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Energies of isoelectronic atomic ions from a successful metageneralized gradient approximation and other density functionals

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We show that the poor performance of approximate Kohn-Sham (KS) density functional theory for highly charged atomic ions is improved dramatically by ensuring that (i) the exchange functional recovers the correct leading term in the Z expansion of the exchange energy (Z is the nuclear charge) and (ii) the correlation functional is bounded under uniform scaling of the density to the high-density limit—i.e., $\lim_{\lambda\to\infty}E_c^{\mathrm{KS}}[n_\lambda] > -\infty$, where $n_\lambda(\mathbf{r})=\lambda^3 n(\lambda\mathbf{r})$. The performance of several density functionals (BLYP, BP86, VS98, HCTH/407, PBE, PKZB, and TPSS) is compared for the 4-, 10-, and 18-electron atomic series spanning values of Z from 4 to 28. Especially accurate results are obtained with the nonempirical metageneralized gradient approximation of Tao, Perdew, Staroverov, and Scuseria (TPSS). High-Z limits of selected exchange and correlation functionals are evaluated and compared with the exact values.

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I. INTRODUCTION

Ground-state atomic isoelectronic series are fundamental models for understanding correlation effects in many-electron systems. As the nuclear charge Z of an N-electron ion increases, the correlation energy approaches a constant for certain values of N and diverges as $-Z$ for others. This paradoxical result [1] follows from conventional perturbation theory using the noninteracting many-electron hydrogenic atom as the zeroth-order approximation, the electron-electron repulsion as the perturbation, and $1/Z$ as the perturbation parameter [2].

Unlike most wave function techniques, approximate density functional theory (DFT) fails badly for these relatively simple systems. For example, the local spin-density approximation (LSDA) to the correlation energy diverges as $-\ln Z$ regardless of N, a concern that was first raised by Perdew and co-workers [3]. Beyond-LSDA functionals also give poor results for highly charged atomic ions, as demonstrated numerically by Jarzęcki and Davidson [4]. They examined several generalized gradient approximations (GGA's) popular in the late 1990s, including the correlation functionals of Perdew (P86) [5], Perdew and Wang (PW91) [6], and Lee, Yang, and Parr (LYP) [7], combined with the Becke (B88) [8] and Hartree-Fock (HF) exchange, as well as the B3PW91 [9], B3LYP [10], and B3P86 hybrids. For most of these functionals, the correlation energy diverges with Z for all N. For LYP, it always approaches a constant. No existing functional can distinguish the two types of correlation energy behavior at large Z. Even when the spurious divergence of the correlation functional is absent, as in BLYP, errors of the total energy proportional to Z arise from the exchange functional approximation. The largest errors for $Z \leqslant 28$ were found [4] for the widely used B3LYP hybrid.

Although a perfect model for the exchange-correlation energy is beyond reach, one can avoid at least some of the failures of present-day DFT by using approximations constructed to have a proper scaling behavior. Levy showed [11] that, for a system whose Kohn-Sham (KS) Hamiltonian is nondegenerate, the exact DFT correlation energy is bounded from below with respect to uniform scaling of the density $n(\mathbf{r})$ to the high-density limit—that is,

$$\lim_{\lambda\to\infty} E_c^{\mathrm{KS}}[n_\lambda] > -\infty, \tag{1}$$

where $n_\lambda(\mathbf{r})=\lambda^3 n(\lambda\mathbf{r})$. Because an atomic ion becomes more and more hydrogenic with increasing Z and because varying Z in hydrogenic ions has the same effect as uniform scaling of the density by $\lambda=Z$, the exact correlation energy of a real ion will go to a constant at large Z if the corresponding N-electron hydrogenic system is nondegenerate. An approximate correlation functional that satisfies Eq. (1) for *all* choices of the unscaled density $n(\mathbf{r})$ will scale to a constant as $Z\to\infty$ for all N.

In contrast to correlation, the DFT exchange energy is strictly linear in λ for all N [12]:

$$E_x^{\mathrm{KS}}[n_\lambda] = \lambda E_x^{\mathrm{KS}}[n]. \tag{2}$$

Although all common approximations to $E_x^{\mathrm{KS}}[n]$ satisfy Eq. (2), they rarely yield the correct exchange energy for a given nonuniform density. For hydrogenic systems like high-Z atomic ions this means that the error in E_x^{KS} will grow linearly with Z at a rate proportional to the deviation of $E_x^{\mathrm{KS}}[n_{Z=1}]$ from the exact value.

Wilson and Levy were the first to explicitly impose the high-density scaling constraint of Eq. (1) on an approximate correlation functional [13]. Some prior functionals, such as

Becke's 1988 correlation [14] and LYP, also respect Eq. (1) for all densities, although they predate the formal proof of it. The numerical real-space cutoff construction [15] that underlies the PW91 and PBE GGA's respects this scaling limit, although the PW91 analytic parametrization does not. More recent nonempirical functionals, such as the GGA of Perdew, Burke, and Ernzerhof (PBE) [16] and the meta-GGA's of Perdew, Kurth, Zupan, and Blaha (PKZB) [17] and Tao, Perdew, Staroverov, and Scuseria (TPSS) [18,19], are constructed to satisfy Eq. (1), among many other exact constraints. The TPSS meta-GGA even gives the correct $E_{\mathrm{x}}^{\mathrm{KS}}[n]$ for ground-state one-electron hydrogenic densities.

