

Pseudopotentials for meta-GGA calculations

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The construction of consistent pseudopotentials for exchange-correlation approximations that depend on the kinetic energy density [meta-generalized gradient approximations (meta-GGAs)] is challenging because of their explicit orbital dependence. However, modern meta-GGAs use the kinetic energy density to distinguish between one- and many-electron regions of space, and therefore, the straightforward use of inconsistent, e.g., GGA-based pseudopotentials, can lead to substantial errors. We here discuss a scheme for constructing pseudopotentials that incorporate the atomic kinetic energy density in the spirit of a core correction. This considerably increases the accuracy of meta-GGA calculations that use pseudopotentials. Examples and tests are presented for the nonrelativistic and the relativistic Troullier-Martins pseudopotential scheme using real-space grid based calculations. We discuss future extensions of the scheme.

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I. INTRODUCTION

Density functional theory (DFT) in the Kohn-Sham [1,2] or the generalized Kohn-Sham [3] scheme has evolved into one of the most often used theories in condensed matter physics, material science, and quantum chemistry. Although DFT is exact in principle, its accuracy in practice depends on the approximation that is used for the exchange-correlation (xc) energy functional. In the past years, meta-GGAs that explicitly depend on the kinetic energy density have become increasingly popular. Meta-generalized gradient approximations (meta-GGAs) can go decisively beyond GGAs in terms of the physics that they can describe: They can distinguish between different types of electronic bonds [4–8], they can incorporate a sizable derivative discontinuity [9,10], and they can capture effects of (ultra-)nonlocality while still being semilocal in terms of their computational cost [11,12]. Thus, meta-GGAs not only allow for a reliable description of bond energies and lengths (see, e.g., Refs. [5,10,13,14]), but they can also significantly increase the accuracy in the prediction of band gaps [9–11,15–17] and response properties [12,18].

Meta-GGAs are thus the most advanced class of semilocal cost functionals. Semilocal xc approximations are particularly popular in solid-state physics and material science. This is, to some extent, explained by the high computational cost associated with Fock exchange in plane-wave [19,20] and real-space [21–23] representations. The latter allow for the efficient numerical solution of the Kohn-Sham equations in periodic and extended finite systems. However, evaluating Coulomb and

Fock integrals so far is a relatively costly step in plane-wave and real-space approaches. As meta-GGAs can introduce some of the physics that Fock exchange can incorporate into hybrid functionals [12], they offer a computationally efficient alternative to hybrids for solid-state calculations.

Consequently, there is a substantial interest in making meta-GGAs available in a technically reliable way for plane-wave and real-space programs, which typically explicitly take into account only the valence electrons. One way of doing so is the Projector Augmented Waves technique and related approaches, in which frozen core states can be used to evaluate meta-GGAs [24,25]. Another way is using *ab initio* norm-conserving pseudopotentials. Using such techniques does not only reduce the computational cost by reducing the number of explicitly calculated electrons and by easing the requirements for the plane-wave cut-off or the real-space grid spacing, but also allows for efficiently taking into account relativistic effects. For many atoms the latter directly affect only the core orbitals and can therefore be incorporated into a pseudopotential. In this way, an effectively nonrelativistic calculation for the valence electrons can incorporate some of the most relevant relativistic effects in an indirect way via the pseudopotential.

In the past, several attempts have been made to improve the accuracy in pseudopotential-based meta-GGA calculations. One of the most important and widely used pseudopotential construction schemes is the one by Troullier and Martins [26], and Ref. [27] reported the construction of Troullier-Martins pseudopotentials for the meta-GGA SCAN. However, subsequent work pointed out that kinetic energy density terms and nonlinear core corrections have been neglected in this work, i.e., it does not yield potentials that are consistent with the original meta-GGA [25]. A different approach pseudized the kinetic energy density in a plane-wave basis for the generation of ultrasoft pseudopotentials [25]. This was not done for general meta-GGAs, but specifically for the Tran-Blaha potential, i.e., a potential-only functional that was empirically designed

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for band gap prediction and does not have a corresponding energy functional. Furthermore, a scheme was proposed to modify the SCAN functional by deriving a regularized variant called rSCAN, which facilitates the construction of consistent pseudopotentials [28] within the generalized Kohn-Sham framework. These pseudopotentials have been successfully employed in r²SCAN calculations [29]. Reference [30] took a step to explicitly take the kinetic energy dependence of meta-GGAs into account in the pseudopotential construction, but the approach was limited to small (1s) core atoms.

It is thus clear that constructing consistent pseudopotentials for meta-GGAs is not easy, and in Sec. II we discuss in detail why a fully consistent construction is challenging. Therefore, it is tempting to use inconsistent pseudopotentials, i.e., ones that were generated for another xc functional [31,32]. In recent tests, it was found that the resulting errors can be small or large depending on the system and the observable [30,32]. However, it is clear from examples [33] and on general grounds [33,34] that pseudopotential inconsistency can seriously limit the predictive power of a calculation. Therefore, improving pseudopotentials for meta-GGA calculations is a relevant task.

In this paper we elucidate the problem of combining meta-GGAs and pseudopotentials in Sec. II. We then develop a core kinetic energy density (CKED) correction scheme in Sec. III that allows to sidestep the serious difficulties in fully consistent meta-GGA pseudopotentials construction while significantly increasing the accuracy. In Sec. IV we extend this scheme to the relativistic case. Thus, we present a derivation and implementation of the CKED in the nonrelativistic as well as the relativistic Troullier-Martins pseudopotential generation scheme. We analyze the validity of our method by comparing pseudopotential-based results to results from all-electron calculations for the meta-GGAs TASK [9] and r2SCAN [14]. We discuss in detail the strengths and the limitations of our present approach, and how it can be developed further in future work. In the Supplemental Material we provide pseudopotentials for all second and third row elements (except the noble gases) as well as for the heavier (relativistic) elements Mo, W, Ag, and Au [35,36].

II. CHALLENGES WHEN COMBINING META-GGAS WITH PSEUDOPOTENTIALS

A. The Troullier-Martins construction reviewed in the light of meta-GGA functionals

The Troullier and Martins scheme [26] is one of the most successful and popular strategies for constructing norm-conserving *ab initio* pseudopotentials. For understanding why constructing such pseudopotentials consistently for meta-GGAs is challenging, it is helpful to recapitulate some of the steps that the Troullier-Martins construction relies on. For the sake of clarity we here refer to the nonrelativistic case.

The first central idea is to transform the all-electron orbitals of an atomic Kohn-Sham calculation with a given xc approximation to smooth pseudo-orbitals. That is, one first self-consistently solves the radial atomic all-electron

Kohn-Sham equation

$$\left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial r^2} + \frac{\hbar^2}{2m} \frac{l(l+1)}{r^2} + v_{\text{KS}}[n](r) \right] r\varphi_{nl}(r) = \varepsilon_{nl} r\varphi_{nl}(r), \quad (1)$$

where spherical symmetry has been assumed, with the Kohn-Sham potential

$$v_{\text{KS}}[n](r) = -\frac{Ze^2}{r} + v_{\text{H}}[n](r) + v_{\text{xc}}[n](r). \quad (2)$$

Z is the atomic number and the density is given by

$$n(r) = \sum_{nls} \Theta_{nls} \frac{\varphi_{nl}(r)^2}{4\pi}, \quad (3)$$

where $\Theta_{nls} = 2(2l+1)$ is the occupation of the nls subshell. Here, the usual product ansatz

$$\varphi_{nlm_l}(\mathbf{r}) = \varphi_{nl}(r) Y_l^{m_l}(\vartheta, \phi) \quad (4)$$

has been used, with $Y_l^{m_l}(\vartheta, \phi)$ denoting the spherical harmonics. Thus $n \in \mathbb{N}$, $l < n$ and $-l \leq m_l \leq l$ correspond to the nonrelativistic quantum numbers.

One then designs smooth pseudo-orbitals

$$\varphi_{nl}^{\text{ps}}(r) = \begin{cases} \varphi_{nl}(r) & \text{for } r \geq r_l \\ r^l \exp(p(r)) & \text{for } r < r_l \end{cases} \quad (5)$$

with a polynomial

$$p(r) = \sum_{i=0}^6 c_{2i} r^{2i}, \quad (6)$$

i.e., the pseudo-orbitals are nodeless and match the all-electron orbitals for large r (see Ref. [26] for details). Here, r_l is the cutoff radius that depends on the quantum number l .

A decisive aspect of the Troullier-Martins construction now is that one inverts the radial equation (1): Inserting the smooth pseudo-orbitals into the equation and inverting it, i.e., solving for the potential, yields the so-called screened pseudopotential

$$v_{\text{ps},l}^{\text{scr}}(r) = \varepsilon_{nl} - \frac{\hbar^2 l(l+1)}{2mr^2} + \frac{\hbar^2}{2mr\varphi_{nl}^{\text{ps}}(r)} \frac{\partial^2}{\partial r^2} (r\varphi_{nl}^{\text{ps}}(r)). \quad (7)$$

For this inversion step to be doable, it is decisive that the potential be local multiplicative.

The final pseudopotential is derived via the unscreening process: The Hartree and xc potentials corresponding to the atomic valence pseudodensity are subtracted from the screened pseudopotential. This yields the effective potential that describes the interaction between the nucleus and the core electrons with the valence electrons.

