

Towards Density Functional Approximations from Coupled Cluster Correlation Energy Densities

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(Semi-)local density functional approximations (DFAs) are the workhorse electronic structure methods in condensed matter theory and surface science. The correlation energy density $\epsilon_c(r)$ (a spatial function that yields the correlation energy E_c upon integration) is central to defining such DFAs. Unlike E_c , $\epsilon_c(r)$ is not uniquely defined, however. Indeed, there are infinitely many functions that integrate to the correct E_c for a given electron density ρ . The challenge for constructing useful DFAs is thus to find a suitable connection between $\epsilon_c(r)$ and ρ . Herein, we present a new such approach by deriving $\epsilon_c(r)$ directly from the coupled-cluster (CC) energy expression. The corresponding energy densities are analyzed for prototypical two-electron systems. To explore their usefulness for designing DFAs, we construct a semilocal functional to approximate the numerical CC correlation energy densities. Importantly, the energy densities are not simply used as reference data, but guide the choice of the functional form, leading to a remarkably simple and accurate correlation functional for the Helium isoelectronic series.

I. INTRODUCTION

There is no doubt that density functional theory (DFT) has had an unrivalled impact on computational chemistry and physics¹⁻⁴ This is because modern realizations of DFT (density functional approximations, DFAs) tend to offer the best compromise between accuracy and computational cost for most applications⁵⁻⁸ This is especially true for semilocal DFAs, where E_{xc} only depends on properties of the electron density, such as the local density and its gradient. Such methods are sometimes referred to as “pure” density functionals, as opposed to, e.g., hybrid functionals which are based on a generalized Kohn-Sham scheme.⁹ Indeed, the early adoption of semilocal DFAs in the quantum chemistry community can be largely attributed to the remarkable accuracy with which, e.g., the semilocal BLYP^{10,11} functional describes energy differences in molecules at a much lower cost than post-Hartree Fock methods such as second-order Møller-Plesset perturbation theory (MP2).¹²

Even though BLYP and other popular semilocal functionals based on the generalized gradient approximation (GGA) were developed in the 1980-90s, they are still widely used. More recent functionals like those of the ω B97 and Minnesota families (both based on Becke’s 1997 power-series approximation) are also commonly applied in chemistry, although mostly in their hybrid variants¹³⁻¹⁵ Similarly, in the solid-state community, the ubiquitous semilocal PBE¹⁶ functional is still the most frequent choice. Here, more recent alternatives, like the constraint-based SCAN¹⁷ functional of Perdew and co-workers and the Bayesian (m)BEEF^{18,19} methods are

also gaining traction.

Of course, there have been highly significant developments beyond semilocal methods. Most prominently, the already mentioned hybrid functionals (e.g. B3LYP or PBE0) complement semilocal DFA exchange with ‘exact’ Hartree-Fock exchange.^{20,21} This makes the functional depend on the occupied Kohn-Sham (KS) orbitals, and not just on the electron density. Particularly in their more recent range-separated variant, these methods are able to extend the applicability of DFT into areas where “pure” DFAs have difficulties, e.g. charge-transfer states or reaction barrier heights.²²⁻²⁴ In (gas-phase) molecular chemistry, these methods have become the *de facto* standard, whereas they are still too computationally demanding for routine application to condensed matter or nanosized systems. The higher computational demand of hybrids is a direct consequence of the fact that the exchange energy now depends on the occupied KS orbitals, and not just on the total electron density.

This is even more critical for correlation functionals beyond the semilocal approximation, which depend on the unoccupied (virtual) KS orbitals as well. Such ‘higher-rung’ functionals are typically based on the random-phase approximation (RPA) or second-order perturbation theory (double-hybrid functionals).²⁵⁻³⁰ This strongly improves their thermochemical accuracy, and allows for the description of van-der-Waals interactions. The virtual orbital dependence of these methods translates to a quite unfavourable formal scaling with the basis-set size (typically $O(N^5)$ or worse, compared to $O(N^3)$ for GGAs). This is further aggravated by the fact that they additionally require larger (correlation consistent) basis sets, though this deficiency is less critical for the more recent range-separated correlation approaches.^{31,32}

Such DFAs are consequently not really comparable

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with ‘lower-rung’ GGAs, in terms of applicability. Instead, they compete with wavefunction methods such as MP2 or CC.