In this work, we demonstrate the progress achieved for high-Z atomic ions with density functionals of this new generation. Our tests involve the 4-, 10-, and 18-electron series. For comparison with the work of Jarzęcki and Davidson [4] we have included BP86 and BLYP, the best performers in that study. We also report here the high-Z limits of selected exchange and correlation functionals for hydrogenic densities.

II. THEORETICAL BACKGROUND

By applying the coordinate transformation $\mathbf{r}_i' = Z\mathbf{r}_i$ to the nonrelativistic Hamiltonian of an N-electron atomic ion with nuclear charge Z, one obtains (in atomic units)

$$\hat{H} = Z^2\left[\sum_{i=1}^{N}\left(-\frac{1}{2}\nabla_i'^2 - \frac{1}{r_i'}\right) + \frac{1}{Z}\sum_{i<j}\frac{1}{r_{ij}'}\right]. \tag{3}$$

This form of $\hat{H}$ suggests a Rayleigh-Schrödinger perturbation treatment using the noninteracting many-electron hydrogenic atom as the unperturbed system, the electron-electron repulsion as the perturbation, and $\alpha = 1/Z$ as the perturbation parameter:

$$\hat{H}\Psi = E\Psi, \tag{4}$$

$$\hat{H} = Z^2(\hat{H}_0 + \alpha\hat{H}_1), \tag{5}$$

$$\hat{H}_0 = \sum_{i=1}^{N}\left(-\frac{1}{2}\nabla_i'^2 - \frac{1}{r_i'}\right), \tag{6}$$

$$\hat{H}_1 = \hat{V}_{\mathrm{ee}} = \sum_{i<j}\frac{1}{r_{ij}'}. \tag{7}$$

The ground-state energy and unnormalized wave function $\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N)$ of the perturbed system are given by

$$E = Z^2E^{(0)} + ZE^{(1)} + E^{(2)} + \frac{1}{Z}E^{(3)} + \cdots, \tag{8}$$

$$\Psi = Z^{3N/2}\left(\Psi^{(0)} + \frac{1}{Z}\Psi^{(1)} + \frac{1}{Z^2}\Psi^{(2)} + \cdots\right), \tag{9}$$

where $\Psi^{(0)}(\mathbf{r}_1', \ldots, \mathbf{r}_N')$, the ground-state eigenfunction of $\hat{H}_0$, is a Slater determinant of spin- and symmetry-constrained hydrogenic orbitals or a linear combination of such determinants if $\Psi^{(0)}$ is degenerate.

The $1/Z$ expansion summarized by Eqs. (4)–(9) was originally applied to the two-electron atomic problem by Hylleraas [20] and later extended to many-electron systems by others [2]. Unlike many other perturbation schemes used in quantum chemistry, the $1/Z$ series actually converges. The extensive literature on the radius of convergence and analytic behavior of the $1/Z$ expansion is reviewed by Baker *et al.* [21].

The Hartree-Fock energy E_{HF} and wave function Φ^{HF} (the best single determinant) of an atomic ion can be represented by similar $1/Z$ expansions [22–24]

$$E^{\mathrm{HF}} = Z^2E_{\mathrm{HF}}^{(0)} + ZE_{\mathrm{HF}}^{(1)} + E_{\mathrm{HF}}^{(2)} + \frac{1}{Z}E_{\mathrm{HF}}^{(3)} + \cdots, \tag{10}$$

$$\Phi^{\mathrm{HF}} = Z^{3N/2}\left(\Phi_{\mathrm{HF}}^{(0)} + \frac{1}{Z}\Phi_{\mathrm{HF}}^{(1)} + \frac{1}{Z^2}\Phi_{\mathrm{HF}}^{(2)} + \cdots\right). \tag{11}$$

Because the unperturbed system is the same in both cases, $E_{\mathrm{HF}}^{(0)} = E^{(0)}$. Thus, the conventional quantum-chemical (QC) correlation energy

$$E_{\mathrm{c}}^{\mathrm{QC}} = \langle\Psi|\hat{H}|\Psi\rangle - \langle\Phi^{\mathrm{HF}}|\hat{H}|\Phi^{\mathrm{HF}}\rangle \tag{12}$$

can be written for atomic ions as [1,25–27]

$$E_{\mathrm{c}}^{\mathrm{QC}}(N,Z) = c_1^{\mathrm{QC}}Z + c_2^{\mathrm{QC}} + \frac{c_3^{\mathrm{QC}}}{Z} + \cdots, \tag{13}$$

where $c_i^{\mathrm{QC}} = E^{(i)} - E_{\mathrm{HF}}^{(i)}$. For ions where $\Psi^{(0)}$ is nondegenerate, $E_{\mathrm{HF}}^{(1)} = E^{(1)}$ too [1], so that the linear coefficient c_1^{QC} vanishes and E_c^{QC} asymptotically approaches c_2^{QC} at large Z. However, if $\Psi^{(0)}$ is degenerate, then $E_{\mathrm{HF}}^{(1)} \neq E^{(1)}$ and the correlation energy can grow linearly with Z. In ground-state atomic ions with $N \leqslant 18$ electrons, the nondegeneracy of $\Psi^{(0)}$ (or degeneracy unmixed with $\hat{H}_1$) occurs only for $N=2$ (^1S), 3 (^2S), 7 ($^4S^{\mathrm{o}}$), 8 (^3P), 9 ($^2P^{\mathrm{o}}$), 10 (^1S), and 11 (^2S).

