Improved Laplacian-level meta-GGA for the weakly-nonlocal solid metals

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We derive and motivate a Laplacian-level meta-GGA (LL-MGGA) targeting accurate groundstate properties of metallic solids. Our model for the orbital-free kinetic energy density restores the fourth-order gradient expansion for exchange to the $r^2$SCAN meta-GGA [Furness et al, J. Phys. Chem. Lett. 11, 8208 (2020)], yielding a LL-MGGA we call OFR2. OFR2 matches the accuracy of SCAN for prediction of common lattice constants and improves the equilibrium properties of alkali metals, transition metals, and intermetallics that were poorly described by both SCAN and $r^2$SCAN. We compare OFR2 to the $r^2$SCAN-L LL-MGGA [D. Mejia-Rodriguez and S.B. Trickey, Phys. Rev. B 102, 121109 (2020)] and show that OFR2 tends to outperform $r^2$SCAN-L for the equilibrium properties of solids, but $r^2$SCAN-L much better describes the atomization energies of molecules than OFR2. Numerical performance is discussed in detail, and our work provides an outlook to machine learning.

I. INTRODUCTION

The central aim of practical Kohn-Sham density functional theory (DFT) \cite{DFT} is an accurate but computationally efficient description of the ground state energy \( E[n_{\uparrow}, n_{\downarrow}] \) and spin-densities \((n_{\uparrow}, n_{\downarrow})\) of all many-electron systems. The exact energy functional in DFT, for a given external potential \( v_{\text{ext}}(r) \), is

\[
E[n_{\uparrow}, n_{\downarrow}] = T_s[n_{\uparrow}, n_{\downarrow}] + U_H[n] + E_{xc}[n_{\uparrow}, n_{\downarrow}] + \int d^3r v_{\text{ext}}(r)n(r) \tag{1}
\]

The noninteracting kinetic energy

\[
T_s[n_{\sigma}] = \int d^3r \tau_{\sigma}(r). \tag{2}
\]

is a volume integral over the positive-definite kinetic energy spin-densities

\[
\tau_{\sigma} = \frac{1}{2} \sum_i f_{i\sigma} |\nabla \phi_{i\sigma}(r)|^2, \tag{3}
\]

which are constructed from the occupied Kohn-Sham orbitals \( \phi_{i\sigma}(r) \), with occupancies \( f_{i\sigma} = 0 \) or 1. The Hartree energy

\[
U_H[n] = \frac{1}{2} \int d^3r n(r) \int d^3r' \frac{n(r')}{|r - r'|} \tag{4}
\]

is the classical electrostatic repulsion between a continuous charge density \( n(r) = n_{\uparrow}(r) + n_{\downarrow}(r) \) and itself. The final term, the exchange-correlation energy \( E_{xc} \), must be approximated in practice. \( E_{xc} \) is generally a small piece of the total energy, but contains all quantum corrections to the semiclassical energy of an inhomogeneous electron gas.

Density functional approximations (DFAs) for \( E_{xc} \) generally fall into two camps: first-principles design and (semi-)empirical design. A first-principles DFA uses known behaviors of the exact \( E_{xc} \) to constrain a general mathematical template, whereas an empirical DFA is fitted to data, particularly to bonded systems. As empirical DFAs cannot be universally accurate by design \cite{Foster2013}, we will primarily discuss first-principles DFAs. More recently \cite{Zhang2020,Trickey2020}, machine learning techniques have been applied to train semi-empirical DFAs. This approach, while still quite new, seems to overcome some of the limitations of empirical DFAs by also incorporating a sufficient number of exact constraints. The most widely-known first-principles DFAs at the time of writing are the local spin density approximation (LSDA or LSDA), and the Perdew-Burke-Ernzerhof generalized gradient approximation (PBE GGA or PBE) \cite{PBE}. Both DFAs satisfy subsets of all known behaviors of the exact \( E_{xc} \): the \( E_{xc} \) of a uniform electron gas, spin-scaling of \( E_x \) \cite{Singwi1973}, the behaviors of \( E_x \) and \( E_{\uparrow} \) under uniform scaling of the position vector \( r \) \cite{Singwi1973,Perdew1986}, among others.

LSDA and the gradient expansion approximation (GEA) \cite{Ceperley1980,Perdew1981} were the first two DFAs to be proposed (simultaneously). The LSDA gives the exact \( E_{xc} \) of a uniform electron gas, and is the zeroth-order approximation to the \( E_{xc} \) of a slowly-varying electron gas. The GEA of a given order describes the response of a uniform electron gas to a static, long-wavelength perturbation \cite{Ceperley1980}. While LSDA generally provides an accurate starting point for describing simple systems, the GEA offers no systematic correction to the LSDA \cite{Perdew1986}. Much labor has been expended to understand why the GEA fails for many real systems (see, especially, \cite{Perdew1986,Perdew1989}), and then to refine it into a broadly accurate GGA like PBE.

In terms of dimensionless variables, a system is considered slowly-varying on the scale of exchange when the
following set of conditions holds
\[ p \ll 1 \] (5)
\[ |q| \ll 1 \] (6)
\[ |1 - \alpha| \ll 1. \] (7)

Unless stated otherwise, we will use Hartree atomic units throughout, \( e^2 = m_e = \hbar = 1 \). \( p \) is a dimensionless gradient of the density
\[ p(n) = \left[ \frac{|\nabla n(r)|}{2k_F(r)n(r)} \right]^2 \] (8)
and \( q \) is a dimensionless Laplacian of the density
\[ q(n) = \frac{\nabla^2 n(r)}{4|k_F(r)|^2 n(r)}, \] (9)
both on the length scale of the exchange energy, the local Fermi wavelength \( 2\pi/k_F(n) \). The local Fermi wave-vector is
\[ k_F(n) = \left[ 3\pi^2 n(r) \right]^{1/3}. \] (10)

\( p \) is an ingredient common to virtually all GGAs, whereas \( q \) is used infrequently. Last,\n\[ \alpha(n, |\nabla n|, \tau) = \frac{\tau(n) - \tau_W(n)}{\tau_{\text{unif}}(n)} \] (11)
is a dimensionless kinetic energy variable, commonly used in meta-GGAs. \( \alpha \to 0 \) when \( \tau \) approaches its lower bound \[17\], the Weizsäcker kinetic energy density
\[ \tau_W(n, |\nabla n|) = \frac{|\nabla n(r)|^2}{8n(r)} \] (12)
\( \alpha = 0 \) thus uniquely identifies one and two-electron systems, where, in the absence of an applied electrostatic field, \( \tau = \tau_W \) exactly. \( \alpha \to 1 \) for a uniform density, with (local) kinetic energy density
\[ \tau_{\text{unif}}(n) = \frac{3}{10} k_F^2(n)n(r). \] (13)
\( \tau_{\text{unif}} \) is also called the Thomas-Fermi kinetic energy density. For a slowly-varying density, \( \tau \) has a known gradient expansion like the GEA \[18\].

These known limits are important, as they permit \( \tau \)-based meta-GGAs to be essentially exact for typical one- and two-electron densities and slowly-varying ones \[19\]. Here, “typical” refers to compact, un-noded \[20\] one-electron densities. Such a balanced description between finite and extended systems is not possible when using \( p \) or \( q \) alone, as we shall demonstrate.

A meta-GGA that depends on \( \alpha \) of Eq. \[11\] can mistakenly identify intershell regions in atoms as slowly-varying \[21\]. The same behavior will be demonstrated for a Laplacian-level meta-GGA. To make an indicator like \( \alpha \) that more uniquely differentiates between finite and extended systems, one must consider the first and second derivatives of \( \tau \) in addition to those of \( n \) \[21\]. DFAs with all those ingredients are not currently available and are challenging to construct or use.

Most common Laplacian-level meta-GGAs (LL-MGGAs) are “de-orbitalizations” of \( \tau \)-based meta-GGAs. These orbital-free meta-GGAs replace the analytic expression for \( \tau \) with an approximate form \( \tau(n, |\nabla n|, \nabla^2 n) \) that may be constrained to recover exact constraints. This will be the primary subject of this work.

The most popular correlation functional in the quantum chemistry community, due to Lee, Yang, and Parr (LYP) \[22\], was originally cast as an empirical Laplacian-dependent meta-GGA. Miehlich et al. \[23\] demonstrated that an integration by parts, such as that used in Appendix \[B\] could eliminate the density-Laplacian in favor of the density-gradient, yielding a conventional GGA. This latter GGA form of LYP is generally what is referred to as LYP, and the Laplacian-dependent variant is not commonly used, to the best of our knowledge. Other authors \[24,25\] have followed similar derivations as the original LYP work, yielding both Laplacian-dependent exchange and correlation functionals.

Similarly, the exchange density matrix expansion (DME) of Negele and Vautherin \[20\], originally derived in the context of nuclear Hartree-Fock theory, leads \[27\] to an exchange energy density
\[ e_x^{\text{DME}}(n, p, q, \alpha) = e_x^{\text{LDA}}(n) \] (14)
with \( e_x^{\text{LDA}} = -3k_F n/(4\pi) \) the local density approximation (LDA) for exchange. The DME was generalized and the \( q \)-dependence removed to construct the Van Voorhis-Scuseria (VS98) \[28\] and the M06-L \[29\] empirical meta-GGAs, both of which are popular in the quantum chemistry community. More recently, a similar \( q \)-independent generalization of the DME was used to construct the Tao-Mo meta-GGA \[30\]. The common thread between LYP, the DME, and subsequent work: density-Laplacian dependence is viewed as a hindrance, and is cleverly eliminated to yield a conventional GGA or \( \tau \)-level meta-GGA.

As will be discussed further, no single level of approximations (GGA, meta-GGA, etc.) in practical DFT can describe all systems with the same level of accuracy. This has been demonstrated empirically, for example, in the derivation of the PBEsol \[31\] GGA. The PBE GGA does not recover the correct second-order GEA coefficient for exchange, but does so for correlation. This choice is understood to improve PBE’s description of atomic and molecular properties at the expense of those of solids \[31,32\]. By contrast, PBEsol \[31\] recovers the second-order GEA coefficient for exchange, but not correlation, and tends to describe solids well, at the expense of atoms and molecules.

Similar, but more nuanced deficits also appear at the meta-GGA level. For example, the strongly constrained and appropriately normed (SCAN) \[19\] and regularized-restored SCAN (\( r^2 \)SCAN) \[33\] meta-GGAs tend to pre-
dict unit cell magnetic moments that are somewhat too large compared to experiment [34–36], whereas GGAs predict quantitatively correct magnetic moments. SCAN also tends to predict longer lattice constants and smaller cohesive energies in alkali metals than PBE [37]. Even the PBE formation energies are substantially too large for these solids. Kingsbury et al. [40] demonstrated that $r^2$SCAN makes modest improvements in $\Delta H_f$ of these three solids, and generally improves SCAN’s description of formation enthalpies for all solids tested. The random phase approximation (which depends upon the occupied and unoccupied orbitals) predicts slightly more accurate formation energies for HfOs and ScPt than SCAN [41]. For the convenience of the reader, we have compiled the results of Refs. [39] and [40], which we present in Sec. IV.F.

A GGA is more nonlocal than the LSDA, because the existence of a derivative is conditioned upon the continuity of a function in the immediate neighborhood of a point $r$. Likewise, both variants of meta-GGAs are more nonlocal than GGAs, as these include higher-order derivatives of the density or Kohn-Sham orbitals. However, because the Kohn-Sham orbitals are highly-nonlocal, implicit functionals of the density, a meta-GGA is more nonlocal than a Laplacian-level meta-GGA. The exchange-correlation energy functional of a semi-local (SL) DFA (LSDA, GGA, or meta-GGA) can be written as

$$E_{\text{xc}}^{\text{SL}}[n, n_\uparrow, n_\downarrow] = \int e_{\text{xc}}(n_t, n_\uparrow, \ldots; r)d^3r,$$  

(15)

where the exchange-correlation energy density $e_{\text{xc}}(r)$ depends explicitly only on local variables, $n_\uparrow(r)$, $\nabla n_\sigma(r)$, $\nabla^2 n_\sigma(r)$, $\tau_{\sigma}(r)$, etc. A hybrid functional, which includes some fraction of single-determinant exchange in its energy density $e_{\text{xc}}$

$$e_{\text{hybrid}}(r) = (1 - a)e_{\text{xc}}(r) + e_{\text{c}}^{\text{SL}}(r)$$  

(16)

$$- \frac{a}{2} \sum_{\sigma} \int \frac{|\rho_1(r\sigma, r'\sigma)|^2}{|r - r'|} dr',$$

is a non-local functional of the Kohn-Sham orbitals $\phi_{i\sigma}(r)$ through the reduced one-body density matrix

$$\rho_1(r\sigma, r'\sigma) = \delta_{\sigma,\sigma'} \sum_i \phi_{i\sigma}^*(r) \phi_{i\sigma}(r') \theta(\varepsilon_F - \varepsilon_{i\sigma}).$$  

(17)

$\delta_{ij} = 1$ if $i = j$ and $0$ if $i \neq j$ is the Kronecker delta, and $\theta(x < 0) = 0$, $\theta(x > 0) = 1$ is the step function. Single-determinant exchange using Eq. [17] delivers the exact exchange energy.

An accurate description of itinerant electron magnetism appears to be best described by more local DFAs. As shown elsewhere [34–36] and here, LSDA, non-empirical GGAs, and Laplacian-level meta-GGAs tend to better predict transition metal magnetic properties than do $\tau$-meta-GGAs. Global hybrids, which use a constant parameter $a$ in Eq. [16] are much more nonlocal and thus even less accurate than meta-GGAs for transition metal magnetism [42]. Range-separated hybrids, generalizations of global hybrids that separate the short- and long-range components of the Coulomb interaction, also tend to predict markedly worse equilibrium properties (e.g., lattice constants and bulk moduli) for structurally simple metals than they do for similarly simple insulators [43]. To the best of our knowledge, no study of extended systems using local hybrids, which use a function $a(r)$ in Eq. [16] have been undertaken. As meta-GGAs and global hybrids are more non-local, it stands to reason that the exchange-correlation holes of elemental transition metals may be surprisingly local, with the gradient terms of GGAs and Laplacian-level meta-GGAs offering meaningful corrections to LSDA.

The search for a computationally efficient DFA that is highly accurate for nearly all systems of interest has not yet found an unequivocal choice. It has, however, shown that inclusion of exact constraints is perhaps the single most powerful aspect of DFA design [44]. In this work, we determine the utility of an orbital-free meta-GGA designed to augment the constraints of the underlying parent $\tau$-level meta-GGA.

Why does the exact density functional for the exchange-correlation energy display a weaker nonlocality in metallic solids than in molecules and non-metallic solids? A clue is provided by the exact expression [45, 46]

$$E_{\text{xc}} = \frac{1}{2} \int d^3r n(r) \int d^3r' \frac{n_{\text{xc}}(r', r)}{|r' - r|},$$  

(18)

where $n_{\text{xc}}(r', r)$ is the density at $r'$ of the coupling-constant-averaged exchange-correlation hole around an electron at $r$. Starting from the exact exchange hole, correlation makes the exchange-correlation hole more negative at $r' = r$, with a faster decay to zero as $|r' - r| \to \infty$. At long range, the exchange hole density in a solid is screened by a dielectric constant which is finite in nonmetals but infinite in metals. In the uniform electron gas [47], for example, the exact exchange hole (averaged over oscillations) at long range decays as $|r' - r|^{-1}$, while the exact exchange-correlation hole (averaged over oscillations) density decays much faster as $|r' - r|^{-5}$. As the exact exchange-correlation hole becomes more deeper and more localized around its electron, the exact exchange-correlation energy functional becomes less non-local in the electron density. For example [48], the optimum fraction $a$ of exact exchange in a global hybrid functional is the inverse of a long-wavelength dielectric constant, and vanishes for a metal. Thus, highly nonlocal information (e.g., the fundamental energy gap, the dielectric constant, or the descriptors of Ref. [21]) is required to determine the level of nonlocality expressed in an approximate density functional.
II. ORBITAL-FREE META-GGAS

Orbital-free variants of τ-level meta-GGAs may be the most common LLMGGAs to date. Mejía-Rodríguez and Trickey [19, 49] have spearheaded a general-purpose “de-orbitalization” procedure to replace the analytic τ with an approximate form given by the Perdew and Constantin parameterization of τ [51].

