGA\textsubscript{K}\_GGA4) order, the first of which is well-behaved and plateaus to an error of $|\Delta E| = O(10^{-12}E_h)$, while the latter is ill-behaved and plateaus at $|\Delta E| = O(10^{-5}E_h)$.

The convergence for the 2007 kinetic energy functional of Perdew and Constantin\textsuperscript{154} (MGGA\textsubscript{K}\_PC07) is slow and depends on the parameters used. With the original parameters, slow convergence to $|\Delta E| = O(10^{-8}E_h)$ for N with $O(2500)$ grid points is observed. With the parameters reoptimized by Mejia-Rodriguez and Trickl\textsuperscript{155} for deorbitalization of the SCAN family (MGGA\textsubscript{K}\_PC07\_OPT), the functional plateaus to a quadrature error of $|\Delta E| = O(10^{-5}E_h)$ for Ar.

The 2009 reduced derivative approximation (MGGA\textsubscript{K}\_RDA) kinetic energy functional of Karasiev et al.\textsuperscript{156} is similarly characterized by slow convergence. Sharp oscillatory features are observed for Ar, and errors around $|\Delta E| = O(10^{-7}E_h)$ are still observed with $O(2500)$ grid points.

The 2016 CSK1, CSK4, CSK-LOC1, and CSK-LOC4 kinetic energy functionals of Cancio, Stewart, and Kunal\textsuperscript{157} (MGGA\textsubscript{K}\_CSK1, MGGA\textsubscript{K}\_CSK4, MGGA\textsubscript{K}\_CSK\_LOC1, and MGGA\textsubscript{K}\_CSK\_LOC4, respectively) converge slowly, with the slowest convergence observed for nitrogen. More than 500 radial points are necessary to converge N to $\mu E_h$ accuracy, and quadrature errors of $|\Delta E| = O(10^{-10}E_h)$ remain with $O(2500)$ grid points with CSK4 and CSK-LOC4 showing rapid oscillations.

The 2018 semilocal Pauli–Gaussian (XC\_MGGA\_K\_PGSL025) kinetic energy functional of Constantin, Fabiano, and Della Sala\textsuperscript{158} appears quite ill-behaved, quickly plateauing to $|\Delta E| = O(10^{-4}E_h)$.

F. The SCAN family

The most interesting examples of ill-behaved functionals are the recent meta-GGAs constructed from first principles: although the TPSS functional was found to be well-behaved, its successors are not. The MS0\textsuperscript{159} (MGGA\textsubscript{X}\_MS0) and MS2\textsuperscript{160} (MGGA\textsubscript{X}\_MS2) functionals require about twice the number of quadrature points to reach machine precision compared to TPSS: 500 and 550, respectively, with the more recent MS2 requiring more points than MS0.

The successor to MS0 and MS2 is the MVS functional (MGGA\textsubscript{X}\_MVS)\textsuperscript{161} which again roughly doubles the required number of quadrature points: most of the studied atoms reach machine precision with 1000 radial quadrature points, while N requires about 1300 radial quadrature points.

Finally, the SCAN functional\textsuperscript{25} (MGGA\textsubscript{X}\_SCAN, shown in figure 4)—which is well-known to be numerically ill-behaved—clearly problematic as is shown by its remarkably slow convergence rate. Around 600 radial quadrature points are required to reach microhartree precision, and errors around $|\Delta E| = O(10^{-10}E_h)$ persist even with $O(2500)$ radial quadrature points.

The regularized SCAN (rSCAN) functional (MGGA\textsubscript{X}\_RSCAN, shown in figure 4) was designed to fix the issues with numerical behavior in SCAN\textsuperscript{25} Although the convergence is clearly improved for Ne, the functional is still found to converge extremely slowly to the quadrature limit at fixed density for the other atoms: a similar $|\Delta E| = O(10^{-10}E_h)$ level error is observed even with $O(2500)$ radial quadrature points.