Kohn-Sham DFT relies on a different definition of the correlation energy. In the constrained search formulation [28] of KS DFT,

$$E_{\mathrm{c}}^{\mathrm{KS}}[n] = \langle\Psi|\hat{T} + \hat{V}_{\mathrm{ee}}|\Psi\rangle - \langle\Phi_n^{\mathrm{KS}}|\hat{T} + \hat{V}_{\mathrm{ee}}|\Phi_n^{\mathrm{KS}}\rangle, \tag{14}$$

where $\hat{T}$ and $\hat{V}_{\mathrm{ee}}$ are the kinetic energy and electron-electron repulsion operators, respectively, while Φ_n^{KS} is the noninteracting wave function (often a single determinant of KS orbitals) that yields the same ground-state density $n(\mathbf{r})$ as Ψ and minimizes $\langle\hat{T}\rangle$.

Finally, correlation energy functionals intended to be used in combination with the nonlocal HF exchange approximate yet another quantity defined by

$$E_{\mathrm{c}}^{\mathrm{HF}}[n] = \langle\Psi|\hat{T} + \hat{V}_{\mathrm{ee}}|\Psi\rangle - \langle\Phi_n^{\mathrm{HF}}|\hat{T} + \hat{V}_{\mathrm{ee}}|\Phi_n^{\mathrm{HF}}\rangle. \tag{15}$$

Here Φ_n^{HF} is the single determinant that minimizes the expectation value of the operator $\hat{T} + \hat{V}_{\mathrm{ee}}$ and yields the exact ground-state density.

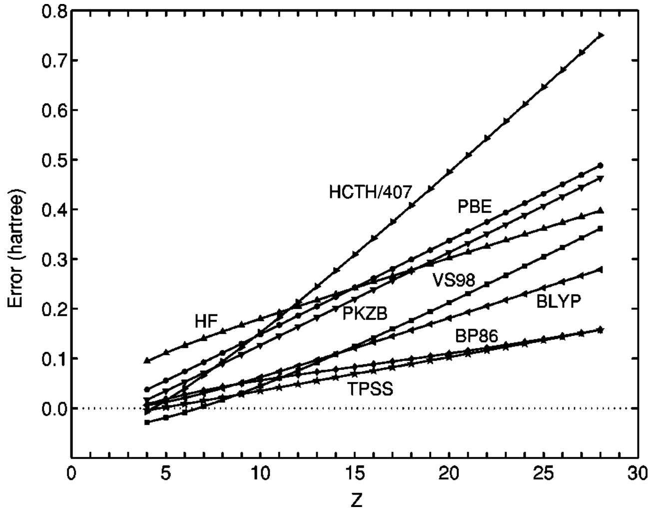

FIG. 1. Errors in the total energy $(E-E_{\mathrm{exact}})$ as functions of nuclear charge Z for the 4-electron [Be] series computed with the Hartree-Fock (HF) method and with approximate density functionals for exchange and correlation.

It is clear from the definitions that, for an atom with given N and Z, $E_{\mathrm{c}}^{\mathrm{QC}} \geqslant E_{\mathrm{c}}^{\mathrm{HF}} \geqslant E_{\mathrm{c}}^{\mathrm{KS}}$. Thus, if $E_{\mathrm{c}}^{\mathrm{QC}}$ diverges to $-\infty$ as $Z \to \infty$, so necessarily do $E_{\mathrm{c}}^{\mathrm{HF}}$ and $E_{\mathrm{c}}^{\mathrm{KS}}$. Moreover, when $\Psi^{(0)}$ is nondegenerate, the large-Z limit of $E_{\mathrm{c}}^{\mathrm{KS}}$ is finite and so necessarily are those of $E_{\mathrm{c}}^{\mathrm{HF}}$ and $E_{\mathrm{c}}^{\mathrm{QC}}$. It should be also noted here that nonempirical approximations like PBE or TPSS model $E_{\mathrm{c}}^{\mathrm{KS}}[n]$, because they are based upon exact properties of $E_{\mathrm{c}}^{\mathrm{KS}}[n]$, such as a finite second-order gradient expansion. The second-order gradient coefficient of $E_{\mathrm{c}}^{\mathrm{QC}}$ probably diverges [29].