This construction has two primary benefits: a more localized exchange-correlation hole, and potential for greater numerical efficiency [52]. We posit that the more localized exchange-correlation holes of metals, including “atypical metals”, are unexpectedly local, a suggestion made long ago [53]. Thus meta-GGAs like SCAN and \( r^2 \)SCAN tend to make their holes too non-local, and more insulator-like. Indeed, Ref. [52] demonstrates that an orbital-free version of SCAN and \( r^2 \)SCAN predict smaller magnetic moments in the ferromagnets (when evaluated at the same geometry), and that the orbital-free variants tend to predict more accurate lattice constants of simple metals. However, the orbital-free variants worsen the cohesive energies of simple metals, presumably because these energy differences involve atoms as well as metallic solids.

Mejía-Rodríguez and Trickey have shown [52] that an orbital-free version of \( r^2 \)SCAN, called \( r^2 \)SCAN-L, has a computational cost similar to PBE in solids. Such a meta-GGA, which promises high accuracy and stability, is the central aim of their work and ours. Our work adds to their pioneering work by restoring the gradient expansion to their pioneering work by restoring the gradient expansion of the approximate τ.

The Perdew-Constantin (PC) [51] expressions approximate τ using an enhancement factor construction similar to that of semi-local exchange energies,

\[
\tilde{\tau}_s(n, p, q) = \tau_{\text{unif}}(n)F_{\text{s}}^{\text{PC}}(p, q).
\] (19)

We use the “s” subscript to indicate a single-electron property, i.e., \( F_{\text{s}} \) is used to approximate the non-interacting kinetic energy density. Such a description is useful because the kinetic energy and exchange energy share the same spin-scaling relationship [6]

\[
T_s[n_{\uparrow}, n_{\downarrow}] = \frac{1}{2}(T_s[2n_{\uparrow}] + T_s[2n_{\downarrow}]). \quad (20)
\]

For sufficiently slowly-varying densities,

\[
\lim_{\substack{p \to 1 \\
q \to 1}} F_s^{\text{PC}}(p, q) \to F_{\text{SVL}} = 1 + \frac{5}{27}p + \frac{20}{9}q + \Delta, \quad (21)
\]

where \( \Delta \) stands for generalized fourth-order gradient expansion terms. Because it employs only the variables \( p \) and \( q \), the Perdew-Constantin model recovers only the second-order gradient expansion of τ, although it also recovers the fourth-order gradient expansion of \( T_s \).

For iso-orbital regions,

\[
F_s^{\text{PC}}(p, q) \to F_W = 5p/3 = \tau_W/\tau_{\text{unif}} \quad (22)
\]

To approximately recover the iso-orbital limit of τ, the PC model interpolates between these limits

\[
F_s^{\text{PC}}(p, q) = F_W + \Delta^{\text{PC}} f_{ab}(\Delta^{\text{PC}}) \quad (23)
\]

\[
\Delta^{\text{PC}} = F_{\text{SVL}} - F_W. \quad (24)
\]

From Eq. (11), it can be seen that \( \Delta^{\text{PC}} f_{ab}(\Delta^{\text{PC}}) \) approximates \( \alpha \). The PC interpolation function is a smooth, non-analytic two-parameter function

\[
f_{ab}(z) = \begin{cases} 
0, & z \leq 0 \\
\left[ 1 + \frac{g_1a(z)}{g_2a(z)} \right]^b, & 0 < z < a \\
1, & z \geq a
\end{cases} \quad (25)
\]

\[
g_1a(z) = \exp \left( \frac{a}{a - z} \right) \quad (26)
\]

\[
g_2a(z) = \exp \left( \frac{a}{z} \right). \quad (27)
\]

The PC model assumes that \( \Delta^{\text{PC}} \leq 0 \) indicates an iso-orbital density, and that \( \Delta^{\text{PC}} \geq 0 \) indicates a sufficiently slowly-varying density. For a uniform density, \( \Delta^{\text{PC}} = 1 \). Thus, \( a < 1 \) is needed to ensure recovery of both the uniform limit of τ and its low-order gradient expansion for weakly-inhomogeneous densities.

For slowly-varying densities,

\[
\Delta^{\text{PC}} \to 1 - 40p/27 + 20q/9 + \Delta. \quad (28)
\]

If \( a < 1 \), as in the Perdew-Constantin work [51], then

\[
f_{ab}(\Delta^{\text{PC}}) \to 1 - 40p/27 + 20q/9 + \Delta + O(\nabla n^6), \quad (29)
\]

because the derivatives

\[
\left. \frac{d^k f_{ab}}{d(\Delta^{\text{PC}})^k} \right|_{\Delta^{\text{PC}} = 1} = 0 \quad (30)
\]

for all \( k > 0 \). However, if \( a > 1 \), as it is in the Mejía-Rodríguez and Trickey re-parameterization (MRT) [19] of the PC functional, then \( f_{ab} \) no longer has a trivial Taylor series about \( \Delta^{\text{PC}} = 1 \),

\[
f_{ab}(\Delta^{\text{PC}}) = f_{ab}(\Delta^{\text{PC}}) + f'_b(1)(\Delta^{\text{PC}} - 1) + O((\Delta^{\text{PC}} - 1)^2). \quad (31)
\]

The MRT parameters are \( a = 1.784720 \) and \( b = 0.258304 \); then the coefficients in the Taylor series of \( f_{ab}(\Delta^{\text{PC}}) \) are

\[
f_{ab}(1) = \left[ \frac{1 + g_1a(1)}{g_2a(1) + g_1a(1)} \right]^b \approx 0.906485 \quad (32)
\]

\[
f'_b(1) = b \left[ \frac{1 + g_1a(1)}{g_2a(1) + g_1a(1)} \right]^{b+1} 
\times \left\{ \frac{g_1'a(1)g_2a(1) - 1 - g_2'a(1) + 1 + g_1a(1)}{g_1a(1) + g_2a(1)} \right\} 
\approx 0.353363. \quad (33)
\]

For reference,

\[
g_1'a(z) = \frac{a}{(a - z)^2}g_1a(z) \quad (34)
\]

\[
g_2'a(z) = -\frac{a}{z^2}g_2a(z). \quad (35)
\]
Note that \( \Delta_{PC} - 1 = O(\nabla n^2) \), and \((\Delta_{PC} - 1)^2 = O(|\nabla n|^4)\) to lowest order. As \( f_{ab}(1) \neq 0 \) in the MRT model, the gradient expansion of the MRT \( \tau \) no longer agrees with the known expansion, including the LSDA (uniform density) term,

\[
\tau_{\text{MRT}}(n, p, q) = \left[ 0.906485 + 1.143167p \right. \\
+0.785250q + O(|\nabla n|) \left. \right] \tau_{\text{uni}}(n). \tag{36}
\]

Compare this to the exact expansion

\[
\tau_{\text{GGA}}(n, p, q) = [1 + 0.185185p \\
+2.222222q + O(|\nabla n|)] \tau_{\text{uni}}(n). \tag{37}
\]

Most critically, the uniform density limit is broken, since \( f^{\text{MRT}}_{ab}(1) \neq 1 \). Consider the restoration of exact constraints to the rSCAN meta-GGA \([54]\), which lacks a correct uniform density limit and slowly-varying gradient expansion, by the \( r^2 \text{SCAN} \) meta-GGA \([53]\). It has been shown, by the \( r^2 \text{SCAN} \) authors and by many others \([53, 55, 56]\) that the uniform density limit is critical for describing both solid-state properties and atomization energies of molecules.

The loss of the correct uniform density limit and gradient expansion terms reduces the accuracy of an orbital-free meta-GGA when applied to prototypical solids. Table I compares the XC surface formation energies calculated for the planar jellium surface and clusters from two \( \tau \) meta-GGAs, SCAN \([19]\) and \( r^2 \text{SCAN} \) \([33]\), with their deorbitalized counterparts SCAN-L \([50, 51]\) and \( r^2 \text{SCAN}-L \([52]\). It is clear that SCAN and \( r^2 \text{SCAN} \) provide reasonably accurate descriptions of the jellium surface formation energies, while their deorbitalized counterparts provide less correct descriptions.

III. NEW MODEL OF THE KINETIC ENERGY DENSITY

We present here a simplified construction of an approximate kinetic energy density. This is intended to be as smooth and numerically stable as is possible using the density Laplacian. Previous works attempting to construct an exchange enhancement factor with the density Laplacian demonstrated \([57]\) that the exchange-correlation potential

\[
v_{xc}(r) = \frac{\partial e_{xc}}{\partial n} - \nabla \cdot \left( \frac{\partial e_{xc}}{\partial \nabla n} \right) + \nabla^2 \left( \frac{\partial e_{xc}}{\partial \nabla^2 n} \right) \tag{38}
\]

is easily destabilized when the “curvature” term, rightmost in Eq. (38), is not well-constrained. Note that \( e_{xc} \) is the exchange-correlation energy density, the integrand of the exchange-correlation energy functional. Part of our aim here is to ensure this term is not too badly-behaved, although it is not possible to eliminate all oscillations induced by this term into the Kohn-Sham potential.

The Perdew-Constantin expression for the kinetic energy density enhancement factor \( F_s \) interpolates between the rigorous lower bound

\[
F_W = \frac{5}{3}p \leq F_s \tag{39}
\]

and a regulated fourth-order gradient expansion for \( \tau \), whose asymptotic limit is \( 1 + 5p/3 \). Note that by “asymptotic limit”, we are referring to the limit \( p, |q| \to \infty \), as is typified by, e.g., a density tail. Cancio and Redd \([58]\) have suggested that extrapolating from these limits could be important as the exact \( \tau \) need not be constrained between the iso-orbital and gradient expansion limits. This has been confirmed by Ref. \([59]\) in the density tails of atoms.

The appropriate norms could provide information about how best to extrapolate beyond these two limits, and indeed this is in line with the construction philosophy of SCAN and \( r^2 \text{SCAN} \). However, we have found that a simple interpolation between these two limits more than suffices for accurate descriptions of solids.

To recover the second-order gradient expansion for exchange and correlation in \( r^2 \text{SCAN} \), and the fourth-order gradient expansion for exchange in SCAN, only the second-order gradient expansion of \( \tau \) is needed. Therefore, we aim to recover only the second-order gradient expansion of \( \tau \), and not the fourth-order gradient expansion of \( T_s \). However, as is shown in App. B the fourth-order gradient expansion for exchange can be restored to \( r^2 \text{SCAN} \) by modifying the fourth-order terms in an approximate expression for \( \tau \). Therefore, we will aim to restore this constraint to \( r^2 \text{SCAN} \).

As can be seen from Eq. (11),

\[
\alpha(r) = F_s - \frac{5}{3}p. \tag{40}
\]

\( 0 \leq \alpha < \infty \) is positive semi-definite, therefore we make a model of \( \alpha \) with the same range as the true variable

\[
x(p, q) = 1 - \frac{40}{27}p + \frac{20}{9}q + c_3p^2 e^{-|c_3|p} \tag{41}
\]

\[+ x_4(p, q) \exp \left[ - \left( \frac{p}{c_1} \right)^2 - \left( \frac{q}{c_2} \right)^2 \right] \]

\[x_4(p, q) = b_{qq}q^2 + b_{pq}pq + (b_{pp} - c_3)p^2 \tag{42}\]

\[c_{s \text{RPP}}(x) = \begin{cases} 0, & x < 0 \\
x^4(A + Bx + Cx^2 + Dx^3), & 0 \leq x \leq x_0 \\
x, & x > x_0 \tag{43}\end{cases}\]

\[F_{s \text{RPP}}(p, q) = \frac{5}{3}p + c_{s \text{RPP}}(x(p, q)) \tag{44}\]

We call this model RPP for “\( r^2 \text{SCAN} \) piecewise-polynomial”. Here, \( A, B, C \) are determined by requiring that \( c_s(x) \) is continuous up to its third derivative (a \( C^3 \)
function) in \( x \) at \( x = x_0 \),

\[
A = 20/x_0^3 \quad \text{(45)}
\]
\[
B = -45/x_0^4 \quad \text{(46)}
\]
\[
C = 36/x_0^5 \quad \text{(47)}
\]
\[
D = -10/x_0^6. \quad \text{(48)}
\]

0 < \( x_0 < 1 \), \( c_1, c_2, \) and \( c_3 \) are model parameters determined by minimizing the residual errors of a set of appropriate norms, described below. Their optimal values are

\[
x_0 = 0.819411 \quad \text{(49)}
\]
\[
c_1 = 0.201352 \quad \text{(50)}
\]
\[
c_2 = 0.185020 \quad \text{(51)}
\]
\[
c_3 = 1.53804 \quad \text{(52)}
\]

Note that, by construction, \( \alpha_s(x) \) is a \( C^3 \) function for all \( x \). \( b_{qq} \approx 1.801019, b_{pq} \approx -1.850497, \) and \( b_{pp} \approx 0.974002 \) restore the fourth-order gradient expansion for exchange; their precise values are given in App. \[52\]. Therefore, the XC potential is continuous, but the adiabatic XC kernel is not continuous. The Perdew-Constantin expression belongs to the class of “smooth non-analytic functions,” \( C^\infty \) functions that have Taylor series with zero radius of convergence about at least one point (\( z = 0 \) & \( \alpha \) in the Perdew-Constantin model). The current model has a Taylor series of nonzero convergence radius about \( x = 0, x_0 \). Figure 1 plots the enhancement factor over a range of \( p \) typical for atoms and molecules (where \( 0 \leq p \leq 9 \)).

Our expression for \( \alpha_s \) is intended for use in the \( r^2 \)\( \text{SCAN} \) meta-GGA. The numerical stability of \( r^2 \)\( \text{SCAN} \), coupled with its high-accuracy for non-metallic solids, make it a good candidate for this kind of work, as noted previously \[52\].

The two fourth-order terms in \( x(p, q) \) restore the fourth-order gradient expansion (GEX4) terms to \( r^2 \)\( \text{SCAN} \). The first term, involving \( x_4(p, q) \), is modeled after the \( r^4 \)\( \text{SCAN} \) meta-GGA \[41\]. This meta-GGA restores the GEX4 to \( r^2 \)\( \text{SCAN} \) using the exact \( \tau \), at the price of some numerical stability and general accuracy.

We noticed in our testing that the gradient expansion terms need sharp cutoffs, like those used in \( r^2 \)\( \text{SCAN} \). This is primarily due to the \( b_{qq} q^2 \) and \( b_{pq} p q \) terms, which introduce numerical instabilities if they are not strongly regulated. However, the \( c_3 p^2 \) term, provides more meaningful corrections at large \( p \) than do the gradient expansion terms. For this reason, the damped \( c_3 p^2 \) term has a much longer tail than \( x_4(p, q) \).

For ease of reference, we refer to the new orbital-free \( r^2 \)\( \text{SCAN} \) as “OFR2”, which is also the METAGGA keyword used in our implementation of the subroutines in VASP.

The second-order gradient expansion for \( \tau \) is most useful for solids, where it is unexpectedly accurate in approximating the true \( \tau \). Figure 2 plots the exact kinetic energy density of the jellium surface, second-order gradient expansion for \( \tau \), the OFR2 model derived here (after fitting, described below), and the Weizsäcker kinetic energy density for a bulk density parameter \( \tau_0 = 2, 4 \).
see that OFR2 reasonably approximates $\tau$ in the jellium surface, despite predicting oscillations of too small magnitude and the incorrect phase.

It is also worth noting that SCAN, $r^2$SCAN, and the orbital free variants SCAN-L, $r^2$SCAN-L, and OFR2 are among the first meta-GGAs to respect the tightened bound on the exchange-correlation energy [63].

$$E_x[n] \geq E_{xc}[n] \geq 1.174E_{x}^{\text{LDA}}[n]$$

(53)

where $n$ is an arbitrary density. GGAs like PBE and PBEsol [31] respect a much more conservative bound [61] [62]

$$E_x[n] \geq E_{xc}[n] \geq 1.804E_{x}^{\text{LDA}}[n].$$

(54)

### A. Appropriate norms

Reference [19] described the process of selecting systems for which a given tier of density functional approximation can be expected to be exact, and those for which it can be highly accurate. This idea had been used previously, e.g., PBE recovering the LSDA in the limit of uniform densities, or the Tao-Perdew-Staroverov-Scuseria (TPSS) meta-GGA [63], which was also constrained to be exact for the hydrogen atom. Such auxiliary conditions, which may need to be satisfied by fitting to reference densities, are necessary in the absence of known conditions on the exact exchange-correlation functional (exact constraints, tout court).