Improving correlation functionals without resorting to virtual orbitals is therefore an exciting prospect and the focus of this work. To this end, we adhere to a purist approach to DFT. In general, the exchange-correlation energy is only dependent on the electron density ρ , and can be determined *via* numerical integration of a spatial function:

$$E_{\text{xc}}[\rho] = \int \epsilon_{\text{xc}}[\rho](r) dr \quad (1)$$

Here, $\epsilon_{\text{xc}}[\rho](r)$ is the exchange-correlation energy density. The notation $\epsilon_{\text{xc}}[\rho](r)$ implies that the energy density is both a spatial function (i.e. it has a single scalar value at a given point in space) and a functional of the electron density. In the most general case, the exchange-correlation energy density on a given point r depends on the electron density at all other points. Semilocal approximations like the GGA use a more convenient formulation, where $\epsilon_{\text{xc}}(r)$ only depends on local quantities like the local electron density $\rho(r)$ or its gradient $\nabla\rho(r)$. Furthermore, the exchange and correlation components are usually treated separately, leading to expressions for $\epsilon_{\text{x}}[\rho](r)$ and $\epsilon_{\text{c}}[\rho](r)$. We will focus on the latter.

Within this paradigm, there are two classic approaches to designing DFAs. On one hand, there is the constraint-based philosophy championed by Perdew, Burke, Levy and others.³³⁻³⁵ Here, exact conditions for the DFA are derived from theoretical considerations of model densities such as the homogeneous electron gas or spherical two-electron densities.^{36,37} On the other hand, the property-based approach postulates a parametric form for the exchange-correlation energy density, which is then fitted to accurate reference properties of real molecular or condensed phase systems (often based on higher level calculations).^{18-20,38-41}

In this contribution, we follow a new route to constructing ‘‘pure’’ DFAs, namely by deriving a correlation energy density from *ab initio* coupled cluster (CC) wavefunctions. This can be thought of as an intermediate strategy between the constraint and property-based philosophies. On one hand, the DFA is constructed to reproduce high quality benchmark calculations, as in the property-based approach. On the other hand, it is not based on a predefined fit function. Instead, the functional form emerges naturally from the shape of the correlation energy densities of meaningful model systems, as in the constraint-based approach.

This paper is organized as follows: In the theory section, we discuss the meaning of the exchange and correlation energies in DFT and WFT and motivate why we expect the CC correlation energy density ($\epsilon_{\text{c}}^{\text{CC}}$) to be a useful model for a correlation functional. Then the formalism for computing $\epsilon_{\text{c}}^{\text{CC}}$ is presented. In the results section, we analyze the properties of $\epsilon_{\text{c}}^{\text{CC}}$ for prototypi-

cal two-electron systems. The usefulness of these energy densities is then illustrated by constructing an accurate DFA to the CC correlation energy of the He isoelectronic series.

II. THEORY

We denote occupied molecular orbitals (MOs, $\phi(r)$) with the indices $i, j, k \dots$, virtual MOs by $a, b, c \dots$ and general MOs by $p, q, r \dots$. All calculations are performed in a one-electron basis of atom-centered, normalized basis-functions $\chi_{\mu}(r)$, with indices $\mu, \nu, \sigma \dots$. Following common practice in the CC community, the basis-functions are referred to as atomic orbitals (AOs).

For clarity, it should be noted that the term ‘‘exchange-correlation energy density’’ is often used in the literature for the correlation energy per particle. The exchange-correlation energy per volume (as used in this paper) is in that case often referred to as the exchange-correlation kernel. The latter can be converted into the former by dividing through the electron density.

A. Exchange and Correlation in WFT and DFT

The concepts of exchange and correlation are fundamental to both WFT and DFT. In WFT methods, the correlation energy E_{c} is defined with respect to the Hartree-Fock (HF) energy, and simply describes the difference between HF and the exact non-relativistic energy (i.e. the full configuration interaction limit) in a given basis.⁴² Meanwhile, the exchange energy E_{x} emerges naturally from the HF formalism, due to the antisymmetry of the wavefunction.⁴³

In DFT, exchange and correlation in principle describe the same physical phenomena, but the energies are not referenced to HF. Instead, the KS equations use the variational principle to obtain (given the exact functional) the exact density.² Accordingly, the exact exchange and correlation energies are referenced to that density, and not to the HF one. One would thus not expect the WFT and DFT E_{xc} to be numerically identical unless the HF density is exact, which is only true in some special cases like the homogeneous electron gas and for one-electron systems like the hydrogen atom. From a DFT perspective, the WFT correlation energy thus contains implicit corrections to the classical and exchange energies, which otherwise carry some error due to the approximate HF density.

To understand these differences in detail, it is helpful to consider the individual components to the DFT and CC total energies. In DFT, all energy contributions are written as functionals of the exact ground state density ρ_0 :

$$E_{\text{tot}}^{\text{DFT}} = T_{\text{s}}[\rho_0] + U[\rho_0] + J[\rho_0] + E_{\text{xc}}[\rho_0], \quad (2)$$

with the non-interacting kinetic energy functional T_s and the contributions of the external (U) and the Hartree (J) potentials. Equivalently, these terms can be expressed as functionals of the occupied KS orbitals $\{\phi_i^{\text{KS}}\}$, which is particularly useful for the kinetic energy.