III. *Z* DEPENDENCE OF EXCHANGE AND CORRELATION

To avoid ambiguities associated with various definitions of exchange and correlation, we consider the errors in total DFT energies relative to the exact nonrelativistic values taken from the work of Chakravorty *et al.* [30]. All atomic energies were computed self-consistently with the GAUSSIAN program [31] using Partridge's nearly saturated uncontracted basis sets [32]: Be $(18s)$, B-Ne $(18s,13p)$, Na-Mg $(20s,12p)$, Al-Ar $(20s,15p)$, K $(25s,16p)$, Ca $(23s,16p)$, and Sc-Ni $(23s,15p,11d)$. The d functions for Sc-Ni were dropped, since atomic orbitals with angular momentum $l>1$ do not contribute to the ground-state configurations of spherical 4-, 10-, and 18-electron ions. Grids with more than 200 radial points were found necessary to integrate the electron density in the vicinity of the nucleus. We used the 300-point radial and 974-point angular grids.

Figures 1–3 show the errors for pure DFT exchange-correlation functionals. The most accurate results here are predicted with the BLYP, BP86, and TPSS approximations. TPSS exchange and correlation perform much better together than PBE and PKZB exchange-correlation functionals. The BP86 functional is comparatively accurate even though its correlation component violates Eq. (1), because this violation is only moderate and because the B88 and P86 errors sometimes cancel each other (as in the Ne series). The performance of these approximations can be contrasted with that of recent semiempirical functionals that violate Eq. (1)—specifically, a refitted GGA of Hamprecht, Cohen, Tozer, and Handy (HCTH/407) [33] and the meta-GGA of Van Voorhis and Scuseria (VS98) [34], both of which tend to have large, rapidly increasing, errors. Overall, the best performance in Figs. 1–3 belongs to the nonempirical TPSS meta-GGA.

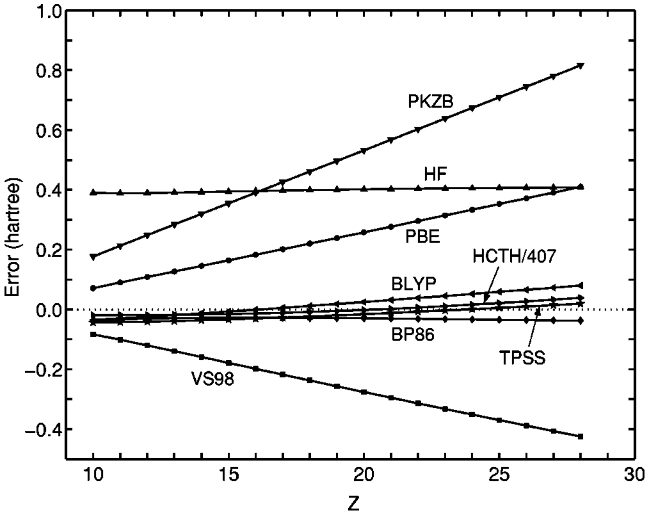

FIG. 2. Same as in Fig. 1 for the 10-electron [Ne] series.

For $N=10$ (Fig. 2), where the true $E_{\mathrm{c}}^{\mathrm{KS}}$ tends to a constant as $Z \to \infty$, the TPSS error remains small for all $Z \leqslant 28$. For $N=18$ (Fig. 3), where the true correlation energy diverges linearly but slowly with Z, the TPSS error also remains small for all $Z \leqslant 28$. For $N=4$ (Fig. 1), where $E_{\mathrm{c}}^{\mathrm{KS}}$ diverges linearly but rapidly with Z, the error of TPSS for $Z \leqslant 28$ is much more serious, but there seems to be a significant cancellation of errors between TPSS exchange and TPSS correlation which can be seen by comparing Fig. 1 to Fig. 4 below.

Figures 4–6 illustrate the performance of the P86, LYP, PBE, PKZB, and TPSS correlation functionals in combination with nonlocal HF exchange. Implicit here is the assump-

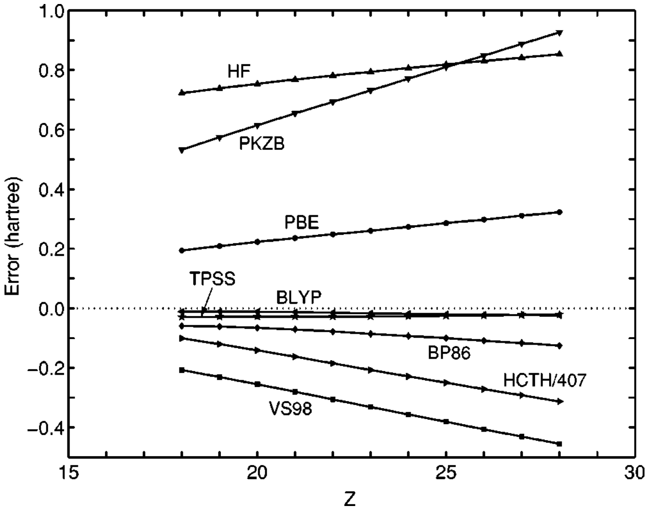

FIG. 3. Same as in Fig. 1 for the 18-electron [Ar] series.