We draw a distinction between first principles functionals, which build in all possible exact constraints prior to determining free parameters with appropriate norms, from empirical functionals. Empirical functionals need not build in exact constraints first, however when the fit is done only with appropriate norms (e.g., rare gas atoms at the GGA level), they often emerge naturally [58] [61]. Empirical functionals often fit to bonded systems. Semi-empirical functionals, like the Beck exchange GGA (B88) [65], build in some constraints prior to determining free parameters by fitting to data sets.

At the LSDA level, the only appropriate norm available is the uniform electron gas, for which “The LSDA” [1] [60] is exact (as opposed to empirical LSDAs [61]). The GGA level can add density-gradient expansions, or the lowest-order large-$Z$ coefficients and the exchange-correlation energies of atoms.

The meta-GGA level can have more freedom. LAPLACIAN-level meta-GGAs (LLMGGAs) exist in standard Kohn-Sham schemes, and have less freedom than $\tau$-meta-GGAs, which exist in a generalized Kohn-Sham scheme. Some of the appropriate norms used in SCAN [19] (the compressed Ar dimer, hydrogen and helium atoms) are not appropriate norms for a LLMGGA, whereas the others (large-$Z$ coefficients to next order and jellium surface formation energies) are still applicable.

We select for our primary appropriate norms the surface formation energies of planar jellium surfaces [65] [69], with $r_s$ values typical of metals ($r_s = 2, 3, 4, \text{and } 5$), and spherical jellium clusters [70] (with typical magic numbers $N = 2, 8, 18, 20, 34, 40, 58, 92, \text{and } 106$). From the spherical jellium clusters, we extract surface formation energies $\sigma_{xc}(r_s)$ and surface curvature energies $\gamma_{xc}(r_s)$ via the liquid drop model [71].

$$\frac{E_{xc}}{N} = \varepsilon_{\text{xc}}^{\text{UG}}(r_s) + 4\pi r_s^2 \sigma_{xc}(r_s) N^{-1/3} + 2\pi r_s \gamma_{xc}(r_s) N^{-2/3}. \quad (55)$$

The surface formation energies extracted from the jellium clusters will, in general, differ from those extracted from the planar surface, although the large-$N$ limit of the spherical clusters is the planar surface. Density functionals that are more sensitive to the shell structure of small-$N$ clusters, e.g., SCAN, predict less accurate $\sigma_{xc}(r_s)$ values than they do for the planar surface. Moreover, to limit the effects of shell-structure oscillations, we always fit the difference $(E_{xc}^{\text{approx}} - E_{xc}^{\text{LSDA}})/N$, as described in Ref. [70].

A Python code was written to generate self-consistent reference LSDA densities for these appropriate norms, and is available publicly from the code repository [72].

As secondary appropriate norms, we use the exchange-correlation energies of the spherically-symmetric noble gas atoms Ne, Ar, Kr, and Xe, using more recent Roothaan-Hartree-Fock reference densities [73] than were used in the construction of SCAN. The code for generating reference atomic densities and extracting large-$Z$ coefficients is also publicly available in the same repository [72].

To determine the model parameters, the objective function

$$\delta = \sqrt{\text{MAPE}_{\text{SA}}^2 + \text{MAPE}_{\text{JS}}^2 + \text{MAPE}_{\text{JC}}^2} \quad (56)$$

where “SA” stands for the exchange-correlation energy of the spherical atoms Ne, Ar, Jr, and Xe, “JS” (“JC”) stands for the jellium planar surface (cluster) $\sigma_{xc}$, and MAPE is the mean absolute percentage error. For the planar jellium surfaces, $r_s \in \{2, 3, 4, 5\}$ were used; for the jellium clusters, $r_s \in \{2, 3, 3.5, 4, 5\}$ were used. The minimization was done in two steps: a Nelder-Mead simplex search, followed by a simple grid search on grids of increasing fineness. The fitting routine stopped when the change in the lowest $\delta$ over a few iterations stagnated.

A plot of the $\alpha_s(z)$ function, compared with similar models [49] [51] [55], is given in Fig. 3. The Cancio-Redd model

$$\alpha_s^{\text{CR}}(z^{\text{CR}}) = 1 + z^{\text{CR}} \{1 - \exp[-1/z^{\text{CR}}]\}^{1/a} \Theta(-z^{\text{CR}})$$

$$+ z^{\text{CR}} \Theta(z^{\text{CR}}) \quad (57)$$

$$z^{\text{CR}} = \frac{40}{27} p + \frac{20}{9} q \quad (58)$$

$$\Theta(z) = \begin{cases} 1 & z \geq 0 \\ 0 & z < 0 \end{cases} \quad (59)$$

for $\delta$. The fitting routine stopped when the change in the lowest $\delta$ over a few iterations stagnated.
Fig. 3 by noting that $\alpha_s(x \approx 1) \approx x$.

Table II shows the appropriate norms used to determine $x_0$: exchange-correlation energies of spherically-symmetric atoms Ne, He, Ar, and Kr; the jellium surface exchange-correlation formation energy, $\sigma_{xc}(r_s)$ found either directly from a planar jellium surface, as in Ref. [69], or indirectly by fitting to Eq. (55), as in Ref. [70]. We have used the RPA+ values of Ref. [75], as well as the fit from Ref. [70] as needed, as reference values for $\sigma_{xc}$. This is done for a few reasons: the RPA alone accounts for 100% of exact exchange and the long-range part of correlation (at least in a metal like the jellium surface); the RPA+ makes a GGA-level correction at short range for the correlation energy; the values of $\sigma_{xc}$ found by RPA+ are comparable to much more sophisticated techniques like the Singwi-Tosi-Land-Sjölander self-consistent spectral function method [77], or careful quantum Monte Carlo (QMC) calculations of finite jellium surfaces [78]. By fitting to Eq. (55) for the total energy, we can also obtain information about the jellium surface total curvature energy $\gamma(r_s)$, which we have compared to available QMC data [79] where possible. For the atoms, we have used Roothan-Hartree-Fock densities from Ref. [73].

### IV. Performance for Real Systems

From the construction of OFR2, one might expect that the form is most accurate for metallic systems, and less accurate for non-metallic ones. While this niche may
seem limited in the grand scope of physical materials, we counter that \( \tau \)-meta-GGAs are already exceedingly accurate for the properties of non-metallic systems. \( \tau \)-meta-GGAs simply exhibit too much nonlocality for simple metallic solids, and this dearth is filled adequately by a Laplacian-level functional.

Panels (a) and (b) of Fig. 4 plot \( p, q, \) and \( \alpha \) in the Cr atom for the up- and down-spin densities, respectively. In the intershell region, \( 0.07 \lesssim r \lesssim 2 \) bohr, both \( p \) and \( q \) are less than one, and there are numerous points where \( \alpha = 1 \). The intershell density would thus be characterized as approximately slowly-varying or metallic by a \( \tau \)-meta-GGA. We define the spin-dependent variables as

\[
p_{\sigma} = p(2n_{\sigma}) = 2^{-2/3} \frac{\left| \nabla n_{\sigma} \right|}{4(3\pi^2)^{2/3}n_{\sigma}^{8/3}}
\]

\[
q_{\sigma} = q(2n_{\sigma}) = 2^{-2/3} \frac{\nabla^2 n_{\sigma}}{4(3\pi^2)^{2/3}n_{\sigma}^{5/3}}
\]

\[
\alpha_{\sigma} = \alpha(2n_{\sigma}, 2\tau_{\sigma}) = 2^{-2/3} \tau_{\sigma} - \frac{\left| \nabla n_{\sigma} \right|^2 / (8n_{\sigma})}{3(3\pi^2)^{2/3}n_{\sigma}^{5/3} / 10}
\]

\[\text{i.e. the density variables as seen by the exchange energy using its spin-scaling relation [6].}\]

Panels (c) and (d) of Fig. 4 plot the errors made in approximating \( \alpha \) with the model of Mejía-Rodríguez and Trickey [49] and the current model, Eq. [44]. Because \( p \) and \( |q| \) are small, the (unregularized) second-order gradient expansion (GE2),

\[
\tau_{\sigma} = \left( 1 + \frac{20}{9} q_{\sigma} + \frac{5}{27} p_{\sigma} \right) \tau_{\text{unif}}(n_{\sigma})
\]

is a reasonable approximation to \( \tau \) in the intershell region only. RPP closely follows the GE2 curve in the intershell region. These semi-local models of \( \alpha \) better describe the intershell region than the core, where they make \( \alpha \) vanish too slowly, or the density tail, where they make \( \alpha \) diverge too quickly. The model of Ref. [49] represents a better overall representation of \( \alpha_{\sigma} \) than the current model.

### A. Lattice constants

All solid-state calculations were performed in the Vienna \textit{ab initio} Simulation Package (VASP) [81,84], version 6.1. We used a \( \Gamma \)-centered \( k \)-point mesh of spacing \( 0.08 \) Å\(^{-1}\), with a plane-wave energy cutoff of 800 eV, except for a few cases, which we discuss below. Energies were converged below \( 10^{-6} \) eV, and calculated using the Blöchl tetrahedron method. For reasons of numerical stability, ADDGRID was set to False. Equilibrium structures were determined using the stabilized jellium equation of state (SJEOS) [85]. 12 single-point energy calculations in a range of \( (1 \pm 0.1)V_{\text{expt.}} \), with \( V_{\text{expt.}} \) the experimental (zero-point energy corrected) equilibrium volume were then performed. To fit hcp structures, we optimized the \( c/a \) packing ratio at fixed volume, and found the optimal \( c/a \) by fitting to a reduced SJEOS. All input files can be found in the code repository.

Some of the standard VASP pseudopotentials cannot accommodate higher plane-wave energy cutoffs. For example, “PAW_PBE Ba_sv 06Sep2000” (“PAW_PBE Pd 04Jan2005”) can accommodate a maximum energy cutoff of about 600 eV (750 eV). Both settings were used here instead of the 800 eV cutoff used for the other solids. The Laplacian-level meta-GGAs exhibited a strong dependence on the number of bands used when the cutoff was exceeded, whereas the GGAs and meta-GGAs did not appear to be similarly affected.
FIG. 4. Square dimensionless density gradient $p$ (blue, solid), density Laplacian $q$ (orange, dashed), and kinetic energy density $\alpha$ (green, dot-dashed) in the Cr atom for the (a) up-spin ($\uparrow$) density, and (b) down-spin ($\downarrow$) density. The density, its derivatives, and kinetic energy density are spherically averaged after sampling 200 azimuthal points on a Gauss-Legendre grid, using Roothaan-Hartree-Fock Slater-type orbitals from Ref. [80]. Vertical dotted lines indicate points $r$ where $\alpha = 1$. The percent error, $100\left(\frac{\alpha_{\text{approx}}}{\alpha} - 1\right)$, made by the model of $\alpha$ from Ref. [49] (MRT; blue, solid) and the present model, RPP (orange, dashed), for the (c) up-spin density and (d) down-spin density. Also shown is the unregularized second order gradient expansion, GE2 (green, dot-dashed), $1 + 20q/9 - 40p/27$. When $p \ll 1$, $|q| \ll 1$, and $|1 - \alpha| \ll 1$, the density can be considered slowly-varying, and a semilocal model of $\tau$ can be approximately accurate.

Table [11] displays the relative error statistics in 20 cubic lattice constants (the LC20 set) [86] made by a variety of common, first-principles functionals: PBEsol [31] (a benchmark GGA for this property), $r^2$SCAN [33], $r^2$SCAN-L [52] and OFR2. Tables XII and XIII of Appendix D present errors in the lattice constants and bulk moduli, respectively, for each solid in the LC20 set.

OFR2 exceeds the performance of $r^2$SCAN and $r^2$SCAN-L overall, for the metals in the set, and for the insulators in the set of lattice constants. However, $r^2$SCAN and PBEsol predict more accurate bulk moduli than do either of the orbital-free $r^2$SCAN meta-GGAs. These results show the bias inherent in each meta-GGA construction: the data used to fit $r^2$SCAN-L was biased towards molecular properties (they used the 18 lightest neutral atoms as a fitting set [39]), whereas the construction of OFR2 is much more biased towards solid state properties. Therefore, the $r^2$SCAN-L results show much stronger performance for the insulating solids. OFR2 is constructed in the spirit of PBEsol, and shows a large gain in performance over its parent functional $r^2$SCAN.

We derive a symmetric expression for the Laplacian contributions to the stress tensor in Appendix C. The total exchange-correlation stress tensor, in a gauge appropriate for a code with periodic boundary conditions, is given by Eq. (C18) reprinted here

$$
\Sigma^i_{\text{xc}} = \int \left[ (\varepsilon_{\text{xc}} - v_{\text{xc}} n) \delta_{ij} - \frac{1}{|\nabla n|} \frac{\partial n}{\partial r_i} \frac{\partial n}{\partial r_j} \frac{\partial \varepsilon_{\text{xc}}}{\partial |\nabla n|} \right] d^3r. \quad (64)
$$

To use the stress tensor to minimize structures, we used a few additional computational parameters, keeping the others unchanged. The magnitudes of forces were converged within 0.001 eV/Å, and all degrees of freedom were permitted to relax (ISIF = 3, IBRION = 2); we verified that no change of symmetry occurred during the minimization. First order Methfessel-Paxton smearing with width 0.2 eV was used for the metals (and Ge for PBEsol and $r^2$SCAN-L), Gaussian smearing of width 0.05 eV was used for the insulators. The mean deviations in the LC20 lattice constants found by the equation of
than 10\(^{-2}\) Å on average, which is satisfied. The deviations are \(a_{\text{SCAN}} - a_{\text{ST}}\).

### Table III

| Functional | Solid (structure) | \(a\) (Å) | \(m_s\) (µB/atom) |
|------------|-------------------|------------|------------------|
| PBEsol     | Fe (bcc)          | 2.783      | 2.094            |
| \(r^2\text{SCAN}\) |                  | 2.864      | 2.64             |
| \(r^2\text{SCAN-L}\) |                | 2.827      | 2.20             |
| OFR2       |                  | 2.791      | 2.12             |
| Expt.      |                  | 2.855      | 1.98 – 2.13      |
| Ni (fcc)   | PBEsol            | 3.465      | 0.620            |
| \(r^2\text{SCAN}\) |                  | 3.478      | 0.74             |
| \(r^2\text{SCAN-L}\) |               | 3.500      | 0.67             |
| OFR2       |                  | 3.463      | 0.66             |
| Expt.      |                  | 3.509      | 0.52 – 0.57      |
| Co (hcp)   | PBEsol            | 2.455      | 1.57             |
| \(r^2\text{SCAN}\) |                  | 2.471      | 1.74             |
| \(r^2\text{SCAN-L}\) |               | 2.494      | 1.66             |
| OFR2       |                  | 2.468      | 1.63             |
| Expt.      |                  | 2.503      | 1.52 – 1.58      |

### Table IV

| Functional | Solid (structure) | \(a\) (Å) | \(c/a\) | \(m_s\) (µB/atom) |
|------------|-------------------|------------|----------|------------------|
| PBEsol     | Ni (fcc)          | 2.455      | 1.615    | 1.57             |
| \(r^2\text{SCAN}\) |                  | 2.471      | 1.623    | 1.74             |
| \(r^2\text{SCAN-L}\) |                | 2.494      | 1.623    | 1.66             |
| OFR2       |                  | 2.468      | 1.623    | 1.63             |
| Expt.      |                  | 2.503      | 1.621    | 1.52 – 1.58      |

As is well known by now [34, 35], some of the most accurate \(\tau\)-meta-GGAs predict correct structures for transition metals, but too large magnetic moments. These works typically look at the simplest ferromagnetic materials, body-centered cubic (bcc) Fe, face-centered cubic (Ni), and hexagonal close-packed (hcp) Co, for which accurate experimental lattice constants are tabulated. However, their magnetic moments are only known within a range of values.