We can now analyze where the challenges arise when trying to realize the Troullier-Martins scheme for meta-GGAs. To give a specific example we refer to the form that many modern meta-GGAs such as SCAN, r2SCAN, TASK and LAK use, i.e., the exchange energy density is written in the form [9,10,14,37]

$$e_x^{\text{mGGA}}[n, \nabla n, \tau] = A_x n^{4/3} F_x[s, \alpha] \quad (8)$$

with $A_x = -(3e^2/4)(3/\pi)^{1/3}$, and e being the elementary charge. The enhancement factor F_x does not only depend on the dimensionless variable

$$s[n, \nabla n] = \frac{|\nabla n|}{2(3\pi^2)^{1/3}n^{4/3}}, \quad (9)$$

and the density

$$n = \sum_{i=1}^N |\varphi_i(\mathbf{r})|^2 \quad (10)$$

(now written not for an atom, but for a general system with N electrons) that also feature in GGAs, but also on

$$\alpha[n, \nabla n, \{\varphi_i\}] = \frac{\tau - \tau^W}{\tau^{\text{unif}}}. \quad (11)$$

Here and in the following,

$$\tau^W[n, \nabla n] = \frac{\hbar^2}{8m} \frac{|\nabla n|^2}{n} \quad (12)$$

denotes the von Weizsäcker kinetic energy density, m the electron mass, and $\tau^{\text{unif}}[n] = A_s n^{5/3}$ with $A_s = (3\hbar^2/10m)(3\pi^2)^{2/3}$ is the uniform density limit of the orbital-dependent kinetic-energy density $\tau(\mathbf{r})$

$$\tau[\{\varphi_i\}](\mathbf{r}) = \frac{\hbar^2}{2m} \sum_{i=1}^N |\nabla \varphi_i|^2. \quad (13)$$

α or τ , respectively, is the decisive quantity that endows meta-GGAs with their special properties via the explicit dependence on the orbitals φ_i [12].

This explicit orbital dependence has the consequence that one needs to choose—just like for any other orbital dependent functional [38]—one of the two possible ways how to use the meta-GGA. One can either take the Kohn-Sham route in which the global multiplicative potential $v_{\text{xc}}(\mathbf{r}) = \delta E_{\text{xc}}/\delta n(\mathbf{r})$ is constructed via the optimized effective potential, or one can resort to generalized Kohn-Sham theory [39], in which the potential is obtained from the functional derivative with respect to the orbitals, $\delta E_{\text{xc}}/\delta \varphi_i^*(\mathbf{r})$.

While meta-GGAs have been used in the Kohn-Sham scheme, e.g., in Refs. [40,41], the majority of meta-GGA calculations use the generalized Kohn-Sham scheme. There are several reasons for this. The generalized Kohn-Sham scheme allows to avoid the numerically involved solution of the optimized effective potential equation, it can endow the frontier eigenvalue gap with physical meaning [11,15,39,42], and propagating the generalized Kohn-Sham equations of time-dependent density functional theory is straightforward [30], while the time-dependent optimized effective potential equation is notoriously difficult to solve [41,43] for systems with more than one spatial dimension.

Consequently, when thinking about constructing pseudopotentials for meta-GGAs, one can think along the Kohn-Sham as well as the generalized Kohn-Sham line. Pseudopotentials based on the optimized effective potential have been generated in the context of exact exchange calculations [44–46]. Devising an analogous Optimized-Effective-Potential-based construction scheme for meta-GGAs could be a way of obtaining consistent pseudopotentials for the

Kohn-Sham use of meta-GGAs. However, as the vast majority of meta-GGA calculations are done in the generalized Kohn-Sham scheme anyhow, it is natural and relevant to also think about the combination of the generalized Kohn-Sham scheme with the Troullier-Martins construction. This requires us to take a look at the structure of the generalized Kohn-Sham potential for a meta-GGA.

Taking the functional derivative with respect to an orbital leads to the potential

$$\hat{v}_{\text{GKS}}^{\text{mGGA}} = v^{\text{loc}} + \hat{v}_{\tau}^{\text{non-loc}}. \quad (14)$$

Here, $v^{\text{loc}}(\mathbf{r}) = (\partial e_{\text{xc}}^{\text{mGGA}}/\partial n) - [\nabla \cdot (\partial e_{\text{xc}}^{\text{mGGA}}/\partial (\nabla n))]$ is a local multiplicative potential similar to the one that one encounters for a GGA. This part is unproblematic in the pseudopotential construction. However,

$$\hat{v}_{\tau}^{\text{non-loc}} = -\frac{\hbar^2}{2m} \left[\nabla \cdot \frac{\partial e_{\text{xc}}^{\text{mGGA}}}{\partial \tau} \right] \nabla \quad (15)$$

is not local multiplicative, but features a final ∇ on the right-hand side. This makes a decisive difference for the Troullier-Martins construction strategy: Because of this derivative the generalized Kohn-Sham equation

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + \hat{v}_{\text{KS}}^{\text{GKS}}[n](\mathbf{r}) \right] \varphi_i(\mathbf{r}) = \varepsilon_i \varphi_i(\mathbf{r}) \quad (16)$$

for a meta-GGA cannot be inverted, i.e., solved for the potential. Thus, the step corresponding to Eq. (7) of the usual Troullier-Martins scheme cannot be carried out.

B. Problems when using LDA or GGA pseudopotentials in meta-GGA calculations

As a generalized Kohn-Sham Troullier-Martins procedure is not feasible, it is tempting to disregard the kinetic energy dependent parts or use inconsistent, e.g., GGA-based pseudopotentials [32]. However, one can easily see that there are cases where this can lead to not just quantitative differences, but serious qualitative failures. For understanding the possible pitfalls, it is helpful to recall that α , or τ^W/τ , in meta-GGAs is typically used to detect one-orbital regions and to ensure specific properties of $e_{\text{xc}}^{\text{mGGA}}$ in such regions. For example, one of the typical conditions that is enforced in this way is zeroing the correlation energy for one-electron systems. This is a correct condition for one-electron systems such as the hydrogen atom. However, consider the case of a sodium atom that is described by a local density approximation (LDA) or GGA pseudopotential that treats only the 3s electron as a valence electron. If one uses such an LDA or GGA pseudopotential in combination with a meta-GGA such as SCAN, r2SCAN, TASK, or LAK, the meta-GGA will detect via its dependence on the kinetic energy density that there is only one valence electron. Consequently, with the pseudopotential the meta-GGA will treat the sodium atom as a one-electron atom, i.e., like hydrogen. This will have erroneous consequences, e.g., the correlation energy will be set to zero in the pseudopotential calculation. In contrast, in an all-electron calculation with the same meta-GGA, the sodium atom will correctly be identified as a many-electron atom. The pseudopotential

calculation will, therefore, be far from reproducing the results of the all-electron calculation.

C. The core kinetic energy density correction idea

The above example shows that one key aspect of improving pseudopotentials for meta-GGA calculations in the generalized Kohn-Sham scheme is to make sure that the ratio of the kinetic energy densities reflects the all-electron situation as well as possible. Therefore, as an important step towards improvement we recall that the kinetic energy density can be split into a core and a valence part,

$$\tau = \tau_c + \tau_v. \quad (17)$$

Since τ depends on the orbitals explicitly, only τ_v can readily be computed from the pseudo valence orbitals $\varphi_i^{\text{ps}}(r)$ during a usual pseudopotential-based calculation according to

$$\tau_v = \frac{\hbar^2}{2m} \left(\sum_{i=(N_{\text{core}}+1)}^N |\nabla \varphi_i^{\text{ps}}|^2 \right), \quad (18)$$

where the sum runs over all valence orbitals of the given system.

However, as the CKED τ_c is a core-orbital property and as the core orbitals are not much influenced by the system environment, the pseudopotential approach allows one to avoid some of the worst consequences of pseudopotential inconsistency in meta-GGA calculations: The key idea is to calculate τ_c in the atomic all-electron calculation and provide it, together with the core density, as an additional component of the pseudopotential. That is, in addition to the core electron density for the nonlinear core correction, the core kinetic energy density is computed and stored as a separate block within the pseudopotential file. Then, following Eqs. (17) and (18), the full τ , rather than just τ_v , can be used in the actual calculations (see Sec. V for a discussion of “smoothing” the core quantities.) In this way, the pseudopotential-based calculation more faithfully resembles the all-electron calculation, and in particular one can thus avoid to falsely identify one-orbital regions.

For the special case of only 1s core orbitals, the idea to extend the Troullier-Martins scheme in this way was already successfully tested [30]. However, the restriction to 1s cores is of course a serious limitation. In the following, we realize this idea for general atoms with multiorbital cores. We find that great improvement is achieved when the CKED $\tau_c(\mathbf{r})$ from an atomic LDA based all-electron calculation is used to supplement the meta-GGA calculation.

III. THE NONRELATIVISTIC CKED CORRECTION

A. Derivation of the nonrelativistic CKED correction scheme

We here consider the case of a closed-shell spin-unpolarized core, i.e.,

$$\tau_c(\mathbf{r}) = \frac{\hbar^2}{2m} \sum_{i=1}^{N_{\text{core}}} |\nabla \varphi_i|^2 = \frac{\hbar^2}{2m} \underbrace{2}_{\text{spin}} \sum_n \sum_l \sum_{m_l=-l}^l |\nabla \varphi_{nlm_l}|^2, \quad (19)$$

where the sums on the right-hand side (here and in the following) run over all core states of one spin. One can use the complex valued product ansatz

$$\varphi_{nlm_l}(\mathbf{r}) = \varphi_{nl}(r) Y_l^{m_l}(\vartheta, \phi) = \frac{R_{nl}(r)}{r} Y_l^{m_l}(\vartheta, \phi) \quad (20)$$

due to the spherical symmetry of the atomic potential. Here, $\varphi_{nl}(r) = \frac{R_{nl}(r)}{r} \in \mathbb{R}$, i.e., in evaluating the absolute values squared the only complex contributions that must be taken into account arise from the spherical harmonics $Y_l^{m_l}$. The transformation of the nonrelativistic CKED into spherical coordinates is demonstrated in detail in the Supplemental Material. One evaluates $\nabla \varphi_{nlm_l}$ in spherical coordinates and exploits that the sum over all m_l quantum numbers can be done analytically for a closed-shell core by using the Unsöld identity for spherical harmonics, and

$$\begin{aligned} \sum_{m_l=-l}^l \left(\left| \partial_{\vartheta} Y_l^{m_l}(\vartheta, \phi) \right|^2 + \frac{m_l^2}{\sin^2(\vartheta)} \left| Y_l^{m_l}(\vartheta, \phi) \right|^2 \right) \\ = \frac{(2l+1)(l+1)l}{4\pi}. \end{aligned} \quad (21)$$

In this way, one arrives at the expression

$$\begin{aligned} \tau_c(\mathbf{r}) &= \tau_c(r) = \underbrace{2}_{\text{spin}} \sum_n \sum_l \tau_{nl}(r) \\ &= 2 \sum_n \sum_l \frac{2l+1}{4\pi} \left[\left(\frac{\partial_r R_{nl}(r)}{r} - \frac{R_{nl}(r)}{r^2} \right)^2 \right. \\ &\quad \left. + \left(\frac{R_{nl}(r)}{r^2} \right)^2 (l+1)l \right], \end{aligned} \quad (22)$$

where Rydberg atomic units ($\frac{\hbar^2}{2m} = 1$) have been used, and all contributions have been added up taking into account their multiplicity. The factor $2(2l+1)$ can be interpreted as the occupation of the l -th subshell.