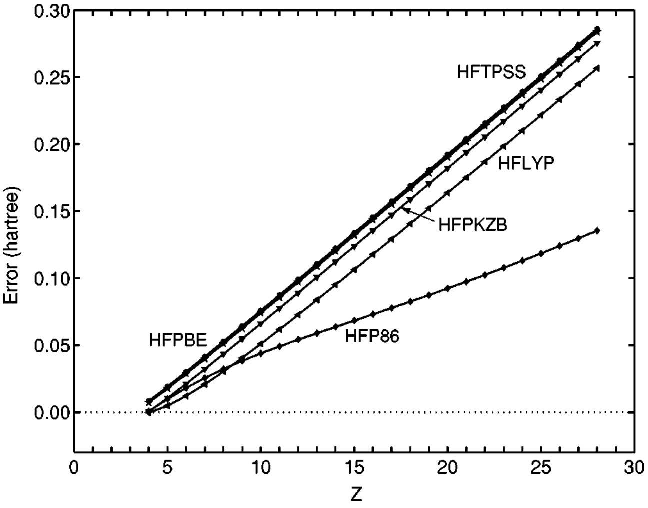

FIG. 4. Errors in the total energy $(E - E_{\text{exact}})$ as functions of nuclear charge Z for the 4-electron [Be] series computed with approximate density functionals for correlation combined with Hartree-Fock (HF) exchange.

tion that these functionals represent E_c^{HF} of Eq. (15) when at least some of them (PBE, PKZB, TPSS) represent E_c^{KS} of Eq. (14). All of these approximations satisfy Eq. (1) except P86, which produces a moderate violation. The plots for VS98 and HCTH/407 are not shown because these functionals were constructed semiempirically to approximate exchange and correlation *together*; when a correlation component is formally separated from them, it shows large errors even at $N = Z$ (e.g., an HCTH/407 error of −0.44 hartree for the Ar atom). Such errors can be compensated by corresponding errors in the exchange at $Z \approx N$, but not for all Z. The P86, VS98, and HCTH/407 correlation energies diverge for all N like $-\ln \lambda$, as does LSDA, but with different constant prefactors.

Note that the errors of LYP, PBE, PKZB, and TPSS, but not P86, approach a constant at high Z for the nondegenerate 10-electron [Ne] configuration and diverge for the degenerate 4- and 18-electron [Be] and [Ar] configurations. The close agreement found in Figs. 4–6 between PBE and TPSS correlation is not a general result; these two functionals predict significantly different correlation contributions to atomization energies of molecules, as can be seen from Table VII of Ref. [19].

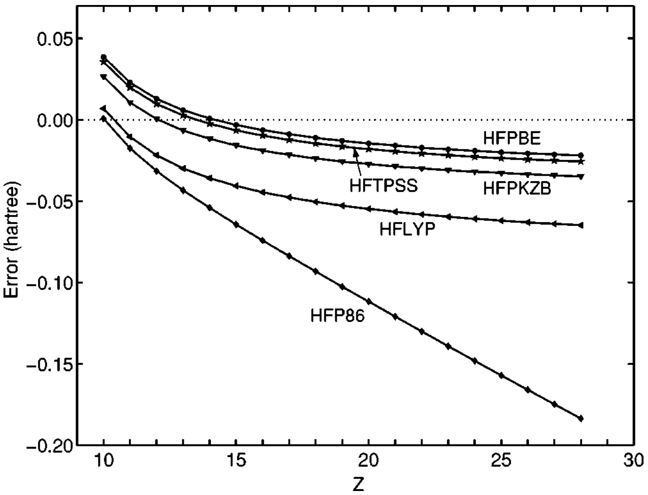

FIG. 5. Same as in Fig. 4 for the 10-electron [Ne] series.

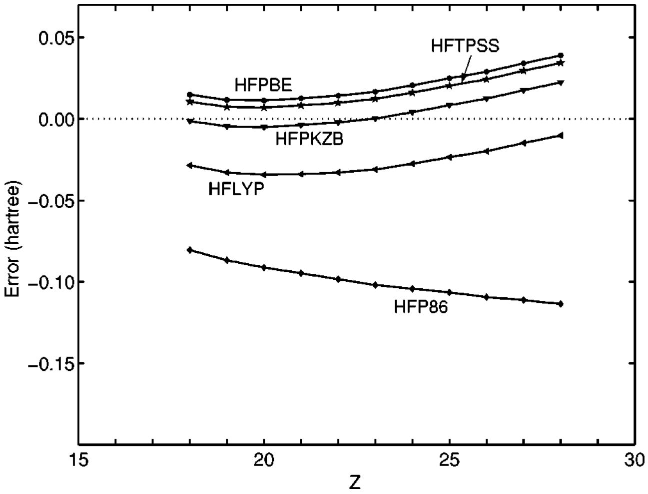

FIG. 6. Same as in Fig. 4 for the 18-electron [Ar] series.