One might anticipate that the greater degree of locality in a LL-MGGA would result in a more local (and in this case, more correct) description of transition metals. Reference [52] compares two first-principles \(\tau\)-meta-GGAs, SCAN [19] and \(r^2\text{SCAN}\) [33], with their de-orbitalized counterparts, which we shall discuss further. The de-orbitalization procedure replaces the \(\tau\)-dependence with a form that depends only upon the density gradient and Laplacian. Both de-orbitalized functionals provide more realistic descriptions of transition metal magnetism.

Consistent with these expectations, OFR2 strikes a balance between the GGA and meta-GGA levels in terms of accuracy. Table V compares PBEsol, a GGA that has been shown to be highly-accurate for describing solid state properties, \(r^2\text{SCAN}\) [33], \(r^2\text{SCAN-L}\) [52], and the OFR2 functional derived here. OFR2 provides more accurate estimates of solid structure than PBEsol, and more accurate magnetic moments than \(r^2\text{SCAN}\).
usual oscillations that could be misinterpreted as shell structure. Using this density,

\[
k_F(r) = (3\pi)^{1/3} e^{-2r/3} \quad (65)
\]

\[
p(r) = k_F^{-2} \quad (66)
\]

\[
q(r) = (1 - 1/r)k_F^{-2} \quad (67)
\]

There is a region near \( r = 1 \) bohr that an LL-MGGA can mistakenly identify as slowly-varying, because \( p \lesssim 1 \), and \( q \) is nearly zero. This induces an artificial shell structure that the \( r^2 \) SCAN KS potential lacks [33], at least in its semi-local part. Some numerical artifacting is possible due to the use of a sixth-order finite difference to calculate portions of the KS potential. It should be noted that the finite difference is only used to evaluate the divergence of \( \partial e_{xc} / \partial (\nabla n_x) \) and Laplacian of \( \partial e_{xc} / \partial (\nabla^2 n_x) \). The actual density derivatives listed previously (and \( \partial e_{xc} / \partial n_x \)) are computed analytically, as they would be in a self-consistent code.

Similarly, Fig. 6 plots the finite difference exchange and correlation potentials in a jellium surface with \( r_s = 2 \), for OFR2 and and \( r^2 \) SCAN-L. As in the other calculations of the jellium surface, reference LSDA densities were used. Both models yield extreme oscillations in the resultant potentials, which can be compared to the potentials of PBEsol shown in Fig. 7 for the same density. PBEsol is expected to yield reasonable predictions of jellium surface properties, by construction. It is clear, without plotting the associated electrostatic potential, that the oscillations dependent in the Laplacian-dependent meta-GGAs will be significant.

**D. Bandgaps**

In a standard Kohn-Sham calculation, the exact exchange-correlation functional would lead to an underestimation of the fundamental (charge) bandgap equal to an amount called the “exchange-correlation derivative discontinuity” [30]. Thus, even though GGAs like PBE often likely come close to approximating the exact Kohn-Sham bandgap [30], only functionals defined within a generalized Kohn-Sham (GKS) scheme with nonzero
derivative discontinuity can give realistic estimates of the fundamental bandgap \[91\]. For this reason, \(\tau\)-meta-GGAs, which are orbital-dependent and thus well-defined within a GKS scheme, can provide surprisingly reliable estimates of the bandgap \[92, 93\]. Similarly, this is the reason why hybrid functionals reliably predict bandgaps \[94\], as the exact exchange functional must be expressed in terms of the Kohn-Sham orbitals.

Analogously, we expect an LL-MGGA to underestimate the fundamental bandgap, but quite accurately approximate the Kohn-Sham bandgap. An LL-MGGA is a standard KS meta-GGA, and thus produces no derivative discontinuity.

Table VI demonstrates this for a subset of the LC20 set of solids. To compute the bandgap, the equilibrium lattice constants from Table XII were used as input to a single total energy calculation. From this, the Fermi energy was extracted, and a new density of states (DOS) grid was defined centered at the Fermi energy, evenly spaced in intervals of 0.01 eV. The calculation was then repeated with the finer DOS grid. Note that VASP is not consistent in defining the position of the Fermi energy: it occasionally lies at the valence band maximum as it should, but can end up at the conduction band minimum.

Interestingly, OFR2 and \(r^2\)-SCAN-L show no consistent behavior with respect to gaps. Of course, both LL-MGGAs severely underestimate the fundamental gap. We are of the view that a general-purpose functional should be able to reliably predict lattice parameters and bandgaps. In this view, the equilibrium geometry is the right geometry for evaluation of the bandgap. An alternate perspective would use the same geometry for each functional to evaluate the bandgap, as in Ref. \[92\].

E. Monovacancy in Platinum

Reference \[38\] found that SCAN curiously predicts a favorable formation of a monovacancy in Pt, and generally. To build upon their work, we also compute the equilibrium lattice constants and vacancy formation energies of Pt using SCAN, \(r^2\)-SCAN, \(r^2\)-SCAN-L, and OFR2. The initial equilibrium lattice constants for face-centered cubic (fcc) Pt were found by fitting to the SJEOS, using the same computational parameters as before. A \(2 \times 2 \times 2\) supercell was constructed using that lattice constant, and the supercell was allowed to further relax (ISIF = 3, IB-RION = 2), using first-order Methfessel-Paxton smearing of width 0.2 eV, and forces converged within 0.001 eV/Å. The total energy was determined from the relaxed supercell structure using the tetrahedron method (ISIGMA = -5). An identical supercell, but with an ion nearest the center of the cell removed, was used to model the monovacancy, and the same procedure was repeated. An \(11 \times 11 \times 11\) \(k\)-point grid was used, consistent with Ref. \[38\].

The monovacancy formation energy

\[
E_{\text{MVF}} = E(N - 1) - \frac{N - 1}{N} E(N),
\]  

(68)

where \(E(N)\) is the total energy of an \(N\)-electron system, are presented in Table VII. We found a small positive monovacancy formation energy for SCAN, OFR2 predicts a slightly larger monovacancy formation energy than PBE. However, PBEsol predicts the most accurate Pt monovacancy formation energy, albeit still underestimating the bottom of the experimental range by about 0.4 eV.
TABLE VII. Monovacancy formation energy and equilibrium geometry of fcc Pt. The experimental, zero-point corrected lattice constant is taken from Ref. [39], and the experimental monovacancy formation energy range is taken from Ref. [38]. Note that the SJEOS-determined lattice constant (second column), which was then performed to relax in the Pt supercell. For all DFAs shown, the supercell lattice constant after relaxation did not change to the stated precision, verifying our implementation of the Laplacian-dependent stress tensor.

| DFA      | \(a_0\) (SJEOS, Å) | \(E_{\text{MNF}}\) (eV) |
|----------|---------------------|-------------------------|
| Expt.    | 3.913               | 1.32–1.7                |
| PBE      | 3.971               | 0.676                   |
| PBEsol   | 3.919               | 0.886                   |
| SCAN     | 3.913               | 0.126                   |
| \(r^2\)SCAN | 3.943               | 0.593                   |
| \(r^2\)SCAN-L | 3.980               | 0.590                   |
| OFR2     | 3.928               | 0.684                   |

F. Intermetallic formation energies

To probe whether \(r^{2}\)SCAN-L and OFR2 improve the \(r^{2}\)SCAN description of intermetallic formation energies, we follow the methodology of Ref. [39]. All initial geometries were taken from the Open Quantum Materials Database (OQMD) [93] [96]. Following Ref. [39], geometries were relaxed allowing all ionic degrees of freedom to change (ISIF = 3), and with first-order Methfessel-Paxton smearing of width 0.2 eV. After relaxation, total energies were determined using the tetrahedron method at fixed geometry. All ions were initialized with a (ferromagnetic) magnetic moment of 3.5 \(\mu_B\). The plane-wave cutoff was 600 eV, and the \(k\)-grid was determined as follows: for a fixed density of \(k\)-points \(\kappa\) (Å\(^{-3}\)), the spacing \(\Delta k\) between adjacent \(k\)-points along each axis (KSPACING tag) is

\[
\Delta k = \left( \frac{\prod_{i=1}^{3} |b_i|}{\prod_{i=1}^{3} \left(\prod_{j=1}^{3} a_j \times a_j \right)} \right)^{1/3}, \tag{69}
\]

where \(a_i\) and \(b_i\) are the direct and reciprocal lattice vectors, respectively, for the initial geometry. As in Ref. [39], we used \(\Delta k = 700\) Å\(^{-3}\), and checked that \(\Delta k\) produced a grid of density of at least \(\Delta k\) density, decreasing \(\Delta k\) if needed. For VPt\(_2\), we needed to manually determine a grid with an equal number of \(k\)-points along each axis to ensure that VASP produced a \(k\)-grid with the right symmetry. Formation energies \(\Delta E_i\) were computed from total energies \(E\) as follows: for compound \(Y = \prod_{i=1}^{M} (X_i)_{x_i}\) composed of \(M\) elements \(X_i\) with multiplicity \(x_i\),

\[
\Delta E_i = \frac{1}{\sum_i x_i} \left[ E(Y) - \sum_{i=1}^{M} x_i E(X_i) \right] / N_i \tag{70}
\]

with \(N_i\) the number of ions in the unit cell for the pure solid \(X_i\).

Our results, along with those of Refs. [39] [40], are presented in Table VIII. None of the DFAs considered here accurately predict the formation energies of these solids, however \(r^2\)SCAN-L and OFR2 improve over SCAN and \(r^2\)SCAN. Although scalar relativistic effects are included in the treatment of core electrons in the VASP pseudopotentials, relativistic corrections (e.g., spin-orbit coupling) for Hf, Os, and Pt may be needed to accurately predict the formation enthalpies of these alloys. Moreover, these uncommon alloys have little representation in the literature. Other experimental references for the formation enthalpies could benefit further analysis.

The tests of intermetallic formation energies described here and in Refs. [39] [40] test the ability of a DFA to predict the correct equilibrium structure, spin-densities, and total energies for a solid and its constituents (or, more unlikely, benefit from a random cancellation of errors). Therefore, a large error in any one predicted property for a single constituent in a given compound can cascade, making it discern which aspect of the test the DFA fails. The subject of density-driven and functional-driven errors [100] is a useful framework for decomposing the various errors in this kind of test. However, we cannot apply this metric without having the exact spin-densities (and geometries).

Systems with a strong sensitivity to perturbations in the Kohn-Sham potential can exhibit density driven errors [101]. Evaluating a semi-local DFA (GGA, meta-GGA) on the Hartree-Fock density can often eliminate density-driven errors in molecules, as has recently been shown for SCAN applied to liquid water [102]. It is unclear what an equivalent density-correction method would be for solid-state calculations, as such a method would need to produce a density with a realistic geometry. A modern periodic Hartree-Fock calculation of face-centered cubic LiH [103] found an equilibrium lattice constant \(a_0 = 4.105\) Å and bulk modulus \(B_0 = 32.3\) GPa, in significant error of the zero-point corrected experimental values \(a_0 = 3.979\) Å and \(B_0 = 40.1\) GPa [104] (and less accurate than the PBE, PBEsol, and SCAN values reported in Ref. [104]). We are unaware of periodic Hartree-Fock calculations for metallic solids.

G. Molecules

Within the quantum chemistry community, the set of six molecular atomization energies (AE6) [105] is a standard way of rapidly evaluating the performance of a DFA for thermochemical properties. Despite containing only six molecules, the results of the test generally indicate the level of accuracy a DFA can have in predicting molecular properties. Table IX presents the results of the AE6 set for \(r^2\)SCAN, \(r^2\)SCAN-L, and OFR2.

These calculations were also performed in VASP. Each atom or molecule was placed in an orthorhombic box of dimensions 10 Å × 10.1 Å × 10.2 Å to sufficiently lower the lattice symmetry and reduce interac-
| $\Delta H_f$ | PBE, Expt. | SCAN, Refs. | r$^2$SCAN, Ref. | LSDA | PBE | PBEsol | SCAN | r$^2$SCAN | r$^2$SCAN-L | OFR2 |
|---|---|---|---|---|---|---|---|---|---|---|
| (eV/atom) | | | | | | | | | | |
| HfOs | $-0.482 \pm 0.052$ | -0.707 | -0.874 | -0.846 | -0.724 | -0.715 | -0.708 | -0.901 | -0.847 | -0.805 |
| ScPt | $-1.086 \pm 0.056$ | -1.212 | -1.473 | -1.308 | -1.233 | -1.214 | -1.204 | -1.461 | -1.301 | -1.243 |
| VPt$_2$ | $-0.386 \pm 0.026$ | -0.555 | -0.726 | -0.601 | -0.562 | -0.548 | -0.566 | -0.712 | -0.592 | -0.524 |

TABLE VIII. Formation enthalpies, in eV/atom, of a few intermetallic elements. The DFT results are formation energies and neglect the $PV$ term in the enthalpy. The experimental formation enthalpy of HfOs is from Ref. [97]; experimental values for ScPt and VPt$_2$ are taken from Ref. [98]. Reference PBE values are taken from Ref. [39]. Reference SCAN values are averages of those reported in Refs. [39] and [40]. Reference r$^2$SCAN values are taken from Ref. [40]. The LSDA uses the Perdew-Zunger parameterization [99] of the uniform electron gas correlation energy.

Table XIX presents the data for each individual solid in Appendix E.

V. OUTLOOK: MACHINE LEARNING AND KINETIC ENERGY DENSITY

Machine learning has already made leaps and bounds in the design of empirical DFAs. The work of Ref. [K] has shown that the most sophisticated $\tau$-meta-GGAs have essentially reached a fundamental limit of accuracy for their level of approximation. The work of Ref. [H] built a local hybrid-level DFA that approximately satisfies frac-
TABLE IX. Comparison of PBE [5], PBEsol [31], $r^2$SCAN [33], $r^2$SCAN-L [52], and OFR2 errors for the set of six atomization energies (AE6) [105]. All values are in kcal/mol (1 eV $\approx$ 23.060548 kcal/mol). Reference values are the non-relativistic, frozen-core values from Table 4 of Ref. [106]. Given that the calculation in VASP is non-relativistic with a frozen-core pseudopotential, these reference values appear to be most appropriate. Mean errors (ME) and mean absolute errors (MAE) are also reported. Absolute total energies have no physical meaning in a pseudopotential calculation, therefore we only report the energy differences (as errors) here.

| Molecule | Reference (kcal/mol) | PBE | PBEsol | $r^2$SCAN | $r^2$SCAN-L | OFR2 |
|----------|----------------------|-----|--------|-----------|------------|------|
| SiH$_4$  | 324.594              | -10.950 | -1.678 | -2.520    | -3.162     | -4.240 |
| SiO      | 192.352              | 3.577 | 11.735 | -5.543    | -4.325     | -5.890 |
| S$_2$    | 103.227              | 12.457 | 26.391 | 7.128     | 7.283      | 9.037 |
| C$_3$H$_4$ | 701.458              | 25.631 | 50.517 | 1.046     | -1.219     | -14.659 |
| C$_2$H$_2$O$_2$ | 632.457             | 30.376 | 60.301 | -3.368    | -3.597     | -14.021 |
| C$_4$H$_8$ | 1145.387             | 30.178 | 75.887 | 2.322     | -3.974     | -18.523 |

$\text{ME} (\text{Å})$ | 0.051 | -0.017 | 0.084 | 0.111 | -0.004 | 0.014 |
$\text{MAE} (\text{Å})$ | 0.061 | 0.019 | 0.095 | 0.114 | 0.055 | 0.039 |
$B_0 \text{ ME} (\text{GPa})$ | -0.105 | -0.056 | -0.164 | -0.329 | 2.481 | 0.008 |
$B_0 \text{ MAE} (\text{GPa})$ | 0.446 | 0.340 | 0.467 | 0.360 | 3.639 | 0.760 |
$E_0 \text{ ME} (\text{eV/atom})$ | -0.072 | -0.005 | -0.083 | -0.092 | -0.100 | -0.099 |
$E_0 \text{ MAE} (\text{eV/atom})$ | 0.072 | 0.022 | 0.083 | 0.092 | 0.100 | 0.099 |

TABLE X. Error statistics in the equilibrium lattice constants $a_0$, bulk moduli $B_0$, and cohesive energies $E_0$ for the alkali metals Li, Na, K, Rb, and Cs. The PBE [5] and PBEsol [31] GGAs, SCAN [19] and $r^2$SCAN [33] $\tau$-meta-GGAs, and $r^2$SCAN-L [52] and OFR2 Laplacian-level meta-GGAs are presented.