We implemented this idea by modifying a local version of the pseudopotential generation code of Froyen, Troullier, and Martins [26,47,48]. The $\tau_c(\mathbf{r})$ calculated according to Eq. (22) is written to the pseudopotential file on the same logarithmic grid that is used for the other components of the pseudopotential. It can then be read in by the electronic structure code for which the pseudopotential is intended, and that electronic structure code must be modified to add $\tau_c(\mathbf{r})$ in the places where the kinetic energy density is used, specifically in the meta-GGA routine.

B. Results part I: Pseudopotential-based calculations using the nonrelativistic CKED

In the following we test which improvement in accuracy can be reached with this CKED correction. To this end, we compare all-electron results to two types of pseudopotential-based calculations: on the one hand, using a “standard” inconsistent pseudopotential without core information, and on the other hand, including the CKED correction discussed above together with the usual nonlinear core correction for the density. The pseudopotential results were obtained with the real-space code BTDFT [23] which we extended to include the CKED correction. The all-electron results were obtained with the codes Amsterdam Density Functional (ADF) [49]

TABLE I. Eigenvalues (EV) and corresponding highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMO-LUMO) gaps (gap) for TASK meta-GGA calculations of Na_4 , Na_6 , Al_2 , and SH with all-electrons (AE), an inconsistent LDA pseudopotential (PP_{std}), and a pseudopotential with core kinetic energy density (CKED) correction (PP_{τ_c}). The “diff”-column shows the difference between the AE and PP_{std} or PP_{τ_c} values, respectively. The CKED is used in combination with the nonlinear core correction for the density throughout.

Na_4						Na_6				
EV in eV	AE	PP_{std}	diff _{std}	PP_{τ_c}	diff _{τ_c}	AE	PP_{std}	diff _{std}	PP_{τ_c}	diff _{τ_c}
LUMO	−1.348	−1.533	0.185	−1.531	0.183	−1.485	−1.696	0.211	−1.556	0.071
HOMO	−2.643	−3.024	0.381	−2.775	0.132	−2.865	−3.326	0.461	−3.016	0.151
	−3.661	−4.323	0.662	−3.847	0.186	−2.869	−3.329	0.460	−3.020	0.151
gap in eV						−4.073	−4.602	0.529	−4.223	0.150
	1.295	1.491	−0.183	1.244	0.051	1.380	1.630	−0.240	1.461	−0.081
Al_2						SH				
EV in eV	AE	PP_{std}	diff _{std}	PP_{τ_c}	diff _{τ_c}	AE	PP_{std}	diff _{std}	PP_{τ_c}	diff _{τ_c}
LUMO	−3.896	−3.927	0.031	−3.965	0.069	−5.181	−4.965	−0.216	−5.053	−0.128
HOMO	−4.579	−4.561	−0.018	−4.677	0.098	−6.677	−6.695	0.018	−6.717	0.040
	−4.579	−4.561	−0.018	−4.677	0.098	−7.275	−7.252	−0.023	−7.274	−0.001
	−6.283	−6.833	0.550	−6.448	0.165	−8.591	−8.696	0.105	−8.713	0.122
	−7.096	−7.569	0.473	−7.249	0.153	−10.571	−10.623	0.052	−10.607	0.036
	−9.203	−9.623	0.420	−9.321	0.118	−11.088	−11.116	0.028	−11.098	0.010
	−10.703	−11.156	0.453	−10.816	0.113	−18.400	−18.712	0.312	−18.429	0.029
gap in eV						−19.899	−20.210	0.311	−19.926	0.027
	0.683	0.634	0.047	0.712	−0.029	1.496	1.730	−0.234	1.663	−0.167

and TURBOMOLE [50,51] (depending on the desired level of relativity and basis set accuracy, see below). We used large aug-cc-pV5Z basis sets to ensure a sufficient accuracy for the all-electron reference values. For the present study we mainly focused on the TASK meta-GGA for exchange combined with LDA correlation [9]. This choice is motivated by the fact that TASK was derived nonempirically with a pronounced kinetic energy dependence. In the Kohn-Sham scheme, the latter leads to a sizable derivative discontinuity, and in the generalized Kohn-Sham scheme, it leads to an eigenvalue gap that can realistically reflect the band gap. Because of the pronounced kinetic energy dependence, neglecting or including τ_c is expected to be particularly relevant for TASK, and the eigenvalues are a particularly sensitive test case. Furthermore, the reliable prediction of band gaps is one of the areas in which meta-GGAs can qualitatively go beyond GGAs [3,11,15], and their use for this purpose has found great interest in recent years [16,17,52–55]. However, in order to demonstrate that our approach is not restricted to TASK and eigenvalues, we also analyzed results for the meta-GGA r2SCAN and some other observables, as discussed below.

The pseudopotential results that we show in the following are based on LDA pseudopotentials. However, we checked that using pseudopotentials based on the PBE-GGA [56] lead to almost identical results with typical eigenvalue differences below 0.005 eV. This confirms that while the inclusion of the CKED is important, it is of lesser importance with which functional the CKED is calculated.

As a first test for the technical correctness of our implementation we compared our results for 1s-core systems, e.g., CO and Benzene, to the results that were obtained earlier [30] by evaluating the CKED correction directly based on the density. The reassuring finding was that eigenvalues and atomization energies agreed, as they should.

We then constructed pseudopotentials including the CKED for all second and third row elements except the noble gases. The detailed data is provided in the Supplemental Material. In Table I we present some characteristic results. The atomic coordinates for the systems discussed in Table I correspond to the structures shown in Ref. [57] (Na clusters), Ref. [58] (SH), and Ref. [59] (Al_2). The coordinates for other systems discussed in the SM were taken from Refs. [58,60,61].

We start by discussing the results that are obtained with the TASK functional for the small sodium clusters Na_4 and Na_6 that are shown in the upper half of Table I. Comparing first the eigenvalues from an all-electron calculation to the calculation using a plain (inconsistent) LDA pseudopotential (in Table I denoted by the subscript “std”) shows noticeable differences (see the column “diff”), with errors as large as ~ 0.7 eV in the occupied eigenvalues, and typical errors in the eigenvalues of ~ 0.5 eV. When looking at the eigenvalue gap, which often is of interest in meta-GGA calculations for condensed matter systems, we see that the errors are somewhat smaller, because the errors in the highest occupied and the lowest unoccupied eigenvalue go in the same direction. However, the errors in the gap nevertheless are at a noticeable ~ 0.25 eV.

When including the CKED correction (values in Table I denoted by the subscript “ τ_c ”), all errors are considerably reduced. The typical errors in the eigenvalues themselves go down to ~ 0.15 eV, and the errors in the gap go down to less than 0.1 eV. The inaccuracy introduced by the use of the pseudopotential is thus reduced to the level at which the accuracy of typical calculations for extended systems is limited anyhow by other approximations, such as the plane-wave cutoff, k-point mesh, or grid size. This is a very reassuring finding.

TABLE II. Eigenvalues (EV) and corresponding HOMO-LUMO gaps (gap) for Na₄, Na₆, Al₂, and SH molecules obtained from r2SCAN meta-GGA calculations. Results are compared for calculations using all-electrons (AE), a standard, inconsistent LDA pseudopotential (PP_{std}), and a pseudopotential with core kinetic energy density (CKED) correction (PP_{τ_c}). The “diff” column reports the deviation of the pseudopotential results from the AE reference, respectively.

Na ₄						Na ₆				
EV in eV	AE	PP _{std}	diff _{std}	PP _{τ_c}	diff _{τ_c}	AE	PP _{std}	diff _{std}	PP _{τ_c}	diff _{τ_c}
LUMO	−1.850	−1.953	0.103	−1.905	0.055	−1.739	−1.715	−0.024	−1.669	−0.070
HOMO	−2.685	−2.779	0.094	−2.700	0.015	−2.973	−3.089	0.116	−2.993	0.020
	−3.804	−3.981	0.177	−3.822	0.018	−2.977	−3.092	0.115	−2.986	0.019
gap in eV	0.835	0.826	0.009	0.795	0.040	−4.088	−4.228	0.140	−4.103	0.015
						1.234	1.374	−0.140	1.324	−0.090
Al ₂						SH				
EV in eV	AE	PP _{std}	diff _{std}	PP _{τ_c}	diff _{τ_c}	AE	PP _{std}	diff _{std}	PP _{τ_c}	diff _{τ_c}
LUMO	−3.643	−3.659	0.016	−3.730	0.087	−5.243	−4.883	−0.360	−5.218	−0.025
HOMO	−4.334	−4.406	0.072	−4.418	0.084	−6.483	−6.499	0.016	−6.506	0.023
	−4.334	−4.406	0.072	−4.418	0.084	−6.846	−6.840	−0.006	−6.863	0.017
	−6.272	−6.370	0.098	−6.332	0.060	−8.347	−8.504	0.157	−8.455	0.108
	−6.904	−7.107	0.203	−6.997	0.093	−10.211	−10.231	0.020	−10.236	0.025
	−9.021	−9.081	0.060	−9.088	0.067	−10.584	−10.589	0.005	−10.606	0.022
	−10.125	−10.292	0.167	−10.243	0.118	−17.909	−17.871	−0.038	−17.863	−0.046
gap in eV	0.691	0.746	−0.055	0.777	−0.086	−19.206	−19.308	0.102	−19.183	−0.023
						1.24	1.615	−0.375	1.288	−0.048

The lower half of Table I shows the same type of comparison for di-aluminium (Al₂) and hydrogen sulfide (SH). The results show the same trends, i.e., with the inconsistent pseudopotentials, eigenvalues deviate by several tenths of an eV from the all-electron eigenvalues. Here, the deviations are particularly large for the deeper eigenvalues. Using the CKED in all cases increases the accuracy and limits the deviation in the eigenvalues to ~ 0.1 eV and the one in the gaps to less than 0.1 eV. The differences are thus reduced to the range that one encounters also with consistent pseudopotentials [45].