Recent functionals that aim to restore constraint adherence to rSCAN—the r\textsuperscript{+}SCAN and r\textsuperscript{4}SCAN functionals\textsuperscript{26} (MGGA\textsubscript{X}\_RPPSCAN and
Figure 3. Quadrature error (equation (18)) for the SCAN meta-GGA exchange functional as a function of the number of radial points.

Figure 4. Quadrature error (equation (18)) for the rSCAN meta-GGA exchange functional as a function of the number of radial points.

Figure 5. Quadrature error (equation (18)) for the r++SCAN meta-GGA exchange functional as a function of the number of radial points.

MGGA_X_R4SCAN, respectively) as well as the r²SCAN (MGGA_X_R2SCAN, shown in figure 6) functional— are also found to behave similarly. The convergence for r++SCAN is strikingly similar to rSCAN, with the main difference being that the good behavior for Ne in rSCAN is lost in r++SCAN. r⁴SCAN has distinctly different behavior to rSCAN and r++SCAN at small numbers of quadrature points, but shares the slow asymptotic behavior for large numbers of grid points and the $|\Delta E| = \mathcal{O}(10^{-8}E_h)$ error with $\mathcal{O}(2500)$ radial quadrature points. The behavior of r²SCAN appears identical to that of r++SCAN.

Holzwarth et al. have recently proposed a modification of r²SCAN to reduce its undesirable numerical instabilities found in fully numerical calculations on atoms. The modification of increasing the $\eta$ parameter from $\eta = 0.001$ in r²SCAN to $\eta = 0.01$ in the r²SCAN01 functional does not result in any better convergence; the r²SCAN01 plots appear similar to the r²SCAN ones. Similar observations can also be made about the corresponding correlation functionals for the whole SCAN family.

Unsurprisingly, the issues also affect the deorbitalized functionals (SCAN-L and r²SCAN-L). Noting that issues with numerical ill behavior were also found above in the PC07 kinetic energy functional used for the deorbitalization, it comes as no surprise that SCAN-L and r²SCAN-L are less well behaved than SCAN and r²SCAN, respectively, and plateau to errors around $|\Delta E| = \mathcal{O}(10^{-8}E_h)$ even with $\mathcal{O}(2500)$ radial quadrature points.

V. SUMMARY AND DISCUSSION

Being able to converge total energies to high precision is of utmost importance for both the theory and applications of DFT. As pointed out in section §I, this requires three things from a given density functional:

1. the total energy must be evaluatable accurately at fixed density,
2. SCF calculations must be easily convergeable, and
3. the complete basis set limit must be reachable.
Any functional that breaks these criteria is deemed numerically ill-behaved.

Inaccuracies in total energy evaluation (criterion 1) may result in a lack of self-consistent field convergence, leading to breaking of criterion 2 that can be a major issue for applications of DFT. Numerical well-behavedness according to all the above criteria is especially important for fully numerical approaches that target sub-\(\mu E_h\) accurate total energies. Likewise, the optimization of atomic basis sets for density functional calculations requires numerically well-behaved functionals, as the basis set parameters—such as the exponent in Gaussian or Slater type orbital basis sets—are typically optimized to sub-\(\mu E_h\) level precision in SCF calculations, even if the basis set truncation error of the Gaussian basis set is larger than this.

We have studied the numerical behavior of all 592 density functionals for three-dimensional systems included in Libxc 5.2.2 according to criterion 1 by employing tabulated Hartree–Fock wave functions for Li, N, Ne, Na, P, and Ar. By examining the convergence of the quadrature of the density functional energy at fixed density, we were able to demonstrate ill-behavedness in a number of recent density functionals.

These results strongly suggest that issues with numerical behavior of DFAs have not been adequately investigated nor addressed by the density functional community. A practical functional needs to converge rapidly to the grid limit for a fixed density with any reasonable quadrature approach. Standard quadrature grids for density functional theory typically employ only \(O(100)\) radial quadrature points even for meta-GGA functionals.