IV. HIGH-*Z* LIMITS OF EXCHANGE FUNCTIONALS

The DFT exchange energy is defined as

$$E_x^{\text{KS}}[n] = \langle \Phi_n^{\text{KS}} | \hat{V}_{\text{ee}} | \Phi_n^{\text{KS}} \rangle - J[n], \tag{16}$$

where Φ_n^{KS} is the KS noninteracting wave function that yields the ground-state density $n(\mathbf{r})$ and

$$J[n] = \frac{1}{2} \int \frac{n(\mathbf{r}_1) n(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2 \tag{17}$$

is the Coulomb repulsion energy. Following Jaręcki and Davidson [35], we consider the expansion

$$E_x^{\text{KS}} = e_1^{\text{KS}} Z + e_2^{\text{KS}} + \frac{e_3^{\text{KS}}}{Z} + \cdots . \tag{18}$$

For hydrogenic densities, the series terminates at the linear term, because Eq. (18) must satisfy Eq. (2) with $\lambda = Z$. Therefore,

$$e_1^{\text{KS}} = E_x^{\text{KS}}[n_{Z=1}^{\text{H}}], \tag{19}$$

where $n_{Z=1}^{\text{H}}(\mathbf{r})$ is the density of a many-electron hydrogenic atom with $Z = 1$. Note that for a nondegenerate hydrogenic system $\Phi_n^{\text{KS}} = \Psi^{(0)}$ and $E_x^{\text{KS}}[n] = E_x^{\text{HF}}[n]$, in which case

$$e_1^{\text{exact KS}} = e_1^{\text{HF}} = E_x^{\text{HF}}[n_{Z=1}^{\text{H}}], \tag{20}$$

where $E_x^{\text{HF}}[n_{Z=1}^{\text{H}}]$ is the HF exchange energy of a many-electron hydrogenic atom. This quantity can be evaluated analytically as shown in the Appendix.

Table I compares e_1^{KS} coefficients for the B88, PBE, PKZB, and TPSS exchange functionals determined by Eq. (19) to the exact HF values of Eq. (20). Only the nondegenerate cases are considered. For the 8- and 9-electron ions, we

TABLE I. Coefficients (in hartrees) of the linear terms in Z expansions of the exchange energy of atomic ions. The exact values e_1^{HF} are determined by Eq. (20) and the coefficients of approximate functionals by Eq. (19) using MATHEMATICA.

N	$-e_1^{\mathrm{HF}}$	$-e_1^{\mathrm{B88}}$	$-e_1^{\mathrm{PBE}}$	$-e_1^{\mathrm{PKZB}}$	$-e_1^{\mathrm{TPSS}}$
2	0.6250	0.6195	0.6119	0.6163	0.6250
3	0.7221	0.7191	0.7120	0.7143	0.7246
7	1.2836	1.2796	1.2704	1.2623	1.2833
8[a]	1.4278	1.4249	1.4148	1.4032	1.4292
9[a]	1.5826	1.5784	1.5674	1.5530	1.5816
10	1.7479	1.7404	1.7286	1.7123	1.7425
11	1.8038	1.7997	1.7886	1.7691	1.8009
m.a.e.[b]		0.0044	0.0141	0.0232	0.0019

[a] Using real $2p$-orbitals with integer occupation numbers.

[b] Mean absolute error.

used nonspherical densities corresponding to the configurations $|\ldots 2p_x 2p_y 2p_z \overline{2p_z}|$ and $|\ldots 2p_x \overline{2p_x} 2p_y \overline{2p_y} 2p_z|$, respectively. Because the three real p orbitals are spatially equivalent, other determinantal functions with the same number of unpaired p electrons and total spin S would yield the same e_1^{KS} and e_1^{HF} values (see also the Appendix).

As seen from Table I, the TPSS exchange has a far more accurate linear term in the expansion of $E_{\mathrm{x}}^{\mathrm{KS}}$ than the other functionals. In the case of the He-like hydrogenic atom ($N=2$) the coefficient e_1^{TPSS} is truly exact because $E_{\mathrm{x}}[n]=E_{\mathrm{x}}[n_\uparrow]+E_{\mathrm{x}}[n_\downarrow]$ and the TPSS meta-GGA was constructed to reproduce the exact exchange energy for ground-state one-electron hydrogenic densities [18,19]. The coefficients e_1^{B88} are also comparatively accurate. This explains why BLYP, BP86, and TPSS functionals have the slowest-growing error in Figs. 1–3.

V. HIGH-Z LIMITS OF CORRELATION FUNCTIONALS

While high-Z limits of $E_{\mathrm{c}}^{\mathrm{QC}}$ are known for all $N \leqslant 11$ cases without degeneracies [26,27], the high-density scaling limits of $E_{\mathrm{c}}^{\mathrm{KS}}$ and $E_{\mathrm{c}}^{\mathrm{HF}}$ cannot be easily determined except in special cases [36]. A link between these quantities was established by Ivanov and Levy [37]. Using a perturbation expansion for the DFT correlation energy [38], they showed that, in the absence of high-Z degeneracies,

$$\lim_{\lambda\to\infty} E_{\mathrm{c}}^{\mathrm{KS}}[n_\lambda^{\mathrm{H}}] \leqslant \lim_{Z\to\infty} E_{\mathrm{c}}^{\mathrm{QC}}(N,Z), \tag{21}$$

where $n^{\mathrm{H}}(\mathbf{r})$ is the N-electron hydrogenic density, with the equality holding for only $N=2$, and

$$\lim_{\lambda\to\infty} E_{\mathrm{c}}^{\mathrm{HF}}[n_\lambda^{\mathrm{H}}] = \lim_{Z\to\infty} E_{\mathrm{c}}^{\mathrm{QC}}(N,Z) \tag{22}$$

for all numbers of electrons.