Table II shows the same comparison for the same systems for the r2SCAN functional. The influence of the CKED correction is less pronounced for r2SCAN than for TASK. This is in line with r2SCAN’s weaker dependence on the kinetic energy density. However, also with r2SCAN, some eigenvalues are in error as much as 0.36 eV (SH) and 0.2 eV (Al₂) when using the inconsistent pseudopotential. The CKED reduces these errors to less than 0.1 eV. Thus, also for r2SCAN the CKED improves the agreement with the all-electron results.

For the sake of completeness we also looked at two larger molecular systems, bacteriochlorophyll (BChl) and a naphthalenediimide derivative (NDI-1), for which Ref. [30] reported that pseudopotential inconsistency is not a major issue. Both contain third row atoms with bigger cores, namely sulfur (NDI-1) and magnesium (BChl). We again compared all-electron results to the results from the inconsistent pseudopotential and the pseudopotential with CKED correction. In agreement with Ref. [30] we find that for these systems, using an inconsistent pseudopotential does not introduce significant errors. We further find that introducing the CKED correction does neither improve nor worsen the results noticeably, with differences in the eigenvalues mainly below 0.1 eV when comparing the CKED correction to standard inconsistent pseudopotential results. This observation can be

explained by the fact that both molecules contain mostly atoms with very small (1s) cores and only a few heavier atoms, and therefore the overall effect of the inconsistency between τ and τ_v is smaller and can average out. A peculiar case is Na₂. For Na₂ we noticed that using the nonrelativistic CKED does not yield any improvement, while using the relativistic CKED calculations were harder to converge but did lead to improved results. To understand this observation, note that in the Na atom there is just one valence orbital and it is of s character. Thus, due to proximity to the core it can be more strongly affected by relativistic effects. For larger Na systems with more orbitals, this becomes less relevant.

Summing up the nonrelativistic case, one can say that including the CKED correction can generally be recommended, as it improves the accuracy in the cases in which pseudopotential inconsistency is an issue for meta-GGAs, and it retains the accuracy in the cases in which inconsistent pseudopotentials already work fine. In line with what one would naturally expect, pseudopotential inconsistency tends to be less of a problem in systems with small cores, and a larger problem for systems with larger cores. This, however, forces us to consider a further extension of the CKED correction scheme: Larger cores occur in particular for heavy atoms, and with increasing atomic number, relativistic effects become increasingly important. As relativistic effects change the form of the kinetic energy density substantially, the CKED correction must be extended to the relativistic case.

IV. THE RELATIVISTIC CKED CORRECTION

A. Relativistic Kohn-Sham theory and Troullier-Martins pseudopotentials

For heavy atoms in which spin-orbit coupling is nonnegligible, a fully relativistic, spin-polarized Kohn-Sham approach

is important for constructing physically meaningful pseudopotentials. Under the assumption of spherical symmetry [also see Sec. IV B, especially Eq. (38)], the problem reduces to solving the coupled system of radial Kohn-Sham equations derived from the Dirac Hamiltonian [62,63]:

$$\hbar c \left(\frac{\partial}{\partial r} + \frac{\kappa}{r} \right) \varphi_i(r) = (\varepsilon - v_{\text{KS}}[n](r) + 2mc^2) \chi_i(r), \quad (23)$$

$$\hbar c \left(-\frac{\partial}{\partial r} + \frac{\kappa}{r} \right) \chi_i(r) = (\varepsilon - v_{\text{KS}}[n](r)) \varphi_i(r), \quad (24)$$

where

$$v_{\text{KS}}[n](r) = -\frac{Ze^2}{r} + v_{\text{H}}[n](r) + v_{\text{xc}}[n](r), \quad (25)$$

$$n(r) = \sum_i \Theta_i \frac{\varphi_i(r)^2 + \chi_i(r)^2}{4\pi r^2}. \quad (26)$$

Here, i is a generalized index labeling a set of relativistic quantum numbers $n j \kappa$. Furthermore, m is the electron mass and c is the velocity of light. The functions $\varphi_{n j \kappa}(r)$ and $\chi_{n j \kappa}(r)$ denote the radial parts of the major and minor components of the Kohn-Sham Dirac spinors, respectively, in the standard representation [cf. Eq. (38)]. The quantity Θ_i represents the occupation of the $n j \kappa$ subshell. Furthermore, $\varepsilon = E - mc^2$ denotes the Kohn-Sham energy relative to the rest energy, where E is the relativistic total energy. The nonrelativistic quantum numbers n , l , m_l , and s are replaced by their relativistic counterparts: the principal quantum number n , the total angular momentum j satisfying $|l - s| \leq j \leq l + s$, the total angular momentum number m_j , and [64,65]

$$\kappa = \begin{cases} -(l + 1) = -(j + 1/2) & \text{for } j = l + 1/2 \\ l = +(j + 1/2) & \text{for } j = l - 1/2 \end{cases}$$

$$\text{with } |\kappa| = j + 1/2. \quad (27)$$

In general, one can now proceed along lines analogous to the nonrelativistic case to derive a relativistic Troullier-Martins pseudopotential. However, due to the presence of two coupled Kohn-Sham Eqs. (23) and (24) in the relativistic formalism, the concept of “inverting” the Kohn-Sham equation to obtain the screened pseudopotential becomes less straightforward than in the nonrelativistic case.

However, one may exploit the fact that for valence electrons—whose pseudo-orbitals are to be constructed—the orbital-energy ε is small and the Kohn-Sham potential $v_{\text{KS}}[n](r)$ is small outside of the core region, i.e., the major and minor component become only weakly admixed. Under this approximation, the small-component radial function $\chi_i(r)$ in Eq. (24) may be replaced by

$$\chi_i(r) \simeq \frac{\hbar}{2mc} \left(\frac{\partial}{\partial r} + \frac{\kappa}{r} \right) \varphi_i(r) \quad (28)$$

to obtain the effective Schrödinger-like equation with the quantum number κ replacing l [66–68]:

$$\left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial r^2} + \frac{\hbar^2}{2m} \frac{\kappa(\kappa + 1)}{r^2} + v_{\text{KS}}[n](r) \right] \varphi_i(r) = \varepsilon \varphi_i(r). \quad (29)$$

Within this form, the Troullier-Martins formalism can be applied in a manner analogous to the nonrelativistic case,

enabling the construction of relativistic norm-conserving pseudopotentials.

B. Deriving and implementing the CKED in the relativistic case

To properly account for effects such as spin-orbit coupling in heavy atoms, relativistic Troullier-Martins pseudopotentials are indispensable [62,66,67]. Consequently, incorporating the CKED in the pseudopotential demands that the CKED be derived consistently within the relativistic Kohn-Sham formalism. We checked that simply using the upper component of the Kohn-Sham single-particle spinor as a pseudo-wave function to evaluate a pseudorelativistic kinetic energy density τ_c via the nonrelativistic formula (22) provides no benefit in meta-GGA calculations when the resulting pseudopotential is employed. This indicates that a fully relativistic treatment of the CKED is necessary. In relativistic Kohn-Sham theory, following Refs. [63,69] the noninteracting kinetic energy can be expressed as

$$T_s = \frac{1}{2} \int d^3r \left\{ \sum_{\substack{k \\ \varepsilon_k \leq \varepsilon_F}} \underline{\Psi}_k^\dagger(\mathbf{r}) [-i\hbar c \alpha^\mu \partial_\mu + \gamma^0 mc^2] \underline{\Psi}_k(\mathbf{r}) - \sum_{\substack{k \\ \varepsilon_F < \varepsilon_k}} \underline{\Psi}_k^\dagger(\mathbf{r}) [-i\hbar c \alpha^\mu \partial_\mu + \gamma^0 mc^2] \underline{\Psi}_k(\mathbf{r}) \right\}. \quad (30)$$

Here, k is a generalized index labeling a set of relativistic quantum numbers $n j m_j \kappa$, the energy ε_F is the Fermi energy, and the matrix

$$\gamma^0 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad (31)$$

is the 0-th of the four-component standard Dirac matrices γ^μ . Omitting the integral yields an expression for the kinetic energy density. Since the energy of all core orbitals is below the Fermi energy, only states with $\varepsilon_k \leq \varepsilon_F$ contribute to the CKED. Thus, the second term on the right-hand side of Eq. (30) can be omitted. Furthermore, the inclusion of the rest energy mc^2 in the kinetic energy has no nonrelativistic counterpart. However, for the CKED approaches to be consistent, the nonrelativistic and the relativistic CKED should match in the limit of weak relativistic effects, i.e., in the case of weakly relativistic atoms and an appreciable distance to the core. Furthermore, the relativistic and nonrelativistic kinetic energies of weakly relativistic atoms such as oxygen or sodium should be very close to each other. This is the case if and only if the mc^2 term is omitted. We further verified for the example of the weakly relativistic atoms oxygen and sodium that the two formulations of the CKED agree with each other, except in the immediate vicinity of the nucleus; a region that contributes negligibly to the total energy. Based on these considerations, we conclude that the rest energy can be safely omitted in our ansatz for the CKED. Combining these arguments, Eq. (30)

simplifies to the following expression for the CKED:

$$\begin{aligned}\tau_c(\mathbf{r}) &= \frac{1}{2} \sum_k^{N_{\text{core}}} -i\hbar c \underline{\Psi}_k^\dagger(\mathbf{r}) \alpha^\mu \partial_\mu \underline{\Psi}_k(\mathbf{r}) \\ &= \frac{1}{2} \sum_k^{N_{\text{core}}} c \underline{\Psi}_k^\dagger(\mathbf{r}) (\underline{\alpha} \cdot \hat{\mathbf{P}}) \underline{\Psi}_k(\mathbf{r}),\end{aligned}\quad (32)$$

where $\alpha^\mu = \gamma^0 \gamma^\mu$. Since the atomic core states are stationary, the time component of the relativistic covariant derivative vanishes. Thus, α^μ reduces to $\underline{\alpha}$, a three-component vector of 4×4 matrices with the 2×2 Pauli matrices σ_j on the off-diagonals:

$$\underline{\alpha} = \begin{pmatrix} \begin{pmatrix} 0 & \sigma_1 \\ \sigma_1 & 0 \end{pmatrix} \\ \begin{pmatrix} 0 & \sigma_2 \\ \sigma_2 & 0 \end{pmatrix} \\ \begin{pmatrix} 0 & \sigma_3 \\ \sigma_3 & 0 \end{pmatrix} \end{pmatrix}. \quad (33)$$