We will model the function $\theta(z)$, which determines the mixing between Weizsäcker and gradient expansion limits. Moreover, $\theta(z)$ should permit extrapolation for arbitrary positive $z$, as suggested by Cancio and Redd [53]. Then for the appropriate norms considered here – the neutral noble gas atoms Ne, Ar, Kr, and Xe, and the jellium surfaces of bulk densities $\tau_s = 2, 3, 4, 5$ – take a reference density and compute

$$\theta(z) = \frac{\tau - F_W(p)}{z(p, q)}.$$  

As we are reducing a two-variable function $\theta(z(p, q))$ to a single-variable function $\theta(z)$, it is useful to bin the values of $\theta$ within a narrow range of $z$.

The form selected for $\theta$ satisfies three constraints: the Weizsäcker lower bound, the uniform density limit, and the second-order gradient expansion terms. A machine can learn these constraints approximately by penalizing their violation, but cannot satisfy them by construction as a human-designed model can. Because the “exact” $\theta(z)$ is complicated, we need an expression which has sufficient freedom for fitting. Consider the $M$-parameter.
Parameterized mixing function $\theta(z)$ of Eq. \ref{eq:theta} that determines the optimal mixing fraction between Weizsäcker and second-order gradient expansion kinetic energy densities. Acceptable (pole-free and non-negative $\theta(z \geq 0)$) parameter sets $M = 3, 4, 6, & 11$ are displayed. Solid points are the binned $\theta(z)$ data taken from the appropriate norms: the neutral noble gas atoms Ne, Ar, Kr, and Xe, and the jellium surfaces of bulk densities $\tau = 2, 3, 4, 5$.

\begin{equation}
\theta(z) = \begin{cases}
0, & z < 0 \\
10^b \left[1 + b_1 z + b_2 z^2\right] \left[1 + \sum_{i=1}^{M} c_i z^i\right]^{-1}, & z \geq 0
\end{cases}
\end{equation}

\begin{equation}
b_1 = 3 + \sum_{i=1}^{M} (5 - i) c_i
\end{equation}

\begin{equation}
b_2 = \sum_{i=1}^{M} c_i - b_1,
\end{equation}

where $b_1$ and $b_2$ are chosen such that $\theta(1) = 1$ (to satisfy the uniform density limit) and $\theta'(1) = 0$ (to recover the second-order gradient expansion terms). It appears that $\theta(z > 1) \propto a \log z$, for constants $a$ and $b$, however this model can approximately recover that behavior. The minimum power of $z$ in the numerator is chosen to allow for sufficient smoothness of the exchange-correlation potential for $z \approx 0$.

We considered $2 \leq M \leq 20$; for $M \geq 5$, $\theta$ can be bounded as $z \to \infty$. A non-linear least-squares fit was used to determine the $c_i$. We discarded parameter sets for which the denominator of $\theta$ had positive polynomial roots or for which $\theta(z > 0) < 0$. The possible acceptable parameters found were for $M = 3, 4, 6, & 11$, as shown in Fig. \ref{fig:theta}. Clearly, $M = 3$ or 4 do not represent reliable extrapolations for $z \to \infty$. $M = 6$ appears to represent the most realistic, long-tailed extrapolation for $z \to \infty$, however $M = 11$ more accurately captures the apparent oscillations in $\theta(z)$.

Thus we emphasize the need for human decision in these kinds of highly-empirical DFA design. Both $M = 6$ or $M = 11$ deliver similar performance for the appropriate norms, as shown in Table \ref{tab:orbitalFree}}, however the $M = 6 \theta$ is much smoother and is thus likely more numerically stable. It is purely for reasons of numeric stability that the HLM models have been deferred to this section. While we do not present plots of the $r^2\text{SCAN} + \text{HL}6$ or $\text{HL}11$ Kohn-Sham potential for the simple systems considered here, we have computed them and determined they are wholly unrealistic.

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|c|}
\hline
& \textbf{$r^2\text{SCAN}$} & \textbf{SCAN} \\
\hline
\textbf{M} & \textbf{RGA} & \textbf{JS} & \textbf{JC} & \textbf{RGA} & \textbf{JS} & \textbf{JC} \\
\hline
3 & 0.73 & 9.20 & 11.48 & 0.95 & 6.71 & 10.39 \\
4 & 0.91 & 2.82 & 1.15 & 1.01 & 2.87 & 3.74 \\
6 & 0.53 & 3.60 & 2.61 & 0.55 & 1.51 & 2.11 \\
11 & 0.48 & 3.73 & 2.72 & 0.49 & 1.53 & 1.88 \\
\hline
\end{tabular}
\caption{Orbital free $r^2\text{SCAN}$ and SCAN appropriate norm performance using the highly-parameterized mixing function $\theta(F_W - F_{GE2})$ of Eq. \ref{eq:theta} compared to the orbital-dependent variants (bottom row). Increasing the number of parameters $M$ generally improves the fidelity of the approximate $\tau$, at the cost of more rapid oscillations. The mean absolute percentage errors of the rare gas atom (RGA) exchange-correlation energies, jellium surface (JS) exchange-correlation surface formation energies, and jellium cluster exchange-correlation surface formation energies are shown.}
\end{table}

\section{Conclusions}

We developed a model Laplacian-level meta-GGA that is an orbital-free or “deorbitalized” variant of $r^2\text{SCAN}$ \cite{OFR2}. Moreover, we showed that this model, OFR2, could recover the fourth-order gradient expansion for exchange. We have extensively tested OFR2 against an existing deorbitalization of $r^2\text{SCAN}$, $r^2\text{SCAN-L}$ \cite{OFR2}, which breaks the uniform density limit of $r^2\text{SCAN}$.

OFR2 appears to improve upon $r^2\text{SCAN}$ for the lattice constants of solids, matching or exceeding the accuracy of SCAN, $r^2\text{SCAN-L}$ and OFR2 more accurately describe transition-metal magnetism than $r^2\text{SCAN}$, which drastically over-magnetizes the unit cell. OFR2 better describes the structural properties of alkali metals than $r^2\text{SCAN}$ and $r^2\text{SCAN-L}$, but not their cohesive energies. We therefore recommend OFR2 for an orbital-free description of solids.

For an orbital-free description of molecules, we recommend $r^2\text{SCAN-L}$, which retains the accuracy of $r^2\text{SCAN}$ for the AE6 set \cite{AE6} of atomization energies. OFR2, which targets properties of metallic solids, bridges the gap between high GGA-level errors ($> 10$ kcal/mol average errors) and lower meta-GGA-level errors ($< 5$ kcal/mol average errors).

Laplacian-level meta-GGAs are generally more challenging to obtain well-converged results with at higher...
convergence settings. Some PBE pseudopotentials also appear to be less transferrable to Laplacian-level meta-GGAs than τ-meta-GGAs. This finding tracks with that of Mejía-Rodríguez and Trickey [52], who found that GW potentials were less transferrable. Laplacian-level meta-GGAs might have a particular niche for exploratory purposes: if benchmark-quality results are not desired, these can often match or surpass the accuracy of their τ-meta-GGA counterparts.

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CODE AND DATA AVAILABILITY

The Python 3 and Fortran code used to fit the orbital free r2SCAN is made freely available at the code repository [72]. Data files needed to run this code, general purpose Fortran subroutines, and VASP subroutines are included there as well.
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Appendix A: Implementing the Laplacian in VASP

Rather than use the standard definition of the potential, White and Bird [108] have suggested an alternate way to compute the potential on a grid of $M$ finite points $\mathbf{R}$. This robust method is used in many standard plane wave libraries, including VASP. We outline the method below.

Their analysis was tailored to the specific case of periodic boundary conditions, thus we define the reciprocal lattice vectors of the unit cell as $\mathbf{G}$. Using Fourier series, we can write the density variables as

$$ n(\mathbf{r}) = \sum_G n(\mathbf{G}) e^{i \mathbf{G} \cdot \mathbf{r}} \quad (A1) $$

$$ n(\mathbf{G}) = \frac{1}{M} \sum_{\mathbf{R}} n(\mathbf{R}) e^{-i \mathbf{G} \cdot \mathbf{R}} \quad (A2) $$

$$ \nabla n(\mathbf{r}) = i \sum_G G n(\mathbf{G}) e^{i \mathbf{G} \cdot \mathbf{r}} \quad (A3) $$

$$ \nabla^2 n(\mathbf{r}) = -\sum_{G,R} G^2 n(\mathbf{G}) e^{i \mathbf{G} \cdot \mathbf{r}} \quad (A4) $$

Now let the discrete $E_{\text{xc}}$ within a cell volume $\Omega$ be

$$ \bar{E}_{\text{xc}} = \frac{\Omega}{M} \sum_{\mathbf{R}} \epsilon_{\text{xc}}(n(\mathbf{R}), \nabla n(\mathbf{R}), \nabla^2 n(\mathbf{R})) \quad (A5) $$

with $\epsilon_{\text{xc}} = \epsilon_{\text{xc}}(\mathbf{R})$. One can approximate the variations in $\bar{E}_{\text{xc}}$ using

$$ \delta \bar{E}_{\text{xc}} = \frac{\Omega}{M} \sum_{\mathbf{R}} \frac{d\bar{E}_{\text{xc}}}{dn(\mathbf{R})} \delta n(\mathbf{R}) \equiv \sum_{\mathbf{R}} \bar{\epsilon}_{\text{xc}}(\mathbf{R}) \delta n(\mathbf{R}) \quad (A6) $$

then the discrete potential $\bar{\epsilon}_{\text{xc}}$ is represented as

$$ \bar{\epsilon}_{\text{xc}}(\mathbf{R}) = \frac{\partial \epsilon_{\text{xc}}}{\partial n(\mathbf{R})} + \sum_{\mathbf{R}'} \left\{ \frac{\partial \epsilon_{\text{xc}}}{\partial \nabla n(\mathbf{R'})} \cdot \frac{d(\nabla n(\mathbf{R'}))}{dn(\mathbf{R})} \right\} \quad (A7) $$

It’s now trivial to insert the Fourier series representations of the total derivatives on the RHS of the last equation. Note that the density gradient vector is never used in PBE-like GGAs, thus we can replace the derivatives with respect to $\nabla n$

$$ \frac{\partial}{\partial (\nabla n)} = \frac{\nabla n}{|\nabla n|} \cdot \frac{\partial}{\partial |\nabla n|} \quad (A8) $$

The discrete potential then becomes

$$ \bar{\epsilon}_{\text{xc}}(\mathbf{R}) = \frac{\partial \epsilon_{\text{xc}}}{\partial n(\mathbf{R})} + \frac{1}{M} \sum_{\mathbf{G},\mathbf{R}} \left\{ i \mathbf{G} \cdot \frac{\nabla n(\mathbf{R'})}{|\nabla n(\mathbf{R'})|} \right\} \left( \frac{\partial \epsilon_{\text{xc}}}{\partial \nabla^2 n(\mathbf{R'})} \right) e^{i \mathbf{G} \cdot (\mathbf{R'} - \mathbf{R})} \quad (A9) $$

Appendix B: Restoring the fourth-order gradient expansion for exchange to r^2SCAN

This section builds upon the derivation of r^2SCAN presented in Ref. [44]. By construction, r^2SCAN recovers the exact second-order gradient expansion for exchange, but not the fourth-order terms. It will be shown in a forthcoming
work that r²SCAN severely overestimates the magnitude of the fourth-order gradient expansion coefficients. The exact exchange enhancement factor has a fourth-order gradient expansion in \( p \) and \( q \) \cite{10}

\[
F_x = 1 + \frac{10}{81} p + \frac{146}{2025} q^2 - \frac{73}{405} pq + \mathcal{O}(|\nabla n|^6). \tag{B1}
\]

Note that the coefficient of \( pq \) is known within some uncertainty, as is the coefficient of \( p^2 \). We take the best estimates from Ref. \cite{10}.

However, an orbital-free r²SCAN can be made to recover the right fourth-order gradient expansion for exchange. This is accomplished by using different fourth-order terms in the gradient expansion of the approximate \( \tau(p, q) \) than those that appear in the gradient expansion of the exact \( \tau \) \cite{18}. To maintain the second-order gradient expansion constraint of r²SCAN, we retain the correct second-order gradient expansion of \( \tau \),

\[
\frac{\tau(p, q)}{\tau_0} = 1 + \frac{5}{27} p + \frac{20}{9} q + b_{pq} q^2 + b_{qp} pq + b_{pp} p^2 + \mathcal{O}(|\nabla n|^6). \tag{B2}
\]

The iso-orbital indicator used in r²SCAN is the numerically-stable

\[
\bar{\alpha} = \frac{\tau - \tau_W}{\tau_0 + \eta \tau_W} \tag{B3}
\]

where \( \eta = 0.001 \) \cite{23}. It can be seen that the gradient expansion of the approximate \( \bar{\alpha}(p, q) \) is

\[
\bar{\alpha}(p, q) = 1 - \frac{5(8 + 9\eta)}{27} p + \frac{20}{9} q + b_{pq} q^2 + \left( b_{pp} - \frac{100\eta}{27} \right) pq + \left( b_{pp} + \frac{200\eta}{81} + \frac{25\eta^2}{9} \right) p^2 + \mathcal{O}(|\nabla n|^6). \tag{B4}
\]

Note that the gradient expansion of \( \bar{\alpha} \) using the exact \( \tau \) cannot be expressed in terms of a polynomial in \( p \) and \( q \).