In CC, similar components are computed in terms of the HF orbitals $\{\phi_p^{\text{HF}}\}$:

$$E_{\text{tot}}^{\text{CC}} = T_s[\{\phi_i^{\text{HF}}\}] + U[\{\phi_i^{\text{HF}}\}] + J[\{\phi_i^{\text{HF}}\}] + K[\{\phi_i^{\text{HF}}\}] + E_c[\{\phi_p^{\text{HF}}\}] \quad (3)$$

Here, $K[\{\phi_i^{\text{HF}}\}]$ is the HF exchange energy.

Given the exact exchange-correlation functional and full CC expansion, both expressions lead to the same energy ($E_{\text{tot}}^{\text{DFT}} = E_{\text{tot}}^{\text{CC}}$). It is therefore tempting to equate the last term in the DFT expression with the last two terms of the CC formula leading to:

$$E_c[\{\phi_i^{\text{HF}}\}] \approx E_{\text{xc}}[\rho_0] - K[\{\phi_i^{\text{HF}}\}] \quad (4)$$

However, this is an approximation because $\sum_i |\phi_i^{\text{HF}}|^2$ does not yield the exact ground-state density. Accordingly, for $E_{\text{tot}}^{\text{CC}}$ to be exact, E_c^{CC} must also contain corrections to all other terms in the energy expression:

$$E_c[\{\phi_i^{\text{HF}}\}] = E_{\text{xc}}[\rho_0] - K[\{\phi_i^{\text{HF}}\}] + \Delta T_s + \Delta U + \Delta J, \quad (5)$$

where $\Delta T_s = T_s[\rho_0] - T_s[\{\phi_i^{\text{HF}}\}]$, and so on.

When constructing a correlation functional based on CC reference data, we are essentially hoping for a high accuracy of eq. (4). In particular that,

$$E_{\text{x}}[\rho_0] \approx K[\{\phi_i^{\text{HF}}\}] \quad (6)$$

and

$$\sum_i |\phi_i^{\text{HF}}|^2 \approx \rho_0 \quad (7)$$

Indeed, these conditions are related, since the exact DFT exchange can be computed analogously to the HF case, but using $\{\phi_i^{\text{KS}}\}$ instead of $\{\phi_i^{\text{HF}}\}$, leading to

$$E_c[\{\phi_i^{\text{HF}}\}] = E_c[\rho_0] + \Delta K + \Delta T_s + \Delta U + \Delta J, \quad (8)$$

The difference between the WFT and DFT correlation energies thus boils down to the difference between $\{\phi_i^{\text{KS}}\}$ and $\{\phi_i^{\text{HF}}\}$. While the exact KS orbitals are generally not available (because a general expression for the exact $E_{\text{xc}}[\rho_0]$ is unknown), it has been observed that Brueckner theory offers an excellent approximation to $\{\phi_i^{\text{KS}}\}$.^{44,45} Very briefly, the idea behind the Brueckner CC approach is to rotate the HF orbitals in such a way that the T_1

contribution to the correlation energy vanishes. This is equivalent to introducing a (non-local) correlation potential into the HF equations.⁴⁶

If the chosen CC expansion is exact (see below), the total energies of the canonical and Brueckner CC methods are identical. However, the individual components on the r.h.s. of eq. (3) change. Specifically, the sum of the first four terms (the reference energy) becomes less negative, while the last term (the correlation energy) becomes more negative by the same amount.

In the following we apply the CC singles and doubles expansion (CCSD) to two electron systems. We can use canonical and Brueckner CC calculations to numerically estimate the accuracy of eq. (4) for this case. For the He atom, the correlation energy difference between a canonical CCSD and Brueckner CCD calculation is $2.6 \times 10^{-5} E_h$ (see the Supporting Information, table S1). Consequently, the approximation made in eq. (4) is very good in this particular case.

In a more general vein, it can be noted that HF electron densities are often surprisingly good. Indeed they are often better than self-consistent GGA densities as observed by Bartlett, Burke and others.⁴⁷⁻⁴⁹

Note, however, that the above discussion is no longer valid if semilocal exchange functionals are used (in particular for molecular systems). Semilocal correlation functionals cannot describe the type of static (left-right) correlation that is evident, e.g. when dissociating the hydrogen molecule in a spin-restricted calculation. As was observed by Handy and others, this contribution is instead emulated by GGA exchange functionals.⁵⁰

The case is different for atomic systems, however. Many classic GGA functionals are based on the approximate equivalence of exchange and correlation in DFT and WFT for atoms. For example, Becke's 1988 exchange functional was fitted to HF exchange energies of atoms, and the Lee-Yang-Parr (LYP) correlation functional is derived from the Colle-Salvetti formula, which expresses the WFT correlation energy of the Helium atom in terms of the corresponding HF density matrix.^{10,11} Even functionals which are not based on WFT at all (such as the already mentioned SCAN functional and the "nearly correct asymptotic property" NCAP functional) show reasonably good numerical agreement with the WFT based exchange and correlation energies of noble gas atoms.^{17,51}