Furthermore, $\hat{\mathbf{P}} = -i\hbar \nabla$ denotes the momentum operator. With this simplification, the expression for the CKED is transformed into spherical coordinates. To this end, one first derives the expression

$$\underline{\alpha} \cdot \hat{\mathbf{P}} = \underline{\alpha}_r \left[\hat{P}_r + \frac{i\hbar}{r} \begin{pmatrix} \hat{K} & 0 \\ 0 & \hat{K} \end{pmatrix} \right], \quad (34)$$

where the equality results from using the radial momentum operator

$$\hat{P}_r = \frac{\hbar}{i} \left(\partial_r + \frac{1}{r} \right) \quad (35)$$

and the spin-orbit operator

$$\hat{K} = 1 + \frac{1}{\hbar} \underline{\sigma} \cdot \hat{\mathbf{L}}, \quad (36)$$

including the spin-orbit-coupling $\underline{\sigma} \cdot \hat{\mathbf{L}}$. Here, $\underline{\sigma}$ is a vector containing the Pauli-matrices and $\hat{\mathbf{L}}$ is the angular momentum operator. $\underline{\alpha}_r$ is the projection of $\underline{\alpha}$ onto the radial direction resulting in a 4x4 matrix with the radial Pauli matrix σ_r :

$$\underline{\alpha}_r = \frac{\mathbf{r}}{r} \cdot \underline{\alpha} = \begin{bmatrix} 0 & \frac{\mathbf{r}}{r} \cdot \underline{\sigma} \\ \frac{\mathbf{r}}{r} \cdot \underline{\sigma} & 0 \end{bmatrix}. \quad (37)$$

Analogous to the nonrelativistic case, a product ansatz can be employed to separate the total four-component Dirac-Kohn-Sham spinor $\underline{\Psi}_k$ into radial and angular parts. To this end, one first transforms to the so-called bispinor representation, where the spinor is decomposed into a major component Φ_k and a minor component X_k . Under the assumption of spherical symmetry, each component can be expressed as a product of a radial function and a two-component spinor spherical harmonic—also known as Pauli spinor—encapsulating all angular dependences in the form

$$\underline{\Psi}_k = \begin{pmatrix} \Phi_k \\ X_k \end{pmatrix}(\mathbf{r}) = \begin{pmatrix} \frac{\varphi_{njk}(r)}{r} \mathcal{Y}_{jm_j}^{(j\pm\frac{1}{2})}(\phi, \vartheta) \\ \frac{\chi_{njk}(r)}{ir} \sigma_r \mathcal{Y}_{jm_j}^{(j\pm\frac{1}{2})}(\phi, \vartheta) \end{pmatrix}, \quad (38)$$

cf. Eqs. (23), (24). For improved clarity, radial function indices are suppressed in the following. Since $\underline{\alpha}_r$ in Eq. (37) is a hollow symmetric matrix, the action of operator (34) on the ansatz (38) interchanges the major and minor components, resulting in

$$c \underline{\alpha} \cdot \hat{\mathbf{P}} \underline{\Psi}_k = c \sigma_r \left(\hat{P}_r + \frac{i\hbar}{r} \hat{K} \right) \begin{pmatrix} X_k \\ \Phi_k \end{pmatrix}. \quad (39)$$

The upper component of this expression now leads to

$$\begin{aligned}c \sigma_r \left(\hat{P}_r + \frac{i\hbar}{r} \hat{K} \right) X_k &= c \sigma_r \left(\hat{P}_r + \frac{i\hbar}{r} \hat{K} \right) \frac{\chi(r)}{ir} \sigma_r \mathcal{Y}_{jm_j}^{(j\pm\frac{1}{2})}(\phi, \vartheta) \\ &\stackrel{(41)}{=} c \left[\left(\frac{\hat{P}_r}{i} + \frac{\hbar\kappa}{r} \right) \frac{\chi(r)}{r} \right] \mathcal{Y}_{jm_j}^{(j\pm\frac{1}{2})} \\ &\stackrel{(41)}{=} c \left[\left(-\frac{\hbar}{r} \partial_r + \frac{\hbar\kappa}{r^2} \right) \chi(r) \right] \mathcal{Y}_{jm_j}^{(j\pm\frac{1}{2})} \\ &\stackrel{\hat{P}_r(\frac{\chi}{r}) = -\frac{i\hbar}{r} \partial_r \chi}{=} c \left[\left(-\frac{\hbar}{r} \partial_r + \frac{\hbar\kappa}{r^2} \right) \chi(r) \right] \mathcal{Y}_{jm_j}^{(j\pm\frac{1}{2})}.\end{aligned}\quad (40)$$

Here, we have used that the spinor spherical harmonics are eigenfunctions of the spin-orbit operator $\hat{K}$ [64], i.e.,

$$\hat{K} \mathcal{Y}_{jm_j}^{(j\pm\frac{1}{2})} = -\kappa \mathcal{Y}_{jm_j}^{(j\pm\frac{1}{2})} \quad (41)$$

with the negative of the relativistic quantum number κ as the eigenvalue, cf. Eq. (27) (also see Ref. [64] for a detailed discussion). Similarly, the lower component yields

$$\begin{aligned}c \sigma_r \left(\hat{P}_r + \frac{i\hbar}{r} \hat{K} \right) \Phi_k &= c \sigma_r \left(\hat{P}_r + \frac{i\hbar}{r} \hat{K} \right) \frac{\varphi(r)}{r} \mathcal{Y}_{jm_j}^{(j\pm\frac{1}{2})}(\phi, \vartheta) \\ &\stackrel{(41)}{=} c \sigma_r \left[\left(\hat{P}_r - \frac{i\hbar\kappa}{r} \right) \frac{\varphi(r)}{r} \right] \mathcal{Y}_{jm_j}^{(j\pm\frac{1}{2})} \\ &\stackrel{(41)}{=} c \sigma_r \left[\left(-\frac{i\hbar}{r} \partial_r - \frac{i\hbar\kappa}{r^2} \right) \varphi(r) \right] \mathcal{Y}_{jm_j}^{(j\pm\frac{1}{2})} \\ &\stackrel{\hat{P}_r(\frac{\varphi}{r}) = -\frac{i\hbar}{r} \partial_r \varphi}{=} c \sigma_r \left[\left(-\frac{i\hbar}{r} \partial_r - \frac{i\hbar\kappa}{r^2} \right) \varphi(r) \right] \mathcal{Y}_{jm_j}^{(j\pm\frac{1}{2})}.\end{aligned}\quad (42)$$

Finally, to complete the expression required for writing the relativistic CKED from Eq. (32) in spherical coordinates, the scalar product between Eq. (39) and the Hermitian conjugate (daggered) bi-spinor

$$\underline{\Psi}_k^\dagger c \underline{\alpha} \cdot \hat{\mathbf{P}} \underline{\Psi}_k \quad (43)$$

must be computed. The first term in the sum, arising from the product of the upper components, yields

$$\begin{aligned}\Phi_k^\dagger c \sigma_r \left(\hat{P}_r + \frac{i\hbar}{r} \hat{K} \right) X_k &= \frac{\varphi(r)}{r} c \left[\left(-\frac{\hbar}{r} \partial_r + \frac{\kappa\hbar}{r^2} \right) \chi(r) \right] |\mathcal{Y}_{jm_j}^{(j\pm\frac{1}{2})}|^2 \\ &= \frac{\varphi(r)}{r} c \left[\left(-\frac{\hbar}{r} \partial_r + \frac{\kappa\hbar}{r^2} \right) \chi(r) \right] |\mathcal{Y}_{jm_j}^{(j\pm\frac{1}{2})}|^2\end{aligned}\quad (44)$$

and the second term resulting from the product of the lower components is

$$\begin{aligned}
 & X_k^\dagger c \sigma_r \left(\hat{P}_r + \frac{i\hbar}{r} \hat{K} \right) \Phi_k \\
 & \stackrel{\sigma_r^2 = |\sigma_r|^2 = 1}{=} \frac{\chi(r)}{-ir} \mathcal{Y}_{jm_j}^{(j \pm \frac{1}{2})\dagger} c \left[\left(-\frac{i\hbar}{r} \partial_r - \frac{i\hbar\kappa}{r^2} \right) \varphi(r) \right] \mathcal{Y}_{jm_j}^{(j \pm \frac{1}{2})} \\
 & = \frac{\chi(r)}{r} c \left[\left(\frac{\hbar}{r} \partial_r + \frac{\hbar\kappa}{r^2} \right) \varphi(r) \right] |\mathcal{Y}_{jm_j}^{(j \pm \frac{1}{2})}|^2. \quad (45)
 \end{aligned}$$

Finally summing up the two contributions results in the expression

$$\begin{aligned}
 \underline{\Psi}_k^\dagger c \underline{\alpha} \cdot \hat{\mathbf{P}} \underline{\Psi}_k & = |\mathcal{Y}_{jm_j}^{(j \pm \frac{1}{2})}|^2 \hbar c \left[\frac{\chi(r)}{r^2} \left(\partial_r + \frac{\kappa}{r} \right) \varphi(r) \right. \\
 & \quad \left. + \frac{\varphi(r)}{r^2} \left(-\partial_r + \frac{\kappa}{r} \right) \chi(r) \right]. \quad (46)
 \end{aligned}$$

Analogously to the nonrelativistic τ_c , the total relativistic expression must be independent of any angular variables. This follows from the relativistic generalization of the Unsöld identity for spherical harmonic spinors [65,70,71]

$$\sum_{m_j=-j}^j \mathcal{Y}_{jm_j}^{(j \pm \frac{1}{2})\dagger} \mathcal{Y}_{jm_j}^{(j \pm \frac{1}{2})} = \frac{2j+1}{4\pi}, \quad (47)$$

whose proof is outlined in the Supplemental Material.