We turn our attention to the enhancement factor \( F_x^{r²SCAN} \),

\[
F_x^{r²SCAN} = \{ h_x'(p) + f_x(\bar{\alpha})[h_x^0 - h_x^1] \} g_x(p). \tag{B5}
\]

In r²SCAN, \( g_x(p) \) is a non-analytic smooth function, with Taylor series \( 1 + \mathcal{O}(|\nabla n|^{\infty}) \). Therefore, \( g_x(p) \) does not contribute to the gradient expansion of the enhancement factor beyond order zeros. Note that \( h_x^0 = 1 + k_0 \), where \( k_0 = 0.174 \). As is done in Ref. \cite{14} to construct the model r⁴SCAN functional, we seek a Taylor expansion of \( F_x \) in \( p \) and \( \bar{\alpha} - 1 \), which approximately define the slowly-varying limit,

\[
F_x^{r²SCAN} = 1 + h_x'(0) p + \frac{h_x''(0)}{2} p^2 + \left[ f_x'(1)(\bar{\alpha} - 1) + f_x''(1)(\bar{\alpha} - 1)^2 \right] \left[ 1 + k_0 - 1 - h_x'(0)p - \frac{h_x''(0)}{2} p^2 \right] + \mathcal{O}(|\nabla n|^6). \tag{B6}
\]

Here, \( h_x'(0) = dh_x^1/d\bar{\alpha}(0) \), etc. Now, \( (\bar{\alpha} - 1) \) contains terms of both second- and fourth-order, whereas \((\bar{\alpha} - 1)^2 \) and \((\bar{\alpha} - 1)p \) contain terms of fourth- and sixth-order,

\[
(\bar{\alpha} - 1)^2 = \frac{400}{81} q^2 - \frac{200(8 + 9\eta)}{243} pq + \frac{25(8 + 9\eta)^2}{729} p^2 + \mathcal{O}(|\nabla n|^6) \tag{B7}
\]

\[
(\bar{\alpha} - 1)p = \frac{20}{9} pq - \frac{5(8 + 9\eta)}{27} p^2 + \mathcal{O}(|\nabla n|^6). \tag{B8}
\]

Thus the expression can be simplified as

\[
F_x^{r²SCAN} = 1 + h_x'(0) p + k_0 f_x'(1)(\bar{\alpha} - 1) + \frac{h_x''(0)}{2} p^2 - h_x'(0)f_x'(1)(\bar{\alpha} - 1)p + \frac{k_0}{2} f_x''(1)(\bar{\alpha} - 1)^2 + \mathcal{O}(|\nabla n|^6). \tag{B9}
\]

After inserting Eq. \cite{B4} for the gradient expansion of the approximate \( \bar{\alpha} \), yielding the OFR2 enhancement factor,

\[
F_x^{OFR2} = 1 + \left[ h_x'(0) - \frac{5(8 + 9\eta)}{27} k_0 f_x'(1) \right] p + \frac{20}{9} k_0 f_x'(1) q + \left[ \frac{200}{81} f_x''(1) + f_x'(1)b_{pq} \right] k_0 q^2 \tag{B10}
\]

\[
- \left[ \left( \frac{100\eta}{27} - b_{pq} \right) k_0 f_x'(1) + h_x'(0)f_x'(1) \right] \frac{20}{9} q + \left[ \frac{100(8 + 9\eta)}{243} k_0 f_x''(1) \right] pq
\]

\[
+ \left[ \frac{h_x''(0)}{2} + \left( b_{pp} + \frac{200\eta}{81} + \frac{25\eta^2}{9} \right) k_0 f_x'(1) + \frac{5(8 + 9\eta)}{27} h_x'(0)f_x'(1) + \frac{25(8 + 9\eta)}{1458} k_0 f_x''(1) \right] p^2 + \mathcal{O}(|\nabla n|^6). \]
As was shown in Ref. [44], the divergence theorem may be used to eliminate the term linear in \( q \) in favor of a term linear in \( p \) plus a gauge function. Suppose an enhancement factor can be separated as \( F_x = \tilde{F}_x + n^{-4/3}\nabla \cdot \mathbf{G}_x \). Under integration over a volume \( \Omega \) with bounding surface \( \partial \Omega \), the exchange energy is

\[
E_x[n] = \int_\Omega F_x \left[ \nabla \cdot \mathbf{G}_x - \frac{6}{5} \left( \frac{\nabla n}{(4\pi^2)^{3/3} n^{1/3}} \right) \right] d^3v.
\]

Provided that the integral of \( \mathbf{G}_x \) vanishes at the bounding surface, \( F_x \) and the “integrated-by-parts” \( \tilde{F}_x \) will yield the same exchange energy and potential, but different exchange energy densities. Note that \( A_x = -3(3\pi^2)^{1/3}/4\pi \). As is easily seen,

\[
qn^{4/3} = \frac{P}{3} n^{4/3} + \nabla \cdot \left[ \frac{\nabla n}{4(3\pi^2)^{3/3} n^{1/3}} \right],
\]

therefore the overall gauge function is \( n^{-4/3}\nabla \cdot [n^{-1/3}\nabla n]/[4(3\pi^2)^{2/3}] \). Then the integrated-by-parts enhancement factor is

\[
\tilde{F}_x^{OFR2} = 1 + \left[ \frac{5(4 + 9\eta)}{27} k_0 f'_x(1) \right] p + \left[ \frac{200}{81} f'_x(1) + f'_x(1) b_{pq} \right] k_0 q^2
\]

\[
- \left[ \left( \frac{100\eta}{27} - b_{pq} \right) k_0 f'_x(1) + h'_x(0) f'_x(1) \right] p q + \left[ \frac{h'_x(0)}{2} + \left( b_{pp} + \frac{200\eta}{81} + \frac{25\eta^2}{9} \right) k_0 f'_x(1) + \frac{5(8 + 9\eta)}{27} h'_x(0) f'_x(1) + \frac{25(8 + 9\eta)^2}{1458} k_0 f''_x(1) \right] q^2 + O(|\nabla n|^6).
\]

Now equate the terms in Eq. B13 with the terms of matching order in Eq. B1 to constrain \( \tilde{F}_x^{OFR2} \) to have the correct fourth-order gradient expansion,

\[
h'_x(0) - \frac{5(4 + 9\eta)}{27} k_0 f'_x(1) = \frac{10}{81}
\]

\[
\frac{200}{81} f'_x(1) + f'_x(1) b_{pq} = \frac{146}{2025}
\]

\[
\left( \frac{100\eta}{27} - b_{pq} \right) k_0 f'_x(1) + \frac{20}{9} h'_x(0) f'_x(1) + \frac{10(8 + 9\eta)}{243} k_0 f''_x(1) = \frac{73}{405}
\]

\[
\left( \frac{h'_x(0)}{2} + \left( b_{pp} + \frac{200\eta}{81} + \frac{25\eta^2}{9} \right) k_0 f'_x(1) + \frac{5(8 + 9\eta)}{27} h'_x(0) f'_x(1) + \frac{25(8 + 9\eta)^2}{1458} k_0 f''_x(1) \right) q^2 = 0.
\]

By construction, in \( r^2 \)SCAN, \( h'_x(0) \) is constrained to satisfy Eq. B14 Therefore we need only solve for the \( b_i \),

\[
b_{qq} = \frac{146}{2025} \left[ f'_x(1) \right]^{-1} \frac{1}{f''_x(1)} \approx 1.8010191875490722
\]

\[
b_{pq} = -1 \left[ f'_x(1) \right]^{-1} \left[ \frac{200}{81} f'_x(1) + f'_x(1) b_{pq} \right] k_0 \approx -1.850497151349339
\]

\[
b_{pp} = -1 \left[ f'_x(1) \right]^{-1} \left[ \frac{h'_x(0)}{2} + \frac{5(8 + 9\eta)}{27} h'_x(0) f'_x(1) + \frac{25(8 + 9\eta)^2}{1458} k_0 f''_x(1) \right] \approx 0.974002499350257.
\]

In \( r^2 \)SCAN [33], the interpolation function \( f_x \) is a piecewise function, but is a polynomial for \( 0 \leq \varpi \leq 2.5 \),

\[
f_x(0 \leq \varpi \leq 2.5) = \sum_{i=0}^{7} c_{xi} \varpi^i
\]

\[
f'_x(1) = \sum_{i=1}^{7} i c_{xi} \approx -0.9353000875519996
\]

\[
f''_x(1) = \sum_{i=2}^{7} i(i-1)c_{xi} \approx 0.8500359204920018,
\]

\[
f''_x(1) = \sum_{i=0}^{7} \varpi^i c_{xi} \approx 0.8500359204920018.
\]
with the coefficients $c_{xi}$ taken from rSCAN \cite{54}. The $h^i_x$ function is unique to r$^2$SCAN,
\begin{equation}
    h^i_x(p) = 1 + k_1 - k_1[1 + x(p)/k_1]^{-1}
\end{equation}
\begin{equation}
    x(p) = \left\{ \frac{5(4 + 9\eta)}{27} k_0 f'_x(1) \exp[-p^2/k_1^2] + \frac{10}{81} \right\} p,
\end{equation}
therefore
\begin{equation}
    h'_x(0) = \frac{5(4 + 9\eta)}{27} k_0 f'_x(1) + \frac{10}{81} \approx 0.0026357640358089796
\end{equation}
\begin{equation}
    h''_x(0) = -\frac{2h'_x(0)^2}{k_1} \approx -0.00021376160161427815.
\end{equation}

It should be noted that the fourth-order terms in $\tau(p, q)$ are positive semi-definite, as they can be written in the form
\begin{equation}
    b_{qq} q^2 + b_{pq} pq + b_{pp} p^2 = \left( \sqrt{b_{qq} q^2} + \frac{b_{pq}}{2 \sqrt{b_{qq}}} p \right)^2 + \left( b_{pp} - \frac{b_{pq}^2}{4b_{qq}} \right) p^2,
\end{equation}
and $b_{pp} - b_{pq}^2/(4b_{qq}) > 0$.

**Appendix C: Laplacian-dependent stress tensor**

Also of use in practical calculations is the exchange-correlation stress tensor, $\Sigma^{ij}_{xc}$, defined as \cite{109}
\begin{equation}
    \Sigma^{ij}_{xc} = \int_\Omega n(r) r_j \frac{\partial v_{xc}}{\partial r_i} \, \! \! dr^3
\end{equation}
where the system volume is $\Omega$. We take $r_1 = x$, $r_2 = y$, and $r_3 = z$. Thus the exchange-correlation stress density,
\begin{equation}
    \sigma^{ij}_{xc} = n(r) r_j \frac{\partial v_{xc}}{\partial r_i}
\end{equation}
is only defined up to a certain gauge, like the exchange-correlation energy density $e_{xc}$. The gauge can be chosen up to the curl of a tensor, as the divergence of this tensor must yield the force on the system due to the exchange-correlation potential \cite{110}. An overall choice of sign corresponds to consideration of internal or external stresses (for example, VASP appears to use the opposite sign convention as Eq. \cite{C2}). Moreover, the stress tensor and its density should be symmetric.

While Eq. \cite{C1} is well-defined in a finite system, the term linear in $r_j$ makes this intractable in an extended system. Following Ref. \cite{109}, we therefore take the system volume $\Omega$ to be finite, and seek an expression for $\sigma^{ij}_{xc}$ that is independent of the boundary conditions. The latter expression will be well-defined as the thermodynamic average in an extended system. Consider that
\begin{equation}
    \sigma^{ij}_{xc} = \frac{\partial}{\partial r_i} (nr_j v_{xc}) - v_{xc} n \delta_{ij} - v_{xc} r_j \frac{\partial n}{\partial r_i},
\end{equation}
where $\delta_{ij} = 1$ if $i = j$ and 0 if $i \neq j$ is the Kronecker delta. In a finite system, the integral of the total derivative will vanish, as it can be evaluated on a bounding surface at infinity. Thus we will collect all terms that involve total derivatives and use those as a choice of gauge.

Suppose that an exchange-correlation functional depends upon $n, |\nabla n|$, and $\nabla^2 n$, and further that $e_{xc}$ and $v_{xc}$ are the exchange-correlation energy density and potential, respectively,
\begin{equation}
    E_{xc} = \int e_{xc}(n, |\nabla n|, \nabla^2 n) \, \! \! dr^3
\end{equation}
\begin{equation}
    v_{xc} = \frac{\partial e_{xc}}{\partial n} - \frac{\partial}{\partial r_k} \left[ \frac{\partial e_{xc}}{\partial (\nabla n)} \right] + \frac{\partial}{\partial r_k} \frac{\partial}{\partial r_k} \left( \frac{\partial e_{xc}}{\partial \nabla^2 n} \right).
\end{equation}
We use the Einstein or summation convention, wherein repeated indices imply summation,
\begin{equation}
    \frac{\partial}{\partial r_k} \frac{\partial e_{xc}}{\partial (\nabla n)} = \sum_{k=1}^{3} \frac{\partial}{\partial r_k} \frac{\partial e_{xc}}{\partial (\nabla n)},
\end{equation}
and the shorthand $\partial_k n \equiv \partial n / \partial r_k$. Then

$$\sigma_{xc}^{ij} = -v_{xc} n \delta_{ij} - \left[ \frac{\partial e_{xc}}{\partial n} - \frac{\partial}{\partial r_k} \left( \frac{\partial e_{xc}}{\partial (\partial_k n)} \right) + \frac{\partial}{\partial r_k} \frac{\partial}{\partial r_k} \left( \frac{\partial e_{xc}}{\partial (\partial_k n)^2} \right) \right] r_j \frac{\partial n}{\partial r_i} + \frac{\partial}{\partial r_i} (nr_j v_{xc}) . \quad \text{(C6)}$$

We can express the gradient of $e_{xc}$ as

$$\frac{\partial e_{xc}}{\partial r_i} = \frac{\partial e_{xc}}{\partial n} \frac{\partial n}{\partial r_i} + \frac{\partial e_{xc}}{\partial (\partial_k n)} \frac{\partial (\partial_k n)}{\partial r_i} + \frac{\partial e_{xc}}{\partial (\partial_k n)^2} \frac{\partial^2 (\partial_k n)}{\partial r_i} + \frac{\partial^2 e_{xc}}{\partial (\partial_k n)^3} n r_i \frac{\partial n}{\partial r_i} . \quad \text{(C7)}$$

and thus replace

$$\sigma_{xc}^{ij} = -v_{xc} n \delta_{ij} - r_j \frac{\partial e_{xc}}{\partial r_i} + r_j \frac{\partial e_{xc}}{\partial (\partial_k n)} \frac{\partial (\partial_k n)}{\partial r_i} + r_j \frac{\partial e_{xc}}{\partial (\partial_k n)^2} \frac{\partial^2 (\partial_k n)}{\partial r_i} + r_j n \frac{\partial}{\partial r_i} \frac{\partial e_{xc}}{\partial (\partial_k n)} \frac{\partial n}{\partial r_i} \frac{\partial e_{xc}}{\partial (\partial_k n)}$$

$$- \frac{\partial n}{\partial r_i} \frac{\partial}{\partial r_k} \frac{\partial}{\partial r_k} \left( \frac{\partial e_{xc}}{\partial (\partial_k n)} \right) + \frac{\partial}{\partial r_i} (nr_j v_{xc} - r_j e_{xc}) . \quad \text{(C8)}$$

Rearranging the term

$$r_j \frac{\partial e_{xc}}{\partial (\partial_k n)} \frac{\partial^2 (\partial_k n)}{\partial r_i} = \frac{\partial}{\partial r_k} \left[ r_j \frac{\partial n}{\partial r_i} \frac{\partial e_{xc}}{\partial (\partial_k n)} - \delta_{ik} \frac{\partial n}{\partial r_i} \frac{\partial e_{xc}}{\partial (\partial_k n)} - r_j \frac{\partial n}{\partial r_i} \frac{\partial e_{xc}}{\partial (\partial_k n)} \right] , \quad \text{(C9)}$$

shows that it partly cancels with another term in Eq. C8

$$\sigma_{xc}^{ij} = (e_{xc} - v_{xc} n) \delta_{ij} - \frac{\partial n}{\partial r_i} \frac{\partial e_{xc}}{\partial (\partial_k n)} + r_j \frac{\partial e_{xc}}{\partial (\partial_k n)^2} \frac{\partial^2 (\partial_k n)}{\partial r_i}$$

$$- r_j \frac{\partial n}{\partial r_i} \frac{\partial}{\partial r_k} \frac{\partial}{\partial r_k} \left( \frac{\partial e_{xc}}{\partial (\partial_k n)} \right) + \frac{\partial}{\partial r_i} (nr_j v_{xc} - r_j e_{xc}) + \frac{\partial}{\partial r_k} \left[ r_j \frac{\partial e_{xc}}{\partial (\partial_k n)} \frac{\partial n}{\partial r_i} \frac{\partial e_{xc}}{\partial (\partial_k n)} \right] . \quad \text{(C10)}$$

Now, assuming that $\partial n / \partial r_k$ has equal mixed partials,

$$\frac{\partial^3 n}{\partial r_k \partial r_k \partial r_i} = \frac{\partial^3 n}{\partial r_k \partial r_i \partial r_k} ,$$

we rearrange

$$r_j \frac{\partial e_{xc}}{\partial (\partial_k n)^2} \frac{\partial^2 (\partial_k n)}{\partial r_i} = \frac{\partial}{\partial r_k} \left( r_j \frac{\partial e_{xc}}{\partial (\partial_k n)^2} \frac{\partial (\partial_k n)}{\partial r_i} \right) - \delta_{jk} \frac{\partial e_{xc}}{\partial (\partial_k n)^2} \frac{\partial^2 (\partial_k n)}{\partial r_i} - r_j \frac{\partial^2 n}{\partial r_i} \frac{\partial e_{xc}}{\partial (\partial_k n)^2}$$

$$= \frac{\partial}{\partial r_k} \left( r_j \frac{\partial e_{xc}}{\partial (\partial_k n)^2} \frac{\partial (\partial_k n)}{\partial r_i} \right) - \frac{\partial e_{xc}}{\partial (\partial_k n)^2} \frac{\partial^2 (\partial_k n)}{\partial r_i} - \frac{\partial}{\partial r_k} \left( r_j \frac{\partial n}{\partial r_i} \frac{\partial e_{xc}}{\partial (\partial_k n)} \right)$$

$$+ \delta_{jk} \frac{\partial n}{\partial r_i} \frac{\partial}{\partial r_k} \frac{\partial}{\partial r_k} \left( \frac{\partial e_{xc}}{\partial (\partial_k n)^2} \right) + r_j \frac{\partial n}{\partial r_i} \frac{\partial}{\partial r_k} \frac{\partial}{\partial r_k} \left( \frac{\partial e_{xc}}{\partial (\partial_k n)^2} \right)$$

$$= \frac{\partial}{\partial r_k} \left( r_j \frac{\partial e_{xc}}{\partial (\partial_k n)^2} \frac{\partial (\partial_k n)}{\partial r_i} \right) - \frac{\partial n}{\partial r_i} \frac{\partial}{\partial r_k} \frac{\partial}{\partial r_k} \left( \frac{\partial e_{xc}}{\partial (\partial_k n)^2} \right) + \frac{\partial n}{\partial r_i} \frac{\partial}{\partial r_k} \frac{\partial}{\partial r_k} \left( \frac{\partial e_{xc}}{\partial (\partial_k n)^2} \right) - 2 \frac{\partial e_{xc}}{\partial (\partial_k n)^2} \frac{\partial^2 n}{\partial r_i} \frac{\partial e_{xc}}{\partial (\partial_k n)}$$

$$+ r_j \frac{\partial n}{\partial r_i} \frac{\partial}{\partial r_j} \frac{\partial}{\partial r_j} \left( \frac{\partial e_{xc}}{\partial (\partial_k n)^2} \right) . \quad \text{(C11)}$$