It has also been found empirically that WFT and DFT correlation energies are compatible, as reflected in the success of double hybrid functionals, which describe E_c as a linear combination of GGA and MP2 correlation.²⁵

B. Correlation Energy Densities from WFT

The connection between WFT and DFT has long been the subject of intensive research. Most prominently, such efforts have been directed at the exchange-correlation potential, V_{xc} .⁵²⁻⁵⁸ These studies have underscored the limitations of most semi-local approximations to V_{xc} , particu-

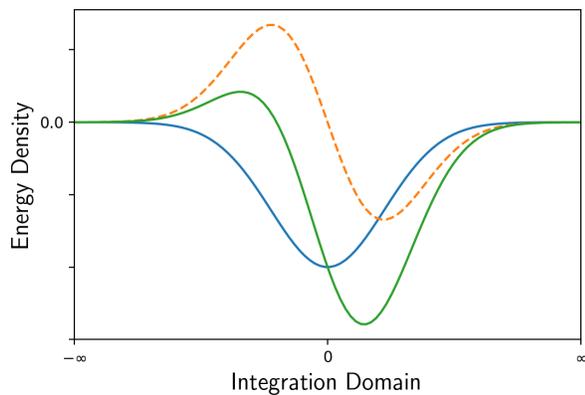


FIG. 1. Schematic depiction of correlation energy densities (blue and green) that differ by a function that integrates to zero over the integration domain (dashed orange line).

larly those that are the functional derivatives of common DFAs^{59,60}. Such *ab initio* potentials are also essential components of some of the higher-rung DFAs methods mentioned above.^{61–63}

Knowledge of V_{xc} does not provide a route to the corresponding functional E_{xc} , however. The latter requires an expression for the exchange correlation energy density $\epsilon_{xc}(r)$, as given in eq. (1). Unfortunately, an inherent difficulty with defining $\epsilon_{xc}(r)$ is that it is not unique. In principle, the only condition is that integrating this function over all space yields the exchange-correlation energy. Adding any function that integrates to zero to an ansatz for $\epsilon_{xc}(r)$ therefore yields equally valid energy densities that may look completely different (see Fig. 1).⁶⁴ In this sense, $\epsilon_{xc}(r)$ is arbitrary. However, not all possible energy densities are mappable to the electron density in an efficient way. A systematic way for defining $\epsilon_{xc}(r)$ for different systems from *ab initio* calculation allows exploring this mapping, and therefore represents a promising starting point for designing new DFAs.

One strategy to this end is relating $\epsilon_{xc}(r)$ to the exchange-correlation hole potential.^{56,65} This offers a systematic route to calculating $\epsilon_{xc}(r)$, given that the one- and two-particle density matrices are known. This has, e.g., been done for configuration interaction wavefunctions with single and double excitations (CISD).⁵⁶ More recently, Vyboishchikov used modified “local” two-electron integrals to calculate the correlation energy density $\epsilon_c(r)$ at the MP2 and CISD level.⁶⁶ These functions were used to construct a simple local correlation functional for spherically confined atoms.

C. CC Correlation Energy Densities

In the following we introduce a new method to calculate an $\epsilon_c(r)$ from first principles, namely one that integrates to the CC correlation energy. The approach has several advantages: (1) By virtue of being CC-based, it

is automatically size-extensive (unlike truncated CI). (2) Only integrals and amplitudes that are available in any standard CC code are required. (3) The $\epsilon_c(r)$ obtained in this manner is by construction topologically similar to the electron density, making it amenable to semilocal approximations (see below).

In CC, the ground-state wavefunction Ψ_{CC} is defined with respect to a reference determinant ψ_0 as:⁶⁷

$$\Psi_{CC} = e^T \psi_0 \quad (9)$$

$$T = T_1 + \dots + T_n \quad (10)$$

By truncating T at double (N=2), triple (N=3), or quadruple (N=4) excitations one obtains specific CC methods, abbreviated as CCSD, CCSDT, and CCSDTQ respectively.^{67–69} An important feature of these methods is that they are exact for systems with a number of electrons smaller or equal to the highest excitation level (i.e. CCSD is exact for two-electron systems).