With these expressions one can evaluate the relativistic CKED and finds

$$\begin{aligned}
 \tau_c(\mathbf{r}) & = \frac{1}{2} \sum_{n,j,m_j,\kappa} \underline{\Psi}_{njm_j\kappa}^\dagger(\mathbf{r}) c \underline{\alpha} \cdot \hat{\mathbf{P}} \underline{\Psi}_{njm_j\kappa}(\mathbf{r}) \\
 & \stackrel{(47)}{=} \frac{1}{2} \sum_n \sum_j \sum_{\kappa} \underbrace{\frac{2j+1}{4\pi}}_{\sum_n \sum_l \sum_{s_z}} \hbar c \left[\frac{\chi_{nj\kappa}(r)}{r^2} \left(\partial_r + \frac{\kappa}{r} \right) \right. \\
 & \quad \left. \cdot \varphi_{nj\kappa}(r) + \frac{\varphi_{nj\kappa}(r)}{r^2} \left(-\partial_r + \frac{\kappa}{r} \right) \chi_{nj\kappa}(r) \right]. \quad (48)
 \end{aligned}$$

The radial derivatives appearing in the expression can be directly computed from the radial Dirac equations, eliminating the need for *a posteriori* numerical finite differences. Analogously to the nonrelativistic procedure, the final step is to incorporate this relativistic CKED into the relativistic LDA pseudopotential and subsequently employ it in nonrelativistic meta-GGA calculations.

C. Results part II: Pseudopotential-based calculations using the relativistic CKED

To analyze the improvement achieved by amending pseudopotentials with the relativistic CKED, we performed ground-state calculations for the TASKx + LDAC functional again using the pseudopotential-based real-space grid code BTDFIT [23]. Furthermore, we also analyzed a set of systems using the meta-GGA r2SCAN. The pseudopotentials were again generated using a version of the Froyen-Troullier-Martins code [26,47,48] which we modified to calculate and include τ_c in the output pseudopotential as explained

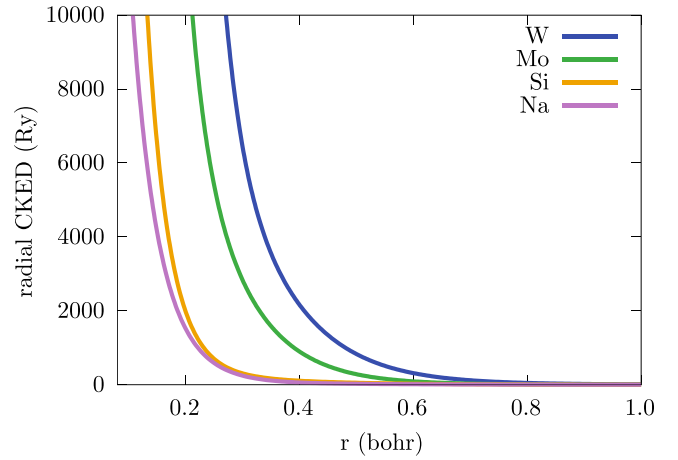


FIG. 1. The relativistic CKED as a function of the radial coordinate for the atoms W and Mo, and the nonrelativistic CKED for the atoms Si and Na. See main text for discussion.

above, now employing the fully relativistic Troullier-Martins scheme. As test systems we look at small clusters of tungsten trioxide (WO_3) and molybdenum trioxide (MoO_3) (geometries from Ref. [72]), denoted as $n\text{WO}_3$ and $n\text{MoO}_3$, where n is the number of WO_3 or MoO_3 units, respectively. These clusters adopt hollow cage- or ring-like geometries, corresponding to typical motifs of finite size metal oxides. Furthermore, we include as paradigmatic test cases the Au_2 dimer and the AgO_3^+ cation (geometries from Refs. [73,74] and [75], respectively) in our analysis, with details provided in the Supplemental Material.

Due to the large nuclear charge in Mo, W, Ag, and Au, relativistic effects such as spin-orbit coupling become increasingly relevant. When computing the relativistic CKED, we observed that it can reach values of several thousand Rydbergs in close proximity to the nucleus. This is illustrated in Fig. 1, which shows the radial decay of the unmodified relativistic CKED for tungsten and molybdenum, and the nonrelativistic CKED for silicon and sodium. The figure shows that, while decaying rapidly, the relativistic CKED values near the nucleus are found to be significantly larger than their nonrelativistic counterparts. This can pose a potential numerical challenge if these large values need to be resolved in the actual pseudopotential calculation. However, for our real-space grid calculations, focusing on the region of space that corresponds to a typical grid spacing, i.e., 0.1 bohr to 0.3 bohr, shows that the numerical consequences are not as severe as one might think. Due to the rapid decay of the CKED, the values relevant for the calculation—evaluated at grid points not exactly coinciding with the atomic positions—are several orders of magnitude smaller than the maximum values. Thus, the large CKED values at the nucleus are not much sampled by the finite grid spacing. The conclusion from this analysis is supported by direct numerical tests. We explored the accuracy and stability of directly using τ_c without any smoothing in our real-space grid-based calculations with a grid-spacing of 0.3 bohr by varying the position of the molecular systems on the grid. In the systems studied here, the inclusion of the CKED not only reduced the computational cost, but also im-

proved the numerical stability, with no noticeable dependence on the system's position on the grid. One has to be aware of, though, that implementations that do not use a real-space grid but other techniques can be more sensitive to the large values of τ_c . In such cases, a smoothing procedure might be beneficial, as discussed in Sec. V.

For relativistic systems, an additional complication arises when trying to assess the accuracy of a pseudopotential. As mentioned previously, the typical situation is that one wants to incorporate the effects of relativity into the pseudopotential and use the relativistic pseudopotential in a calculation in which the valence electrons are treated nonrelativistically. In an all-electron calculation, however, both core and valence electrons are treated on the same footing, e.g., either relativistically or nonrelativistically. Thus, unlike the nonrelativistic case, there is intrinsically no exact match between the all-electron and the pseudopotential calculation. The situation is complicated further by the fact that approximations to the fully relativistic case can be made at different levels, e.g., the scalar relativistic one. It is *a priori* not clear to which level of relativity in the all-electron calculation a pseudopotential calculation should correspond in which the core was calculated relativistically and the valence electrons nonrelativistically. In the following, we explore these questions with the help of some examples.

As a first step, we compared LDA eigenvalues from nonrelativistic pseudopotential-based calculations using relativistic pseudopotentials to all-electron benchmarks at different levels of relativity (see the Supplemental Material for details). The pseudopotential results matched best to scalar-relativistic all-electron results (obtained with ADF), and this comparison is summarized in Table III. However, although both the all-electron and the pseudopotential consistently use the LDA, deviations as large as 0.114 eV are observed in some eigenvalues. This shows that even in an “ideal” comparison, larger deviations must be expected in the relativistic than in the nonrelativistic case.

As a side remark we furthermore note that the choice of the local component—representing the effective local potential contribution derived in the Kleinman-Bylander transformation [76]—plays a noticeable role for the accuracy of the results. In general, using the p -orbital as the local component for Mo, W, and O lead to the best agreement between all-electron and pseudopotential-based calculations in the cases that we studied. Therefore, in Table IV and V we used $l = 1$ as the local component.

With these insights in mind, we proceed to examine eigenvalues and HOMO-LUMO gaps from TASK-functional-based generalized Kohn-Sham calculations using relativistic LDA pseudopotentials that incorporate the relativistic CKED from Eq. (48). We compare them to the results of inconsistent, unadapted relativistic LDA pseudopotentials. In both cases, the pseudo-orbitals are calculated relativistically, but only in the former case the nonlinear core correction and CKED correction are included. The results for 8WO_3 , 12WO_3 , 3MoO_3 , and 4MoO_3 are presented in Table IV; additional data discussing further WO_3 systems, AgO_3^+ , and Au_2 are provided in the Supplemental Material. Pseudopotential-based results using the inconsistent relativistic LDA pseudopotentials are again labeled “std”, while those employing the adapted pseu-

TABLE III. LDA eigenvalues (EV) and HOMO-LUMO gaps (gap) for WO_3 and MoO_3 clusters from all-electron (AE) and pseudopotential (PP) calculations. Pseudopotential results use relativistic LDA pseudopotentials with nonlinear core correction for the density; AE reference is scalar relativistic with a relativistically adapted QZ4P basis. The “diff” column gives the difference between AE and PP results.