While such grids are often suitable for well-behaved functionals, we have identified a number of density functionals which do not converge to the level of precision required in routine applications even with fixed electron densities, or even if an unseemly large number of radial grid points is used. Significant numerical issues were especially discovered in the whole SCAN family of functionals, and we hope that future functionals will be better behaved in this aspect.

One of the original motivations of this work is the reproducibility of density functional approximations: how can we know if the implementation of a given density functional is correct? The numerical behavior of the density functional is an important aspect to consider in this aspect, as reporting reference energies is highly desirable for enabling reproducibility, as we will discuss in upcoming work. In short, reference energies need to be evaluated accurately, at the quadrature limit, in order to be fully reproducible. Also for this reason, the grid sensitivity of the total energy should be considered as an essential part in the development of new density functionals, as many functionals studied in this work do not appear to allow the determination of sub-\(\mu E_h\) accurate reference energies.

Although we have found several recent first principles meta-GGAs to be numerically ill-behaved, many other recent meta-GGA functionals show quick convergence to the quadrature limit. The key difference between the two kinds of meta-GGA functionals appears to be that the problematic physicists’ first principles functionals include kinetic energy dependence through the \(\alpha\) parameter

\[
\alpha_\sigma = (\tau_\sigma - \tau_\sigma^W)/\tau_\sigma^\text{unif},
\]

where

\[
\tau_\sigma^W = |\nabla n_\sigma|^2/8n_\sigma
\]

and

\[
\tau_\sigma^\text{unif} = (3/10)(6\pi^2)^{2/3}n_\sigma^{5/3}.
\]

This \(\alpha\) parameter is closely related to the curvature of the Fermi hole and to the factor \(D_\sigma = 1 - |\nabla n_\sigma|^2/(8n_\sigma \tau_\sigma)\) that leads to singularities that occur at critical points of the electron density that are known to lead to instabilities. In contrast, the chemists’ functionals are based on a finite domain transformation \(-1 \leq w_\sigma \leq 1\) of the kinetic energy density \(\tau_\sigma w_\sigma\) with

\[
t_\sigma = \frac{\tau_\sigma^\text{unif}}{\tau_\sigma}, \quad w_\sigma = \frac{t_\sigma - 1}{t_\sigma + 1},
\]

which appears to lead to quickly convergent quadratures of the total energy.

Another ingredient

\[
\beta_\sigma(r) = \alpha_\sigma(r) \frac{\tau_\sigma^\text{unif}(r)}{\tau_\sigma(r) + \tau_\sigma^\text{unif}(r)}
\]

was proposed by Furness and Sun and used in the MS2\(\beta\) exchange functional, which is obtained from the numerically ill-behaved MS2\(\beta\) exchange functional by replacing \(\alpha\) with 2\(\beta\). In our tests, MS2\(\beta\)
(MGGA_X_MS2B) appears numerically well-behaved, requiring only slightly more quadrature points to converge to machine precision than the TPSS functional, for instance.

Finally, we wish to reiterate that any nasty behavior in total energy evaluation that occurs at the presently studied fixed atomic densities will also occur in self-consistent calculations. However, some functionals that are well-behaved with respect to the energy may still turn out to be unstable or slowly convergent in self-consistent calculations, if the derivatives exhibit strong oscillations, large values, discontinuities, singularities, and so on, and such numerical ill behavior has been described in the literature for various meta-GGA functionals. These kinds of numerical issues—the breakage of criteria 2 and 3 above—can be probed with self-consistent calculations in extended basis sets. Flexible fully numerical approaches are arguably the strongest acid test for numerical behavior and they will be described in another upcoming manuscript.

CONFLICT OF INTEREST

The authors have no conflicts to disclose.

DATA AVAILABILITY STATEMENT

The data that supports the findings of this study are available within the supplementary material.

SUPPORTING INFORMATION

Plots of the quadrature error for all studied density functionals and radial grids.

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