Inserting this latter equality into Eq. C10 shows further cancellation

$$\sigma_{xc}^{ij} = (e_{xc} - v_{xc} n) \delta_{ij} - \frac{\partial e_{xc}}{\partial (\partial_j n)} \frac{\partial n}{\partial r_i} - 2 \frac{\partial e_{xc}}{\partial (\partial_k n)^2} \frac{\partial^2 n}{\partial r_i} \frac{\partial e_{xc}}{\partial (\partial_k n)} + \frac{\partial}{\partial r_j} \left[ \frac{\partial n}{\partial r_i} \frac{\partial e_{xc}}{\partial (\partial_k n)} \right]$$

$$+ \frac{\partial}{\partial r_i} (nr_j v_{xc} - r_j e_{xc}) + \frac{\partial}{\partial r_k} \left[ r_j \frac{\partial n}{\partial r_i} \frac{\partial e_{xc}}{\partial (\partial_k n)} \right] + \frac{\partial}{\partial r_k} \left[ r_j \frac{\partial e_{xc}}{\partial (\partial_k n)^2} \frac{\partial^2 n}{\partial r_i} \frac{\partial e_{xc}}{\partial (\partial_k n)} - r_j \frac{\partial n}{\partial r_i} \frac{\partial}{\partial r_k} \frac{\partial e_{xc}}{\partial (\partial_k n)^2} \right] . \quad \text{(C12)}$$
Let

\[ \sigma^{ij}_{xc} = \tilde{\sigma}^{ij}_{xc} + G^{ij}_{xc} \]  
\[ \tilde{\sigma}^{ij}_{xc} = (e_{xc} - v_{xc} n) \delta^{ij} - \frac{\partial n}{\partial r_i} \frac{\partial e_{xc}}{\partial (\partial_j n)} - 2 \frac{\partial e_{xc}}{\partial n} \frac{\partial^2 n}{\partial \nabla^2 n \partial r_i \partial r_j} \] \hspace{1cm} (C13)

\[ G^{ij}_{xc} = \frac{\partial}{\partial r_j} \left[ \frac{\partial n}{\partial r_i} \frac{\partial e_{xc}}{\partial \nabla^2 n} \right] + \frac{\partial}{\partial r_i} \left( nr_j v_{xc} - r_j e_{xc} \right) + \frac{\partial}{\partial r_k} \left[ r_j \frac{\partial e_{xc}}{\partial (\partial_k n) \partial r_i} \frac{\partial n}{\partial r_j} \right] \] \hspace{1cm} (C14)

\[ + \frac{\partial}{\partial r_k} \left[ r_j \frac{\partial e_{xc}}{\partial \nabla^2 n} \frac{\partial^2 n}{\partial r_k \partial r_i} - r_j \frac{\partial n}{\partial r_i} \frac{\partial}{\partial r_k} \left( \frac{\partial e_{xc}}{\partial \nabla^2 n} \right) \right]. \] \hspace{1cm} (C15)

The total stress due to the volume integral of \( \sigma^{ij}_{xc} \) and its integrated-by-parts counterpart \( \tilde{\sigma}^{ij}_{xc} \) will be the same provided

\[ \int_{\Omega} G^{ij}_{xc} d^3r = 0, \]  
\[ \int_{\Omega} \tilde{\sigma}^{ij}_{xc} d^3r = \int_{\Omega} (e_{xc} - v_{xc} n) \delta^{ij} d^3r. \] \hspace{1cm} (C16)

again in a finite system. Looking term by term, this requires that the factors multiplying \( r_i \) in \( G^{ij}_{xc} \) vanish faster than \( 1/r \). As the density decays exponentially as \( r \to \infty \) \cite{111}, we can safely assume that the integral of \( G^{ij}_{xc} \) vanishes in a finite system.

As a final note of simplification, modern DFAs tend not to depend upon the direction of the density gradient, only its magnitude,

\[ \frac{\partial e_{xc}}{\partial (\partial_j n)} = \frac{\partial e_{xc}}{\partial |\nabla n|} \frac{\partial}{\partial (\partial_j n)} \left[ (\partial_k n)(\partial_k n) \right]^{1/2} = \frac{1}{|\nabla n|} \frac{\partial n}{\partial r_j} \frac{\partial e_{xc}}{\partial |\nabla n|}, \] \hspace{1cm} (C17)

and thus the stress tensor density \( \tilde{\sigma}^{ij}_{xc} \) appropriate for extended systems is

\[ \tilde{\sigma}^{ij}_{xc} = (e_{xc} - v_{xc} n) \delta^{ij} - \frac{1}{|\nabla n|} \frac{\partial n}{\partial r_i} \frac{\partial n}{\partial r_j} \frac{\partial e_{xc}}{\partial |\nabla n|} - 2 \frac{\partial e_{xc}}{\partial n} \frac{\partial^2 n}{\partial \nabla^2 n \partial r_i \partial r_j}, \] \hspace{1cm} (C18)

and the stress tensor is \( \Sigma^{ij}_{xc} = \int \tilde{\sigma}^{ij}_{xc} d^3r. \)
### Appendix D: Full LC20 data

| Solid (structure) | Reference (Å) | PBEsol | r²SCAN | r²SCAN-L | OFR2 |
|-------------------|----------------|--------|--------|---------|------|
| Li (bcc)          | 3.451          | -0.018 | 0.024  | -0.039  | -0.012 |
| Na (bcc)          | 4.207          | -0.036 | 0.007  | -0.039  | -0.056 |
| Ca (fcc)          | 5.555          | -0.095 | 0.023  | -0.044  | -0.046 |
| Sr (fcc)          | 6.042          | -0.129 | 0.061  | 0.015   | -0.023 |
| Ba (bcc)          | 5.004          | -0.110 | 0.073  | 0.069   | -0.006 |
| Al (fcc)          | 4.019          | -0.004 | -0.032 | -0.046  | -0.029 |
| Cu (fcc)          | 3.595          | -0.026 | -0.013 | 0.017   | -0.028 |
| Rh (fcc)          | 3.793          | -0.013 | 0.012  | 0.037   | -0.006 |
| Pd (fcc)          | 3.876          | -0.003 | 0.037  | 0.062   | 0.006  |
| Ag (fcc)          | 4.063          | -0.011 | 0.044  | 0.076   | 0.002  |
| C (ds)            | 3.555          | 0.001  | 0.007  | 0.014   | 0.023  |
| SiC (zb)          | 4.348          | 0.011  | 0.007  | 0.008   | 0.022  |
| Si (ds)           | 5.422          | 0.014  | 0.018  | 0.001   | 0.009  |
| Ge (ds)           | 5.644          | 0.031  | 0.035  | 0.057   | 0.014  |
| GaAs (zb)         | 5.641          | 0.023  | 0.028  | 0.048   | 0.003  |
| LiF (rs)          | 3.974          | 0.035  | 0.010  | 0.004   | 0.002  |
| LiCl (rs)         | 5.072          | -0.008 | 0.016  | -0.002  | -0.021 |
| NaF (rs)          | 4.57           | 0.066  | 0.011  | 0.016   | 0.020  |
| NaCl (rs)         | 5.565          | 0.041  | 0.026  | 0.005   | -0.022 |
| MgO (rs)          | 4.188          | 0.023  | 0.008  | 0.004   | 0.003  |
| ME (metals)       | -0.044         | 0.024  | 0.011  | -0.020  |
| MAE (metals)      | 0.044          | 0.033  | 0.044  | 0.021   |
| ME (insulators)   | 0.024          | 0.017  | 0.016  | 0.005   |
| MAE (insulators)  | 0.025          | 0.017  | 0.016  | 0.014   |
| ME (total)        | -0.010         | 0.020  | 0.013  | -0.007  |
| MAE (total)       | 0.035          | 0.025  | 0.030  | 0.018   |

TABLE XII. Relative errors ($a_{approx}^0 - a_{ref}^0$) for the LC20 test set of 20 cubic lattice constants, all in Å. Reference experimental equilibrium lattice constants (with zero-point corrections included) are taken from Ref. [87]. We include mean absolute (MAE) and mean errors (ME). The structures considered are face-centered cubic (fcc), body-centered cubic (bcc), cubic diamond structure (ds), rock-salt (rs), and zinc-blende (zb). OFR2 exceeds the accuracy of the parent meta-GGA, r²SCAN in terms of accuracy for the metallic and insulating subsets of LC20, and overall.
| Solid (structure) | Reference (GPa) | PBEsol $r^2$SCAN | $r^2$SCAN-L | OFR2 |
|------------------|----------------|------------------|------------|------|
| Li (bcc)         | 13.1 0.619     | -6.659           | -4.143     | -1.461 |
| Na (bcc)         | 7.9 0.021      | 0.254            | 1.546      | -0.480 |
| Ca (fcc)         | 15.9 2.084     | 1.959            | 3.237      | 3.190 |
| Sr (fcc)         | 12.0 0.397     | -0.627           | 0.019      | 0.269 |
| Ba (bcc)         | 10.6 -1.161    | -2.051           | -1.001     | -1.265 |
| Al (fcc)         | 77.1 4.995     | 15.956           | 20.322     | 14.243 |
| Cu (fcc)         | 144.3 20.498   | 15.450           | -0.281     | 24.019 |
| Rh (fcc)         | 277.1 19.283   | 4.888            | -20.918    | 14.439 |
| Pd (fcc)         | 187.2 17.506   | -0.978           | -19.524    | 11.245 |
| Ag (fcc)         | 105.7 12.824   | -2.764           | -12.636    | 6.744 |
| C (ds)           | 454.7 -5.144   | -5.483           | -21.214    | -28.634 |
| SiC (zb)         | 229.1 -8.101   | -2.166           | -9.657     | -11.991 |
| Si (ds)          | 101.3 -7.744   | -4.034           | -5.194     | -6.490 |
| Ge (ds)          | 79.4 -11.809   | -8.147           | -17.672    | -8.620 |
| GaAs (zb)        | 76.7 -7.721    | -4.104           | -30.596    | -3.777 |
| LiF (rs)         | 76.3 -2.860    | 3.965            | 4.592      | 5.766 |
| LiCl (rs)        | 38.7 -3.517    | -0.413           | -3.648     | -3.061 |
| NaF (rs)         | 53.1 -4.571    | 2.988            | 2.640      | 3.033 |
| NaCl (rs)        | 27.6 -1.714    | -0.103           | 0.791      | 2.324 |
| MgO (rs)         | 169.8 -9.361   | 0.801            | 0.774      | -0.966 |
| ME (metals)      | 7.707 2.743    | -3.338           | 7.094      |       |
| MAE (metals)     | 7.939 4.959    | 8.363            | 7.735      |       |
| ME (insulators)  | -6.254 -1.669  | -7.918           | -5.241     |       |
| MAE (insulators) | 6.254 3.220    | 9.678            | 7.466      |       |
| ME (total)       | 0.726 0.537    | -5.628           | 0.926      |       |
| MAE (total)      | 7.096 4.090    | 9.020            | 7.601      |       |

TABLE XIII. Relative errors ($B_{0}^{\text{approx}} - B_{0}^{\text{ref}}$) for the LC20 test set [56] of bulk moduli for 20 cubic solids, all in GPa (1 eV/Å$^3$ ≈ 160.2176634 GPa). Reference experimental bulk moduli, which include zero-point energy corrections, are taken from Ref. [104]. It should be noted that the $r^2$SCAN and $r^2$SCAN-L values presented here and in Ref. [52] agree to within a few GPa for each solid, generally. In a few cases, like Ge and GaAs for $r^2$SCAN-L or NaCl for $r^2$SCAN and $r^2$SCAN-L, agreement is quite poor. We attribute this to the different pseudopotentials used: Ref. [52] used “no-suffix” pseudopotentials, whereas we used the recommended pseudopotentials from VASP. In these cases, the Ge$_d$ (which treats $d$-semicore states as valence states), Ga$_d$, and Na$_p$ (which treats $p$-semicore states as valence states) pseudopotentials might give very different behaviors than their no-suffix counterparts (which treat fewer electrons as valence electrons).
TABLE XIV. Comparison of the LC20 cubic lattice constants found by fitting (EOS) to the SJEOS and by minimization of the stress tensor (ST) using Eq. [C18]. The deviations are $a_0^{\text{EOS}} - a_0^{\text{ST}}$; mean deviations (MDs) and mean absolute deviations (MADs) are also presented.