8WO ₃				12WO ₃		
EV in eV	AE	PP	diff	AE	PP	diff
LUMO	−5.300	−5.324	−0.025	−6.216	−6.266	0.050
HOMO	−8.505	−8.475	0.030	−8.619	−8.689	0.070
	−8.508	−8.480	0.029	−8.619	−8.699	0.080
	−8.562	−8.540	0.022	−8.955	−9.033	0.078
	−8.573	−8.550	0.022	−8.955	−9.042	0.087
	−9.192	−9.247	−0.054	−8.955	−9.054	0.099
	−9.287	−9.365	−0.078	−8.963	−9.068	0.105
	−9.350	−9.419	−0.069	−8.963	−9.078	0.114
gap in eV	3.205	3.150	0.055	2.403	2.423	−0.020
3MoO ₃				4MoO ₃		
EV in eV	AE	PP	diff	AE	PP	diff
LUMO	−5.272	−5.200	−0.072	−5.351	−5.300	−0.051
HOMO	−8.689	−8.674	−0.015	−8.721	−8.679	−0.041
	−8.701	−8.679	−0.021	−8.725	−8.703	−0.022
	−8.706	−8.690	−0.017	−8.728	−8.712	−0.016
	−9.344	−9.339	−0.004	−8.736	−8.718	−0.018
	−9.349	−9.356	0.007	−9.321	−9.404	0.083
	−9.407	−9.454	0.047	−9.422	−9.421	−0.001
	−9.415	−9.491	0.076	−9.449	−9.434	−0.015
gap in eV	−9.496	−9.517	0.021	−9.457	−9.458	0.001
	3.417	3.474	−0.056	3.369	3.379	−0.010

dopotentials are labeled “ τ_c ”. The “diff” column shows the difference relative to the all-electron reference. Our results are compared to relativistic all-electron calculations performed with ADF [49] using relativistically adapted QZ4P basis sets.

Based on the above discussed results for the LDA, one would expect that the pseudopotential results using the meta-GGA should fit best to scalar relativistic all-electron calculations. However, when doing this comparison we found substantial differences of up to 0.39 eV in the LUMO eigenvalues. When we switched to a higher-level of relativistic formalism in the all-electron calculations—specifically the RA-X2C method (Regular Approach to the Exact two-Component relativistic calculation) [77–81] using the two-component approach including spin-orbit coupling effects—the agreement between the all-electron and the pseudopotential results improved substantially. The improvement was particularly large for the LUMO, while the occupied eigenvalues remained largely unchanged. The RA-X2C method corresponds to an exact transformation of the four-component Dirac-equation to two components [77–81]. Consequently, it can include all relativistic effects while the scalar relativistic approach lacks an accurate incorporation of spin-orbit-coupling corrections. For our systems, the differences between the all-electron-calculations based on the scalar relativistic approach and the full relativistic RA-X2C

TABLE IV. Eigenvalues (EV) and corresponding HOMO-LUMO gaps (gap) for TASK meta-GGA calculations of WO_3 and MoO_3 molecules. The table reports calculations with all electrons (AE), an inconsistent, relativistic LDA pseudopotential (PP_{std}), and a relativistic pseudopotential with core kinetic energy density (CKED) correction (PP_{τ_c}). The all-electron reference is based on relativistic calculations using the RA-X2C approach including spin-orbit coupling effects with relativistically adapted QZ4P basis sets. The “diff” column reports the difference between AE and PP_{std} or PP_{τ_c} values, respectively.

8 WO_3						12 WO_3				
EV in eV	AE	PP_{std}	diff _{std}	PP_{τ_c}	diff _{τ_c}	AE	PP_{std}	diff _{std}	PP_{τ_c}	diff _{τ_c}
LUMO	-4.862	-3.934	-0.929	-4.821	-0.041	-5.645	-4.407	-1.239	-5.761	0.115
HOMO	-8.704	-8.607	-0.097	-8.620	-0.084	-8.810	-9.066	0.256	-8.941	0.131
	-8.709	-8.616	-0.093	-8.685	-0.024	-8.810	-9.069	0.259	-9.003	0.193
	-8.747	-8.661	-0.087	-8.790	0.043	-9.141	-9.383	0.242	-9.208	0.067
	-8.757	-8.674	-0.083	-8.849	0.092	-9.142	-9.391	0.249	-9.276	0.134
	-9.462	-9.596	0.134	-9.515	0.053	-9.142	-9.395	0.253	-9.310	0.168
	-9.580	-9.700	0.120	-9.663	0.083	-9.158	-9.482	0.324	-9.359	0.201
	-9.631	-9.716	0.085	-9.674	0.044	-9.160	-9.501	0.341	-9.397	0.237
	-9.631	-9.716	0.085	-9.674	0.044	-9.160	-9.501	0.341	-9.397	0.237
gap in eV	3.842	4.673	-0.832	3.799	0.043	3.165	4.659	-1.495	3.180	-0.015
3 MoO_3						4 MoO_3				
EV in eV	AE	PP_{std}	diff _{std}	PP_{τ_c}	diff _{τ_c}	AE	PP_{std}	diff _{std}	PP_{τ_c}	diff _{τ_c}
LUMO	-4.767	-3.848	-0.919	-4.914	0.148	-4.749	-4.068	-0.682	-4.841	0.092
HOMO	-8.927	-8.969	0.042	-8.825	-0.103	-8.960	-9.002	0.042	-8.879	-0.081
	-8.940	-8.985	0.046	-8.912	-0.028	-8.962	-9.016	0.054	-8.925	-0.036
	-8.945	-8.988	0.043	-8.950	0.004	-8.965	-9.022	0.057	-8.943	-0.022
	-9.537	-9.780	0.243	-9.598	0.062	-8.970	-9.037	0.067	-8.997	0.027
	-9.584	-9.788	0.205	-9.690	0.106	-9.609	-9.866	0.257	-9.710	0.101
	-9.671	-9.888	0.217	-9.780	0.109	-9.632	-9.890	0.258	-9.732	0.100
	-9.709	-9.936	0.227	-9.862	0.152	-9.673	-9.901	0.228	-9.791	0.118
	-9.718	-10.021	0.303	-9.892	0.174	-9.684	-9.927	0.243	-9.802	0.118
gap in eV	4.160	5.121	-0.961	3.910	0.250	4.211	4.934	-0.723	4.038	0.173

method including spin-orbit coupling are as large as 0.3 eV in the LUMO eigenvalue. The fact that the LUMO is much more strongly affected by the level of relativity than the other orbitals calls for an explanation. Therefore, we take a look at the projected density of states. It reflects the contribution of individual atomic orbitals to the total density of states. Figure 2 shows it for the cluster 12WO_3 . We explicitly verified that the situation is very similar for other WO_3 systems, i.e., Fig. 2

is a representative case. The dotted red line corresponds to the p -orbital contribution from the oxygen atoms, while the dotted blue line represents the d -orbital contribution from tungsten. It is evident that the HOMO is predominantly composed of oxygen p -orbitals, whereas the LUMO is almost exclusively formed by tungsten d -orbitals. Since the eigenvalue κ of the spin-orbit coupling operator is proportional to the orbital angular momentum quantum number l [see Eqs. (41) and

TABLE V. Eigenvalues (EV) and corresponding HOMO-LUMO gaps (gap) for WO_3 and MoO_3 molecules obtained from r2SCAN meta-GGA calculations. The table reports calculations with all electrons (AE), a standard inconsistent, relativistic LDA pseudopotential (PP_{std}), and a relativistic pseudopotential with core kinetic energy density (CKED) correction (PP_{τ_c}). The AE reference is based on relativistic calculations using the RA-X2C approach with spin-orbit coupling and relativistically adapted QZ4P basis sets. The “diff” column reports the deviation of the pseudopotential results from the AE reference.

8 WO_3						3 MoO_3				
EV in eV	AE	PP_{std}	diff _{std}	PP_{τ_c}	diff _{τ_c}	AE	PP_{std}	diff _{std}	PP_{τ_c}	diff _{τ_c}
LUMO	-5.132	-4.687	-0.445	-5.136	0.004	-5.023	-4.634	-0.389	-5.120	0.097
HOMO	-8.579	-8.568	-0.011	-8.637	0.058	-8.785	-8.840	0.055	-8.846	0.060
	-8.584	-8.579	-0.005	-8.639	0.055	-8.797	-8.846	0.048	-8.862	0.065
	-8.635	-8.636	0.001	-8.704	0.069	-8.803	-8.855	0.052	-8.867	0.064
	-8.645	-8.645	0.000	-8.714	0.069	-9.382	-9.539	0.156	-9.493	0.111
	-9.278	-9.419	0.141	-9.422	0.144	-9.427	-9.554	0.128	-9.518	0.091
	-9.411	-9.571	0.160	-9.575	0.165	-8.803	-8.702	0.192	-9.660	0.149
	-9.452	-9.575	0.123	-9.595	0.143	-9.382	-9.717	0.197	-9.677	0.157
	-9.472	-9.585	0.113	-9.603	0.131	-9.427	-9.747	0.185	-9.704	0.142
gap in eV	3.447	3.881	-0.434	3.501	-0.054	3.762	4.206	-0.443	3.755	0.007

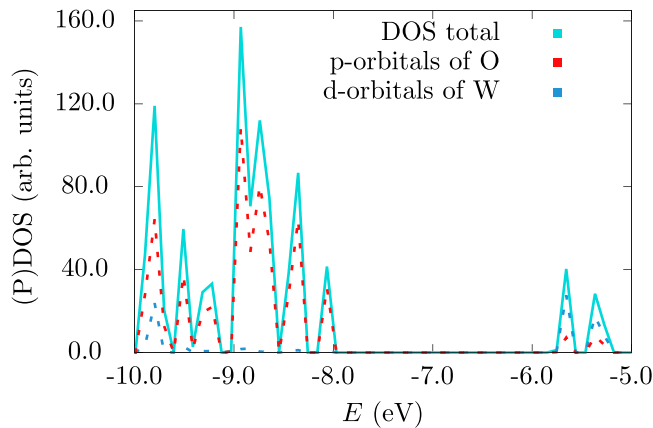


FIG. 2. Projected density of states of 12WO_3 near the HOMO-LUMO gap. The HOMO is dominated by oxygen p -orbitals (red), while the LUMO arises primarily from tungsten d -orbitals (blue). Due to the l dependence of spin-orbit coupling, the LUMO, dominated by d -orbitals ($l = 2$), experiences stronger relativistic corrections than the HOMO ($l = 1$).

(27)], the importance of the relativistic spin-orbit corrections increases with l . Consequently, in tungsten trioxide systems, the LUMO, dominated by d -orbitals ($l = 2$), experiences significantly larger relativistic effects than the HOMO, which arises from p -orbitals ($l = 1$).