Irrespective of the truncation, the CC correlation energy only depends on the single and double amplitudes (t_i^a and t_{ij}^{ab}), while higher than double excitations contribute to the energy indirectly, by coupling with T_1 and T_2 . The correlation energy is calculated as:

$$E_c = \frac{1}{4} \sum_{ijab} (t_{ij}^{ab} + \frac{1}{2} t_i^a t_j^b) \langle ij || ab \rangle = \frac{1}{4} \sum_{ijab} \tau_{ij}^{ab} \langle ij || ab \rangle \quad (11)$$

with $\tau_{ij}^{ab} = t_{ij}^{ab} + \frac{1}{2} t_i^a t_j^b$, and the antisymmetrized two-electron integrals in MO basis defined as

$$\langle ij || ab \rangle = \langle ij | ab \rangle - \langle ij | ba \rangle$$

$$\langle ij | ab \rangle = \int \phi_i(r_1) \phi_a(r_1) \frac{1}{r_{12}} \phi_j(r_2) \phi_b(r_2) dr_1 dr_2 \quad (12)$$

These integrals are obtained from the corresponding AO integrals and the MO coefficients which define ψ_0 , formally via:

$$\langle ij | ab \rangle = \sum_{\mu\nu\sigma\lambda} C_\mu^i C_\nu^j \langle \mu\nu | \sigma\lambda \rangle C_\sigma^a C_\lambda^b \quad (13)$$

We are now looking to transform the coupled cluster correlation energy into a form resembling the DFT expression:

$$E_c[\rho] = \int \epsilon_c[\rho](r) dr \quad (14)$$

We start from the AO-CC approach of Ayala and Scuseria, which is based on an MO to AO transformation of the T-amplitudes:⁷⁰

$$\tau_{\mu\nu}^{\sigma\lambda} = \sum_{ijab} C_{\mu}^i C_{\nu}^j \tau_{ij}^{ab} C_{\sigma}^a C_{\lambda}^b \quad (15)$$

Given these AO amplitudes, the correlation energy can be calculated as:

$$E_c = \frac{1}{4} \sum_{\mu\nu\sigma\lambda} \tau_{\mu\nu}^{\sigma\lambda} \langle \mu\nu || \sigma\lambda \rangle \quad (16)$$

We now partition the energy into atomic or AO contributions, using:

$$E_c = \sum_A E_A = \sum_A \sum_{\mu \in A} e_{\mu} \quad (17)$$

$$e_{\mu} = \frac{1}{4} \sum_{\nu\sigma\lambda} \tau_{\mu\nu}^{\sigma\lambda} \langle \mu\nu || \sigma\lambda \rangle \quad (18)$$

Because the AO basis-functions are normalized, the CC correlation energy can now be written as an integral over space:

$$E_c = \int \sum_{\mu} e_{\mu} |\chi_{\mu}(r)|^2 dr \quad (19)$$

This defines the CC correlation energy density as:

$$\epsilon_c^{\text{CC}}(r) = \sum_{\mu} e_{\mu} |\chi_{\mu}(r)|^2 \quad (20)$$

As noted above, $\epsilon_c^{\text{CC}}(r)$ is topologically similar to the electron density, in the sense that it is a linear combination of atomic densities. As shown in Fig. 1, the shape of the correlation energy density is in principle arbitrary. However, an energy density that is similar to the electron density can be much more easily approximated by a (semi-)local approach.

Using eqs. (15), (16), (18) and (20), $\epsilon_c^{\text{CC}}(r)$ can be calculated for any system, as long as a standard CC calculation is possible. In the following some exemplary calculations for atomic two-electron systems are performed at the CCSD level, using a custom Python program interfaced with the Psi4 program package.^{71,72} Calculations for two-electron ions were performed with a modified uncontracted cc-pV5Z basis set for Helium, where the scaling factor of the orbital exponents was optimized individually for each ion (abbreviated u-5Z).⁷³ In all other DFT calculations, the pcseg-3 basis set of Jensen is used.⁷⁴ Additional CCSD calculations on He-Zn were performed with the core-polarized cc-pwCV(5+d)Z basis.⁷⁵ DFT correlation energies are calculated by numerical quadrature on Lebedev-Treutler (75,302) grids.⁷⁶ All DFT calculations (also for PBE) are performed non-self-consistently using HF densities with the same code.

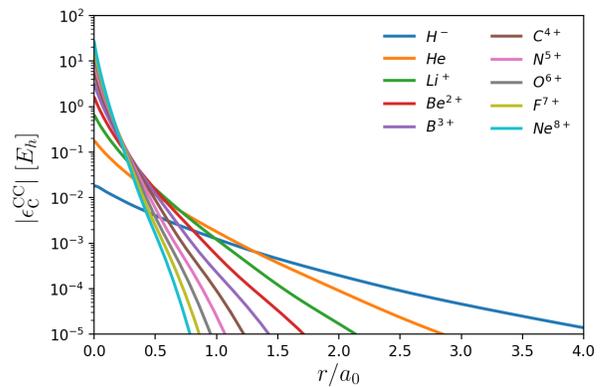


FIG. 2. Plot of correlation energy density against the distance from the nucleus for the Helium isoelectronic series.