Table II lists the high-λ limits of several correlation energy functionals found by applying the appropriate high-density scaling expressions to the N-electron hydrogenic densities (i.e., $\lambda=Z$). For PBE, this expression is Eq. (9) of Ref. [16]. For PKZB and TPSS, which are constructed by self-interaction correction of PBE, the corresponding expressions follow directly from that for PBE. A similar table for LYP and PBE, but not for PKZB or TPSS, was given by Ivanov and Levy [37] (whose LYP limits were later refined in Ref. [38]; see also Refs. [39,40]). As with the exchange functionals, we used nonspherical densities for the 8- and 9-electron atomic ions. This accounts for small discrepancies between our LYP and PBE values and the corresponding values of Ivanov and Levy [37,38] who used spherical densities—i.e., occupation numbers $f_\downarrow(2p_x)=f_\downarrow(2p_y)=f_\downarrow(2p_z)=2/3$ for $N=9$.

TABLE II. High-Z limits (in hartrees) of quantum-chemical (QC) and DFT correlation energies of atomic ions. The QC limits $c_2^{\mathrm{QC}}=\lim_{Z\to\infty}E_{\mathrm{c}}^{\mathrm{QC}}(N,Z)$ are from Refs. [26] ($N\leqslant 10$) and [27] ($N=11$). DFT limits are determined by uniform scaling of hydrogenic densities $n^{\mathrm{H}}(\mathbf{r})$ to the $\lambda\to\infty$ limit, $c_2^{\mathrm{KS}}=\lim_{\lambda\to\infty}E_{\mathrm{c}}^{\mathrm{KS}}[n_\lambda^{\mathrm{H}}]$. The relationship between c_2^{KS} and c_2^{QC} is given by Eq. (21).

N	$-c_2^{\mathrm{QC}}$	$-c_2^{\mathrm{LYP}}$	$-c_2^{\mathrm{PBE}}$	$-c_2^{\mathrm{PKZB}}$	$-c_2^{\mathrm{TPSS}}$
2	0.0467	0.0567	0.0479	0.0579	0.0510
3	0.0537	0.0995	0.0584	0.0672	0.0595
7	0.2373	0.3232	0.2272	0.2388	0.2374
8[a]	0.3064	0.3948	0.3031	0.3182	0.3122
9[a]	0.3694	0.4631	0.3798	0.3974	0.3890
10	0.4278	0.5295	0.4577	0.4764	0.4674
11	0.4577	0.5890	0.4753	0.4935	0.4834

[a] Using nonspherical densities for density functionals (see text).

Note that the PBE, PKZB, and TPSS approximations, which represent $E_{\mathrm{c}}^{\mathrm{KS}}$ of Eq. (14), tend to satisfy the inequality of Eq. (21) for $N\neq 2$, but do not quite show the expected equality for $N=2$. Only PBE violates that inequality, and then only for $N=7$ and 8.

VI. DISCUSSION

The PBE GGA and the PKZB and TPSS meta-GGA's, were designed so that their correlation components would scale to a constant under uniform density scaling to the high-density limit. The result is a qualitatively correct large-Z behavior of the correlation energy for the atomic ions where the noninteracting KS Hamiltonian develops no degeneracy in the high-Z limit. Even so, none of the existing functionals has a correct large-Z behavior for the ions with high-Z degeneracies, because neither the paradigm densities nor the other exact constraints imposed upon GGA's and meta-GGA's bring any information about near degeneracies of the KS noninteracting ground state. Since transition metal atoms display such near degeneracies even at charge neutrality, the accuracy of semilocal functionals must be somewhat limited for systems containing such atoms [41].

The difficulty of the $Z\to\infty$ limit can be understood in another way. The nonempirical correlation functionals (PBE, PKZB, TPSS) all start from and then correct the second-order gradient expansion. The small parameters of this expansion are the dimensionless density gradients $s(\mathbf{r})$ and $t(\mathbf{r})$, as defined in Ref. [16]. As Z goes to infinity, $s(\mathbf{r})\to s(Z\mathbf{r})$

remains bounded but $t(\mathbf{r}) \to Z^{1/2} t(Z\mathbf{r})$ diverges. The second-order gradient expansion of E_c^{KS} then diverges like $+Z$. While the nonempirical GGA fixes much of the resulting error, it is clear that neither functional can be reliable for $Z \to \infty$. On the other hand, the only small parameter for the second-order gradient expansion of E_x is $s(\mathbf{r})$, so GGA's and meta-GGA's can reliably handle the $Z \to \infty$ limit for exchange.

The errors of the total energy for the isoelectronic $N=4$, 10, and 18 atomic series as functions of Z are especially small for the nonempirical TPSS meta-GGA. This functional appears to give accurate large-Z limits of the isoelectronic correlation energy in cases where the exact limit is finite, and also accurate large-Z limits for the isoelectronic exchange energy. Like BP86, PBE, and PKZB and unlike the other functionals tested here, TPSS is exact for an electron gas of uniform density. Like PKZB, it is exact even to second order in ∇ for a slowly varying density. Thus it has a good performance not only for atoms and molecules [42,43], but also for solids and solid surfaces [44,45].