It is a positive finding that the meta-GGA calculation with a relativistically constructed pseudopotential corresponds to the relatively high level of relativity that the RA-X2C approximation including spin-orbit coupling realizes in the all-electron calculation. However, one may ask why the meta-GGA pseudopotential achieves more than the LDA pseudopotential. We assume that this is due to the kinetic energy dependence: The kinetic energy is noticeably influenced by the relativistic effects, and the thus encoded relativistic information can carry over to the pseudopotential calculation. However, one has to be aware that this mechanism is system specific. It works relatively well for systems like the WO_3 clusters, in which the majority of the high-lying occupied orbitals are of p character and thus not too strongly affected by relativistic effects. For Au, where the occupied orbitals are predominantly of d character and thus more strongly affected by relativity, the CKED still leads to significant improvement compared to standard relativistic pseudopotentials, but it does not lead to full relativistic accuracy. A more detailed discussion of the results for Au_2 can be found in the Supplemental Material.

Analyzing the results in Table IV, we find that using inconsistent, unadapted relativistic LDA pseudopotentials in pseudopotential-based TASK calculations leads to large errors compared to the all-electron reference, with deviations reaching up to 1.2 eV. In particular, the LUMO eigenvalue and, for larger systems, eigenvalues near the core deviate significantly from the all-electron result. However, incorporating the CKED into the LDA pseudopotentials significantly improves the accuracy. Both the core-adjacent eigenvalues and the LUMO level benefit substantially from this adaptation, with deviations reduced to less than 0.2 eV in most cases. The enhanced accuracy of the LUMO eigenvalue directly improves the HOMO-LUMO gap: While the unadapted pseu-

dopotentials yield gaps with errors up to 1.5 eV, the adapted pseudopotentials reduce these discrepancies to below 0.25 eV.

Table V presents the same comparison for the r2SCAN functional. Using inconsistent, unadapted relativistic LDA pseudopotentials in r2SCAN calculations yields errors of ~ 0.1 eV in the occupied eigenvalues, less severe than for TASK, due to r2SCAN's weaker dependence on the kinetic energy density. However, the LUMO eigenvalue deviates significantly from the all-electron reference, with a deviation of ~ 0.45 eV. Incorporating the CKED into the pseudopotential significantly improves the accuracy: The deviation in the LUMO eigenvalue is reduced to less than 0.07 eV. This directly reduces the error in the HOMO-LUMO gap, which drops from 0.44 eV to below ~ 0.1 eV.

V. OUTLOOK: CORE CORRECTION CONSISTENCY AND SMOOTHING

In this paper we so far investigated how well the eigenvalues that result from pseudopotentials match the eigenvalues from all-electron calculations. Looking at the eigenvalues is motivated by the fact that the eigenvalues are quantities for which meta-GGAs can go qualitatively beyond GGAs: Whereas structural parameters such as bond lengths can already be, at least in principle, well predicted by GGAs, the eigenvalue gap of a GGA can never match the true fundamental gap, because GGAs intrinsically lack the xc derivative discontinuity. Meta-GGAs, on the other hand, can incorporate this discontinuity and can, therefore, go qualitatively beyond GGAs by predicting a physically relevant generalized Kohn-Sham spectrum [3,11,15]. This is one of the important reasons why meta-GGAs found great interest in recent years [16,17,32,52–55]. While the question of predicting the fundamental gap is relevant not only for molecules, but also for solids, we here focused on molecules in this exploratory study because accurate all-electron references can readily be obtained for molecules.

For completeness, however, we also report some exemplary tests for bond lengths and binding energies. We restrict ourselves to dimers, for which the bond length can easily be accurately determined, and focus on the two systems SH and MgH calculated with the TASK functional. We picked those because among all the dimers that we studied, these are the ones for which the largest improvement in the gap was achieved by the CKED correction, i.e., the CKED is relevant to the eigenvalues. We determined the all-electron equilibrium bond length from energy minimization and took the resulting geometry as the reference equilibrium structure. For this bond length we calculated the atomization energies using all electrons, standard pseudopotentials, and pseudopotentials with CKED correction. We then also determined the bond length corresponding to the energetic minimum in the pseudopotential calculations.

Table VI summarizes the results. For the SH dimer, already the standard pseudopotentials give results that are very close to the all-electron reference for both bond length and atomization energy. The CKED reduces the deviation in the atomization energy further, but on a scale that is already very small. The situation is different for MgH. Using standard inconsistent pseudopotentials leads to an error of 0.1 Å in

TABLE VI. Equilibrium bond lengths and corresponding atomization energies (E_{atom}) for the dimers SH and MgH obtained from TASK meta-GGA calculations. Results from all-electron (AE) calculations are compared to those using a standard inconsistent LDA pseudopotential (PP_{std}) and a pseudopotential with core density and kinetic energy density (CKED) correction (PP_{τ_c}). The “diff” column reports the difference between the pseudopotential and the AE results.

	SH					MgH				
	AE	PP_{std}	diff_{std}	PP_{τ_c}	diff_{τ_c}	AE	PP_{std}	diff_{std}	PP_{τ_c}	diff_{τ_c}
bond length in Å	1.34	1.34	0.00	1.34	0.00	1.77	1.67	0.10	1.73	0.04
E_{atom} in eV	−3.67	−3.64	−0.03	−3.68	0.01	−1.98	−1.46	−0.52	−1.831	−0.15

the bond length and a substantial deviation of 0.52 eV in the atomization energy. The CKED-corrected pseudopotentials reduce the bond length error to 0.04 eV and the atomization energy error to 0.15 eV. Summarizing these results one can say that the errors in bond length and energies that one obtains from inconsistent pseudopotentials can be negligible or appreciable, depending on the system. We expect that generally speaking, structural parameters such as bond lengths will be less sensitive to pseudopotential inconsistency than the eigenvalue spectrum for the following reason: In the eigenvalue spectrum, one orbital being misrepresented will clearly show up. Structural parameters, on the other hand, are largely determined by the density, which sums over all orbitals. Deviations in one orbital are thus less severe and can “average out”. In this sense the eigenvalue spectrum is a particularly sensitive test for pseudopotential accuracy.

When one aims for maximum accuracy, one may wonder whether the large values that the CKED can take close to the nucleus (in particular in the relativistic case, cf. Fig. 1) may cause numerical problems. As mentioned above, we did not encounter such problems in our real-space grid calculations. However, the situation might be different in plane-wave codes. A natural strategy for avoiding such potential difficulties would be to “smooth out” the CKED in the vicinity of the nucleus, similar to the smoothing of the core density that can be used in nonlinear core correction strategies for the density. To check whether such a strategy can, in principle, be compatible with the central idea of the CKED, we conducted a first exemplary test of a smoothing scheme. To this end we replaced the large CKED values near the core with a parabolic function beyond a defined cutoff radius. That is, for distances greater than the cutoff radius, the original CKED values were used, and for smaller distances the smoothed function was used. Using this simple scheme we constructed pseudopotentials for W, O, and Si. For W and O, a cutoff radius of $0.1 a_0$ was used, while for Si we explored cutoffs up to $0.3 a_0$, a range that significantly reduces the maximum CKED values. Using these smoothed pseudopotentials for our finite systems we found that the eigenvalues remained accurate and consistent with those obtained using the original CKED.

This parabolic smoothing only serves as a proof of concept and should not be taken for general pseudopotential construction. When one aims at generally applicable pseudopotentials, one should aim for consistency in the smoothing of n and τ_c , e.g., to preserve the ratio of τ^W/τ as well as possible. Our simple scheme so far did not take this into account. Developing a scheme for consistent smoothing is a relevant task for future work. The reassuring finding from our results here is that the CKED as such leads to pseudopotentials with better

accuracy, and that the large CKED values near the core are not essential for achieving this improved accuracy. Therefore, there is high hope that a consistent smoothing scheme can be developed and will yield reliable results.

VI. CONCLUSION

In summary, we have developed and implemented a systematic approach to improve Troullier-Martins pseudopotentials for meta-GGA calculations. The central idea is to use a core correction for the kinetic energy density. The derived analytical expressions for the CKED in spherical coordinates—in nonrelativistic and relativistic form, respectively—were successfully integrated into the all-electron stage of the Troullier-Martins pseudopotential construction, enabling a more physically consistent treatment of the core electronic structure. Comparisons with high-accuracy all-electron calculations for different molecular systems within the generalized Kohn-Sham approach demonstrate that the adapted LDA-Troullier-Martins pseudopotentials considerably improve the accuracy for eigenvalues and gaps of finite systems. These results underscore the importance of including core kinetic energy density information in pseudopotential-based meta-GGA calculations.

For heavy atoms we found that the inclusion of the relativistic CKED can incorporate significant relativistic corrections into the meta-GGA calculations. This effect was particularly large for the WO_3 and MoO_3 clusters that we studied. Hence, depending on the system and on the orbital character of the frontier states, pseudopotentials incorporating the CKED can yield eigenvalues and gaps comparable to results obtained using a full two-component relativistic all-electron method.

The kinetic energy density is very large in the vicinity of the atomic cores. While this did not lead to problems in our real-space grid calculations, it might cause numerical problems if the pseudopotentials that we provide in the Supplemental Material are used in combinations with other techniques, e.g., in plane-wave codes. We, therefore, tested smoothing the CKED, and discussed how future work can extend the present approach to a consistent smoothing of the core density and the CKED, in extension of existing schemes that smooth (only) the core density [48].

In this paper we focused on the TASK and r2SCAN meta-GGAs, and on eigenvalue differences, but the concept of the kinetic energy density correction is universal. The core idea of our method—adding the CKED during the Troullier-Martins pseudopotential generation scheme—only requires a one-time, atom-specific procedure that can be performed

in advance. Consequently, the use of the adapted pseudopotentials incurs no additional computational cost. Our work shows that this enables pseudopotential-based meta-GGA calculations that can approach the accuracy of all-electron calculations, at the significantly reduced computational cost inherent to pseudopotential methods. This is particularly advantageous for large systems and systems involving heavier elements.

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DATA AVAILABILITY

The data that support the findings of this article are openly available. They are provided as part of the Supplemental Material, and further original data is available in “Data and pseudopotentials for ‘pseudopotentials for meta-GGA calculations’” [35,36].

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