III. RESULTS

As model systems, we calculate $\epsilon_c^{\text{CC}}(r)$ for the two-electron ions from H^- to Ne^{8+} (see Fig. 2). In all cases, the correlation energy density decays in an approximately exponential fashion as a function of the distance from the nucleus, with the individual curves being highly system dependent. Specifically, $\epsilon_c^{\text{CC}}(r)$ decays slowly for the very diffuse H^- ion and quickly for Ne^{8+} . It is furthermore notable that the correlation energy density for He is quite similar to the one obtained by Vyboishchikov’s ‘local 2e-integral’ approach, despite the different mathematical ansatz.⁶⁶

In the supporting information we also include the respective plots for the PBE and LDA correlation functionals (Figs. S1 and S2). While both energy densities are qualitatively similar to Fig. 2, there are important differences. In the LDA case, the functions decay at approximately the same rate as $\epsilon_c^{\text{CC}}(r)$, but they are less curved and display larger values at the nuclear cusp. In contrast, the PBE curves overall decay more quickly and display a more complex shape, with a fast initial decay close to the nucleus followed by a slower asymptotic decay.

From a DFT perspective, the more interesting dependence is between $\epsilon_c^{\text{CC}}(r)$ and ρ (Fig. 3). As the atomic electron densities are monotonically decaying, there is a unique mapping between the two for each ion. Specifically, $|\epsilon_c^{\text{CC}}(r)|$ increases approximately parabolically with ρ . Unsurprisingly, the curves are again somewhat system dependent, however. This simply means that a LDA-like correlation functional cannot represent $\epsilon_c^{\text{CC}}(r)$ exactly for all systems.

If it is to be useful for defining DFAs, it should at least be approximately possible to effectively map $\epsilon_c^{\text{CC}}(r)$ to ρ , however. Furthermore, this mapping should ideally only use readily available local features of the electron density, such as $\rho(r)$ or the reduced density gradient $s = \frac{|\nabla\rho(r)|}{2(3\pi^2)^{1/3}\rho(r)^{4/3}}$. To explore whether this is possible in the presented formalism, we construct a simple GGA

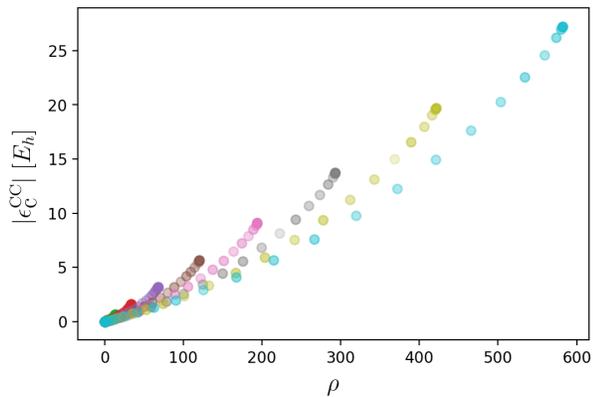


FIG. 3. Plot of correlation energy density against the HF/u-5z electron density for the Helium isoelectronic series.

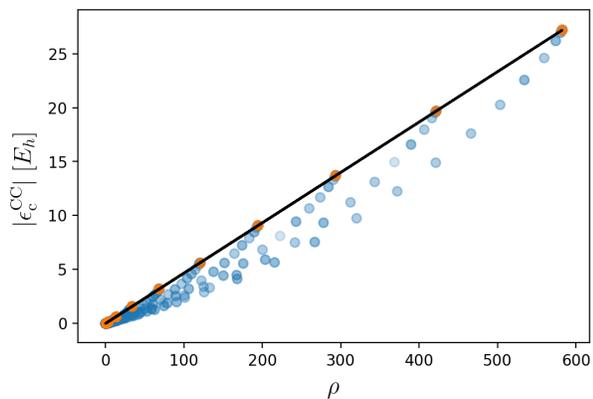


FIG. 4. Plot of $\epsilon_c^{\text{CC}}(r)$ against ρ for the Helium isoelectronic series (blue). Datapoints where the reduced density gradient $s < 0.1$ are shown in orange.

functional to approximate $\epsilon_c^{\text{CC}}(r)$. To this end, only datapoints with $s < 5$ were taken into account, following the observation of Burke, Perdew and coworkers that the energetically relevant range is $0 < s < 3$.⁷⁷

As can be seen in Fig. 4, a simple linear fit allows an accurate description of all datapoints with $s < 0.1$ (i.e. those with approximately “homogeneous electron gas”-like conditions). This is reminiscent of the Wigner functional,^{78,79} which is linear in ρ to leading order, but allows some more flexibility in the low density regime:

$$\epsilon_c^{\text{W}}[\rho(r)] = \frac{c_1 \rho(r)}{1 + c_2 \rho(r)^{-\frac{1}{3}}}, \quad (21)$$

where c_1 and c_2 are coefficients to be defined. Eq. (21) forms the local baseline functional for our GGA (with $c_1 = -0.0468$ and $c_2 = 0.023$).

As shown in Fig. 5, the residual error of $\epsilon_c^{\text{W}}[\rho(r)]$ is strongly dependent on the reduced gradient s . The largest errors are found in the regime between $0 < s < 2$.