Density functionals for exchange and correlation that behave properly under uniform density scaling also have a correct adiabatic connection or coupling-constant integrand [11] and so, when they yield the right answers, do so for the right reasons. Satisfaction of Eq. (1) may not be necessary for the prediction of accurate atomization energies or first ionization energies (see Ref. [42]), but functionals intended to be universally applicable to real systems should satisfy as many constraints on the exact universal functional as possible.

VII. CONCLUSION

The approximate density functionals considered here belong on various rungs of "Jacob's ladder" [46], according to the list of their local ingredients. The first rung, the LSDA, uses only the local spin densities. The second rung, the GGA, uses also the gradients of the spin densities. The third rung, the meta-GGA, uses in addition the Laplacians of the spin densities or the Kohn-Sham orbital kinetic energy density, or both. The fourth rung further uses exact-exchange information. There is also a fifth rung [47], not tested here, which uses all of the occupied and unoccupied Kohn-Sham orbitals and orbital energies. All of these functionals are supposed to yield accurate exchange-correlation energies $E_{xc} = E_x + E_c$ for atoms, molecules, and solids. Semilocal approximations (GGA and meta-GGA) based upon localized hole models should also provide accurate separate exchange energies E_x and correlation energies E_c for neutral atoms, but not for molecules where the separate exact exchange and exact correlation holes are delocalized over more than one center [48]. For atomic ions with $Z \gg N$ (especially for those N that show no hydrogenic degeneracy), the best functionals are the ones that satisfy the exact constraint of Eq. (1), particularly the nonempirical TPSS meta-GGA. It remains an unmet challenge [3] to DFT, as it was in 1981, to achieve a proper large-Z behavior of the correlation energy of atomic ions for all N on the first four rungs of the ladder, although this goal could be achieved on the fifth rung—for example, in a degenerate-case generalization of Görling-Levy perturbation theory [49].

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APPENDIX

In the Hartree-Fock theory, the electron interaction energy for a single Slater determinant Φ is given by

$$V_{ee} = \langle \Phi | \hat{V}_{ee} | \Phi \rangle = J - K, \tag{A1}$$

where J is the Coulomb repulsion and $K = -E_x^{HF}$ is the exchange energy. The latter is obtained as

$$K = \frac{1}{2} \sum_{i,j=1}^{N} K_{ij}, \tag{A2}$$

where N is the number of spin-orbitals $\phi_i(\mathbf{r})\sigma_i$ in Φ and

$$K_{ij} = \delta_{\sigma_i \sigma_j} \int \phi_i^*(\mathbf{r}_1) \phi_j^*(\mathbf{r}_2) \frac{1}{r_{12}} \phi_j(\mathbf{r}_1) \phi_i(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2. \tag{A3}$$

If $\phi_i(\mathbf{r})$ are hydrogenic orbitals, the integrals K_{ij} can be evaluated by Slater's formula [50]

$$K_{ij} = \delta_{\sigma_i \sigma_j} \sum_{k=|l-l'|}^{l+l'} b^k(l^i \mu_l^i, l^j \mu_l^j) G^k(n^i l^i, n^j l^j), \tag{A4}$$

where n^i and l^i are the principal and angular momentum quantum numbers of the ith orbital, μ_l^i is the index referring to the $(2l^i+1)$ degenerate orbitals within the l^i set, b^k are the so-called angle factors, and G^k are integrals over the radial parts of the orbitals, as defined in Ref. [50]. In Eq. (A4), the index k varies in steps of 2.

For hydrogenic orbitals whose angular parts are spherical harmonics in complex form $(\mu_l = m_l = -l, \ldots, +l)$, the values of the angle factors b^k are given by Slater [50]. For real hydrogenic orbitals used in our work, the relevant b^k are as follows: $b^0(s,s)=1$, $b^1(s,p_\mu)=1/3$, $b^0(p_\mu,p_\mu)=1$, $b^0(p_\mu,p_\nu)=0$, $b^2(p_\mu,p_\mu)=4/25$, and $b^2(p_\mu,p_\nu)=3/25$, where $\mu = x,y,z$ and $\mu \neq \nu$.

The integrals over radial hydrogenic orbitals are $G^0(1s,1s)=5/8$, $G^0(2s,2s)=77/512$, $G^0(3s,3s)=17/256$, $G^0(1s,2s)=16/729$, $G^0(1s,3s)=189/32768$, $G^0(2s,3s) = 73008/9765625$, $G^1(1s,2p)=112/2187$, $G^1(2s,2p) = 45/512$, $G^1(3s,2p)=92016/9765625$, $G^0(2p,2p)=93/512$, and $G^2(2p,2p)=45/512$.

In atoms with incompletely filled p shells, a unitary transformation among the p_x, p_y, and p_z functions may change J and K but not V_{ee}. For example, in the case of the $1s^2 2s^2 2p^2$ configuration, determinantal functions $\psi_1 = |\ldots 2p_x \overline{2p_y}|$ and $\psi_2 = |\ldots 2p_x \overline{2p_z}|$ have the same K, but similar determinants of complex p orbitals, $\psi_1' = |\ldots 2p_1 \overline{2p_{-1}}|$ and $\psi_2' = |\ldots 2p_1 \overline{2p_0}|$, have K values that differ by $(3/50)G^2(2p,2p) = 0.005273$ hartree.

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