| Solid (struct) | PBEsol | r$^2$SCAN | r$^2$SCAN-L | OFR2 |
|----------------|---------|------------|-------------|------|
| Li (bcc)       | 3.9698 x 10$^{-3}$ | 9.1842 x 10$^{-3}$ | 1.5553 x 10$^{-2}$ | -9.6238 x 10$^{-3}$ |
| Na (bcc)       | 9.8549 x 10$^{-4}$ | 7.0530 x 10$^{-4}$ | 4.1485 x 10$^{-3}$ | 1.1015 x 10$^{-2}$ |
| Ca (fcc)       | 2.5486 x 10$^{-3}$ | 2.9326 x 10$^{-3}$ | 1.5698 x 10$^{-2}$ | 1.6111 x 10$^{-2}$ |
| Sr (fcc)       | -1.2412 x 10$^{-2}$ | 1.2689 x 10$^{-3}$ | 2.5362 x 10$^{-2}$ | 6.6702 x 10$^{-3}$ |
| Ba (bcc)       | 2.5548 x 10$^{-4}$ | 1.0728 x 10$^{-3}$ | 5.9928 x 10$^{-2}$ | 1.4873 x 10$^{-2}$ |
| Al (fcc)       | 6.1313 x 10$^{-6}$ | -7.9749 x 10$^{-4}$ | 2.6118 x 10$^{-3}$ | 3.0966 x 10$^{-3}$ |
| Cu (fcc)       | 3.0698 x 10$^{-4}$ | 9.6047 x 10$^{-4}$ | 3.5296 x 10$^{-3}$ | 1.4137 x 10$^{-3}$ |
| Rh (fcc)       | 2.9099 x 10$^{-4}$ | 3.6044 x 10$^{-5}$ | 3.8564 x 10$^{-4}$ | 3.7767 x 10$^{-4}$ |
| Pd (fcc)       | -3.3150 x 10$^{-4}$ | -6.9784 x 10$^{-4}$ | -7.5960 x 10$^{-4}$ | -3.4265 x 10$^{-4}$ |
| Ag (fcc)       | 5.6017 x 10$^{-4}$ | 1.2080 x 10$^{-4}$ | 1.2583 x 10$^{-4}$ | 5.0807 x 10$^{-4}$ |
| C (ds)         | 7.3743 x 10$^{-4}$ | 9.5259 x 10$^{-4}$ | 8.4424 x 10$^{-4}$ | 2.6446 x 10$^{-3}$ |
| SiC (zb)       | 6.5009 x 10$^{-4}$ | 6.9223 x 10$^{-4}$ | 1.5169 x 10$^{-3}$ | 2.2265 x 10$^{-3}$ |
| Si (ds)        | 1.5047 x 10$^{-4}$ | 1.8607 x 10$^{-4}$ | -9.5398 x 10$^{-4}$ | 3.3177 x 10$^{-3}$ |
| Ge (ds)        | 4.8177 x 10$^{-4}$ | 1.7996 x 10$^{-3}$ | 1.9719 x 10$^{-3}$ | 3.7134 x 10$^{-3}$ |
| GaAs (zb)      | -1.9404 x 10$^{-4}$ | -3.2999 x 10$^{-4}$ | 1.0211 x 10$^{-2}$ | 3.0868 x 10$^{-3}$ |
| LiF (rs)       | 5.7602 x 10$^{-3}$ | 2.0001 x 10$^{-3}$ | -2.7121 x 10$^{-3}$ | 7.1041 x 10$^{-4}$ |
| LiCl (rs)      | 1.6706 x 10$^{-3}$ | -1.0409 x 10$^{-3}$ | -4.9830 x 10$^{-3}$ | -6.1942 x 10$^{-4}$ |
| NaF (rs)       | 6.0002 x 10$^{-3}$ | 1.7042 x 10$^{-3}$ | 3.5240 x 10$^{-3}$ | 8.9884 x 10$^{-3}$ |
| NaCl (rs)      | 1.6417 x 10$^{-3}$ | -6.9238 x 10$^{-3}$ | 6.5536 x 10$^{-3}$ | 1.8502 x 10$^{-3}$ |
| MgO (rs)       | 1.3037 x 10$^{-3}$ | 1.1726 x 10$^{-3}$ | 7.7154 x 10$^{-5}$ | 1.9402 x 10$^{-3}$ |
| MD             | 7.1911 x 10$^{-4}$ | 7.4993 x 10$^{-4}$ | 7.1316 x 10$^{-3}$ | 3.5979 x 10$^{-3}$ |
| MAD            | 2.0129 x 10$^{-3}$ | 1.7289 x 10$^{-3}$ | 8.0725 x 10$^{-3}$ | 4.6564 x 10$^{-3}$ |
### Appendix E: Full LC23 data

| Solid (structure) | Reference (Å) | PBE | PBEsol | r^2SCAN | r^2SCAN-L | OFR2 |
|------------------|---------------|-----|--------|---------|-----------|------|
| Li (bcc)         | 3.451 -0.012  | -0.008 | 0.018  | 0.029   | -0.021    | 0.010 |
| Na (bcc)         | 4.207 -0.014  | -0.038 | -0.026 | -0.007  | -0.083    | -0.057 |
| K (bcc)          | 5.211 0.072   | 0.004  | 0.111  | 0.139   | -0.042    | -0.006 |
| Rb (bcc)         | 5.58 0.088    | -0.012 | 0.132  | 0.166   | 0.025     | 0.054 |
| Cs (bcc)         | 6.043 0.119   | -0.032 | 0.186  | 0.228   | 0.103     | 0.069 |
| Ca (fcc)         | 5.555 -0.024  | -0.095 | -0.005 | 0.024   | -0.049    | -0.046 |
| Sr (fcc)         | 6.042 -0.020  | -0.129 | 0.042  | 0.062   | 0.007     | -0.018 |
| Ba (bcc)         | 5.004 0.026   | -0.110 | 0.045  | 0.073   | 0.055     | 0.000 |
| Al (fcc)         | 4.019 0.021   | -0.004 | -0.014 | -0.032  | -0.046    | -0.029 |
| Cu (fcc)         | 3.595 0.040   | -0.026 | -0.027 | -0.013  | 0.014     | -0.028 |
| Rh (fcc)         | 3.793 0.031   | -0.018 | -0.014 | 0.011   | 0.031     | -0.010 |
| Pd (fcc)         | 3.876 0.064   | -0.003 | 0.018  | 0.037   | 0.062     | 0.005 |
| Ag (fcc)         | 4.063 0.084   | -0.011 | 0.021  | 0.044   | 0.076     | 0.002 |
| C (ds)           | 3.555 0.018   | 0.002  | 0.001  | 0.008   | 0.015     | 0.024 |
| SiC (zb)         | 4.348 0.032   | 0.011  | 0.004  | 0.007   | 0.008     | 0.023 |
| Si (ds)          | 5.422 0.047   | 0.014  | 0.005  | 0.018   | 0.004     | 0.005 |
| Ge (ds)          | 5.644 0.138   | 0.057  | 0.040  | 0.037   | 0.061     | 0.039 |
| GaAs (zb)        | 5.641 0.121   | 0.043  | 0.024  | 0.031   | 0.056     | 0.024 |
| LiF (rs)         | 3.974 0.099   | 0.042  | 0.005  | 0.022   | 0.039     | 0.043 |
| LiCl (rs)        | 5.072 0.081   | -0.002 | 0.021  | 0.039   | 0.006     | -0.003 |
| NaF (rs)         | 4.57 0.062    | -0.014 | -0.091 | -0.067  | -0.056    | -0.042 |
| NaCl (rs)        | 5.565 0.090   | -0.005 | -0.047 | -0.019  | -0.047    | -0.058 |
| MgO (rs)         | 4.188 0.060   | 0.023  | -0.002 | 0.008   | 0.009     | 0.006 |
| ME (metals)      | 0.037        | -0.037 | 0.037  | 0.058   | 0.010     | -0.004 |
| MAE (metals)     | 0.047        | 0.038  | 0.051  | 0.066   | 0.047     | 0.026 |
| ME (alkalis)     | 0.051        | -0.017 | 0.084  | 0.111   | -0.004    | 0.014 |
| MAE (alkalis)    | 0.061        | 0.019  | 0.095  | 0.114   | 0.055     | 0.039 |
| ME (insulators)  | 0.075        | 0.017  | -0.004 | 0.008   | 0.009     | 0.006 |
| MAE (insulators) | 0.075        | 0.021  | 0.024  | 0.026   | 0.030     | 0.027 |
| ME (total)       | 0.053        | -0.013 | 0.019  | 0.037   | 0.010     | 0.000 |
| MAE (total)      | 0.059        | 0.031  | 0.039  | 0.049   | 0.040     | 0.026 |
| ME (LC20)        | 0.047        | -0.014 | 0.001  | 0.016   | 0.007     | -0.005 |
| MAE (LC20)       | 0.054        | 0.033  | 0.024  | 0.029   | 0.037     | 0.024 |

**TABLE XV.** Relative errors in the equilibrium lattice constants $a_0$ (in Å) for the LC23 set (LC20 augmented with K, Rb, and Cs). The PBE and PBEsol GGAs, SCAN and r^2SCAN meta-GGAs, and r^2SCAN-L and OFR2 Laplacian-level meta-GGAs are presented. Zero-point corrected reference lattice constants are taken from Ref. [87], except for Rb, which is taken from [104]. LC20 error statistics are also reported to demonstrate the level of convergence with respect to the benchmark results presented in Table XII.
| Solid (structure) | Reference $(\text{GPa})$ | PBE | PBEsol | SCAN $r^2$SCAN | $r^2$SCAN-L | OFR2 |
|------------------|--------------------------|-----|--------|----------------|--------------|------|
| Li (bcc)         | 13.1 0.839 0.583 0.596 0.013 1.239 0.045 |     |        |                |              |      |
| Na (bcc)         | 7.9 0.014 0.125 0.163 0.065 -2.894 -0.671 |     |        |                |              |      |
| K (bcc)          | 3.8 -0.207 -0.077 -0.349 -0.360 11.257 1.370 |     |        |                |              |      |
| Rb (bcc)         | 3.6 -0.821 -0.648 -0.905 -0.963 2.295 -1.210 |     |        |                |              |      |
| Cs (bcc)         | 2.3 -0.348 -0.265 -0.324 -0.400 0.509 0.506 |     |        |                |              |      |
| Ca (fcc)         | 15.9 1.327 2.084 2.100 1.879 3.302 3.089 |     |        |                |              |      |
| Sr (fcc)         | 12.0 -0.689 0.399 -0.745 -0.615 -0.108 0.038 |     |        |                |              |      |
| Ba (bcc)         | 10.6 -1.761 -1.162 -2.070 -2.055 -3.387 -1.543 |     |        |                |              |      |
| Al (fcc)         | 77.1 0.260 4.965 1.574 15.934 13.496 11.678 |     |        |                |              |      |
| Cu (fcc)         | 144.3 -6.910 20.643 17.327 16.028 3.719 23.695 |     |        |                |              |      |
| Rh (fcc)         | 277.1 -18.422 21.063 17.606 4.758 -20.703 14.192 |     |        |                |              |      |
| Pd (fcc)         | 187.2 -18.081 17.501 8.447 -0.768 -18.533 11.649 |     |        |                |              |      |
| Ag (fcc)         | 105.7 -16.360 12.857 3.767 -2.716 -14.355 6.616 |     |        |                |              |      |
| C (ds)           | 454.7 -19.906 -3.552 3.901 -3.551 -19.449 -24.790 |     |        |                |              |      |
| SiC (zb)         | 229.1 -16.873 -8.254 -2.853 -2.359 -10.102 -13.234 |     |        |                |              |      |
| Si (ds)          | 101.3 -12.494 -7.742 -1.521 -4.008 -6.276 -6.069 |     |        |                |              |      |
| Ge (ds)          | 79.4 -20.223 -11.949 -7.579 -6.319 -11.531 -8.730 |     |        |                |              |      |
| GaAs (zb)        | 76.7 -14.665 -6.497 -1.881 -2.929 -8.244 -3.676 |     |        |                |              |      |
| LiF (rs)         | 76.3 -8.886 -3.567 3.680 2.138 -0.878 -7.408 |     |        |                |              |      |
| LiCl (rs)        | 38.7 -6.865 -3.591 -2.399 -3.768 -1.930 -1.460 |     |        |                |              |      |
| NaF (rs)         | 53.1 -5.934 -0.959 9.802 6.859 5.564 5.555 |     |        |                |              |      |
| NaCl (rs)        | 27.6 -3.345 -0.746 2.736 1.551 2.196 3.204 |     |        |                |              |      |
| MgO (rs)         | 169.8 -17.938 -9.140 2.450 0.967 -0.729 -0.859 |     |        |                |              |      |
| ME (metals)      | -4.704 6.005 3.630 2.369 -1.850 5.343 |     |        |                |              |      |
| MAE (metals)     | 5.080 6.336 4.306 3.581 7.369 5.869 |     |        |                |              |      |
| ME (alkalis)     | -0.105 -0.056 -0.164 -0.329 2.481 0.008 |     |        |                |              |      |
| MAE (alkalis)    | 0.446 0.340 0.467 0.360 3.639 0.760 |     |        |                |              |      |
| ME (insulators)  | -12.713 -5.600 0.634 -1.142 -5.138 -5.747 |     |        |                |              |      |
| MAE (insulators) | 12.713 5.600 3.880 3.445 6.690 7.498 |     |        |                |              |      |
| ME (total)       | -8.186 0.960 2.327 0.843 -3.284 0.521 |     |        |                |              |      |
| MAE (total)      | 8.399 6.016 4.121 3.522 7.074 6.578 |     |        |                |              |      |
| ME (LC20)        | -9.346 1.153 2.755 1.055 -4.480 0.566 |     |        |                |              |      |
| MAE (LC20)       | 9.590 6.869 4.660 3.964 7.432 7.410 |     |        |                |              |      |

TABLE XVI. Relative errors in the equilibrium bulk moduli $B_0$ (in GPa) for the LC23 set (LC20 augmented with K, Rb, and Cs). The PBE [5] and PBEsol [31] GGAs, SCAN [19] and $r^2$SCAN [33] τ-meta-GGAs, and $r^2$SCAN-L [52] and OFR2 Laplacian-level meta-GGAs are presented. Zero-point corrected reference bulk moduli are taken from Ref. [104]. LC20 error statistics are also reported to demonstrate the level of convergence with respect to the benchmark results presented in Table XIII.
| Solid (structure) | Reference (eV/atom) | PBE | PBEsol | SCAN $r^2$SCAN | $r^2$SCAN-L | OFR2 |
|------------------|---------------------|-----|--------|----------------|-------------|------|
| Li (bcc)         | 1.67 -0.065         | 0.005 -0.105 | -0.096 | -0.060 -0.102 |
| Na (bcc)         | 1.12 -0.033         | 0.038 -0.018 | -0.031 | -0.056 -0.050 |
| K (bcc)          | 0.94 -0.073         | -0.011 -0.074 | -0.089 | -0.100 -0.090 |
| Rb (bcc)         | 0.86 -0.088         | -0.025 -0.097 | -0.111 | -0.131 -0.101 |
| Cs (bcc)         | 0.81 -0.099         | -0.032 -0.121 | -0.131 | -0.154 -0.149 |
| Ca (fcc)         | 1.87 0.032          | 0.233 0.206 | 0.201 | 0.181 0.174 |
| Sr (fcc)         | 1.73 -0.122         | 0.077 0.078 | 0.060 | 0.001 0.078 |
| Ba (bcc)         | 1.91 -0.035         | 0.203 0.117 | 0.077 | -0.006 0.079 |
| Al (fcc)         | 3.43 0.080          | 0.432 0.170 | 0.172 | -0.006 0.016 |
| Cu (fcc)         | 3.51 -0.025         | 0.522 0.375 | 0.350 | -0.018 0.385 |
| Rh (fcc)         | 5.78 -0.021         | 0.933 0.072 | 0.052 | -0.335 0.462 |
| Pd (fcc)         | 3.93 -0.189         | 0.541 0.437 | 0.236 | -0.244 0.363 |
| Ag (fcc)         | 2.96 -0.441         | 0.118 -0.075 | -0.082 | -0.450 -0.037 |
| C (ds)           | 7.55 0.264          | 0.763 -0.051 | -0.090 | -0.196 -0.186 |
| SiC (zb)         | 6.48 -0.012         | 0.411 -0.037 | 0.046 | -0.203 -0.218 |
| Si (ds)          | 4.68 -0.100         | 0.246 0.029 | 0.190 | -0.084 -0.092 |
| Ge (ds)          | 3.89 -0.180         | 0.211 0.246 | 0.133 | -0.314 0.042 |
| GaAs (zb)        | 3.34 -0.158         | 0.233 0.029 | -0.016 | -0.284 0.013 |
| LiF (rs)         | 4.46 -0.023         | 0.085 -0.066 | -0.065 | -0.171 -0.271 |
| LiCl (rs)        | 3.59 -0.189         | -0.056 -0.102 | -0.121 | -0.179 -0.246 |
| NaF (rs)         | 3.97 0.027          | 0.128 0.041 | 0.044 | -0.074 -0.169 |
| NaCl (rs)        | 3.34 -0.181         | -0.071 -0.041 | -0.056 | -0.136 -0.205 |
| MgO (rs)         | 5.2 -0.196          | 0.134 0.062 | 0.055 | -0.060 -0.182 |
| ME (metals)      | -0.083 0.233        | 0.074 | 0.047 | -0.106 0.079 |
| ME (alkalis)     | -0.072 -0.005       | -0.083 | -0.092 | -0.100 -0.099 |
| ME (insulators)  | -0.075 0.208        | 0.011 | 0.012 | -0.170 -0.152 |
| ME (total)       | -0.079 0.222        | 0.047 | 0.032 | -0.134 -0.021 |
| ME (LC20)        | -0.078 0.259        | 0.068 | 0.053 | -0.135 -0.007 |
| ME (LC20)        | -0.078 0.259        | 0.068 | 0.053 | -0.135 -0.007 |

TABLE XVII. Relative errors in the equilibrium cohesive energies $E_0$ (in eV/atom) for the LC23 set (LC20 augmented with K, Rb, and Cs). The PBE [5] and PBEsol [31] GGAs, SCAN [19] and $r^2$SCAN [33] $r$-meta-GGAs, and $r^2$SCAN-L [52] and OFR2 Laplacian-level meta-GGAs are presented. Reference cohesive energies with zero-point and thermal corrections are taken from Ref. [104]. LC20 error statistics are also reported.