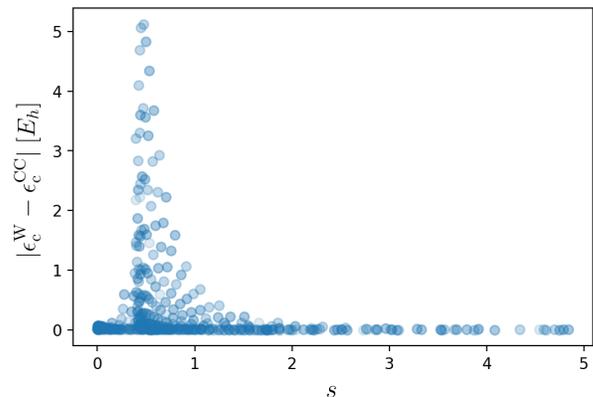


FIG. 5. Plot of residual errors of the $\epsilon_c^{\text{W}}[\rho(r)]$ baseline functional against the reduced density gradient s .

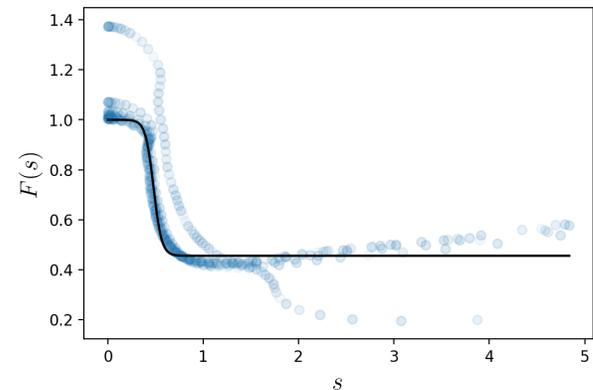


FIG. 6. Numerical (symbols) and analytical (line) enhancement factors for $\epsilon_c^{\text{GGA}}[\rho(r), s]$.

For the full GGA functional, we now choose the enhancement-factor ansatz:

$$\epsilon_c^{\text{GGA}}[\rho(r), s] = \epsilon_c^{\text{W}}[\rho(r)] * F(s) \quad (22)$$

Plotting $\epsilon_c^{\text{CC}}/\epsilon_c^{\text{W}}$ vs. s , gives insight into the numerical distribution of an *ideal* enhancement factor (Fig. 6). Interestingly, all ions from He to Ne^{8+} approximately fall on a curve, whereas the H^- datapoints deviate significantly. This reflects the well-known inability of GGAs to adequately describe atomic anions.⁸⁰ Specifically, semilocal DFAs only attach a fractional electron to an atom in a complete basis-set due to the self-interaction error.^{81,82} This is an inherent limitation of the GGA functional form, not of the CC reference calculations.⁸³ We therefore exclude H^- when fitting parameters, though it is retained in the analysis, for comparison.

The distribution of the numerical enhancement factor in Fig. 6 suggests that $F(s)$ should have a sigmoidal form with the asymptotic behaviour:

$$\lim_{s \rightarrow 0} F(s) = 1 \quad (23)$$

and

$$\lim_{s \rightarrow \infty} F(s) \approx 0.5 \quad (24)$$

We therefore base $F(s)$ on the ‘‘complementary’’ logistic function:

$$F(s) = 1 - \frac{c_3}{1 + e^{-c_4(s-c_5)}}, \quad (25)$$

with coefficients c_{3-5} .

Combining equations (21), (22) and (25), the final functional, which we call ccDF, thus has the simple 5-parameter form:

$$\epsilon_c^{\text{ccDF}}[\rho(r), s(r)] = \frac{c_1 \rho(r)}{1 + c_2 \rho(r)^{-\frac{1}{3}}} \left(1 - \frac{c_3}{1 + e^{-c_4(s-c_5)}} \right) \quad (26)$$

One could optimize these parameters to directly reproduce the numerical $F(s)$ as closely as possible. However, this strategy is not optimal, as $F(s)$ only enters the energy expression as a scaling factor for $\epsilon_c^{\text{W}}[\rho(r)]$. Consequently, it has little effect on the total energy, whenever $\epsilon_c^{\text{W}}[\rho(r)]$ is small. A more promising approach is therefore to use total correlation energies (E_c) as reference data.

A least-squares fit of the GGA parameters to the correlation energies of He to Ne⁸⁺ yields:

$$c_3 = 0.544, c_4 = 23.401, c_5 = 0.479$$

The resulting enhancement factor is a good fit to the numerical $F(s)$ (solid line in Fig. 6), and the ccDF functional accurately reproduces the CCSD correlation energies of He to Ne⁸⁺ (Fig. 7). This figure also includes the PBE correlation energies. Unsurprisingly, ccDF more closely reproduces the CCSD correlation energies than PBE, given that it was fitted to this data. It is, however, notable that this functional achieves very high total accuracies of $10^{-3} E_h$ or better (except for H⁻, see above), given its simple functional form. More importantly, both functionals display the correct qualitative behaviour: As Z increases, the correlation energy converges to a constant value.

As discussed in the Theory section, exact numerical agreement between DFT and WFT correlation energies should generally not be expected. Neither is it necessary for chemical applications. For example, both MP2 and PBE correlation energies will often deviate from more accurate CC values by 10% or more, yet both methods are still quite accurate in terms of energy differences. In fact, even the CCSD/u-5Z values we used for fitting ccDF are only converged to within several milli-Hartree, since the

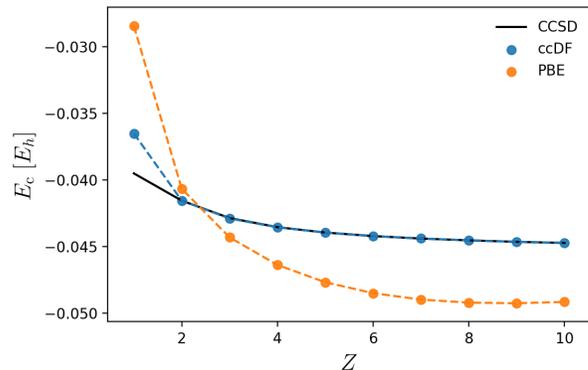


FIG. 7. Correlation energies for He isoelectronics, computed with CCSD, ccDF and PBE.

TABLE I. Exact and DFA correlation energies (in E_h) for closed shell atoms, and the percentage of correlation energy recovered.

Element	Exact	E_c^{ccDF}	E_c^{PBE}	%[ccDF]	%[PBE]
He	0.0453	0.0415	0.0406	91.6	89.7
Be	0.0943	0.0898	0.0861	95.2	91.2
Ne	0.3905	0.2708	0.3476	69.3	89.0
Mg	0.4383	0.3184	0.4120	72.6	94.0
Ar	0.7222	0.5265	0.7088	72.9	98.2
Ca	0.8271	0.5741	0.7778	69.4	94.0
Zn	1.6206	0.9334	1.3979	57.6	86.3
Kr	1.8496	1.1515	1.7640	62.3	95.4

complete basis-set limit for absolute correlation energies of isolated atoms is notoriously difficult to reach.⁸⁴ Still, a useful DFA should reproduce the qualitative behaviour of accurate WFT reference values.

Having established the accuracy of ccDF for two-electron systems, the question arises whether this functional form can also be applied in the many-electron case. To this end, we computed the correlation energies for the closed-shell neutral atoms from He to Kr (table 1), for which highly accurate reference energies are available.^{84,85} Here, ccDF and PBE show qualitatively different behaviour. For He and Be, both functionals recover >90% of the correlation energy. For all other systems, PBE continues to recover 85-100% of the correlation energy while the ccDF values range from 60-70%.

This behaviour can readily be explained by considering the spin-polarized form of the Wigner functional, upon which ccDF is based:⁸⁶

$$\epsilon_c^{\text{W}}[\rho_\alpha(r), \rho_\beta(r), \rho(r)] = \frac{\rho_\alpha(r)\rho_\beta(r)}{\rho(r)} \frac{4c_1}{1 + c_2 \rho(r)^{-\frac{1}{3}}} \quad (27)$$

Here, ρ_α and ρ_β are the up and down-spin densities, respectively. By construction, this functional only describes correlation between electrons of opposite spin

(i.e., the correlation energy for fully spin-polarized systems is zero). Though this is not widely appreciated, the LYP functional actually suffers from the same problem, since the first term in its expansion is exactly eq. (27).^{87–90}

Obviously, closed shell two-electron systems like He only display opposite spin correlation. Similarly, Be possesses filled 1s and 2s orbitals, so that there is only weak core-valence correlation between same-spin electrons, and the bulk of the correlation energy is of opposite-spin nature. ccDF describes these systems quite accurately.

For all other systems, ccDF underestimates the total correlation energy by about one third, presumably due to the missing same-spin contribution. Importantly, this is in good agreement with the relative contribution of same-spin correlation for general many-electron systems, as estimated by Grimme and Head-Gordon in the construction of the spin-component-scaled (SCS) and scaled-opposite-spin (SOS) MP2 methods.^{91,92} For instance, SOS-MP2 simply scales the opposite-spin correlation energy by 1.3 to approximate the full correlation energy.

To further corroborate this interpretation, we turn to the spin component decomposition of the CC energy, which allows computing the opposite-spin contribution to the CC correlation energy as:⁹³

$$E_{c,OS}^{CCSD} = \sum_{ijab} \tau_{ij}^{ab} \langle ij|ab \rangle \quad (28)$$

As shown in Fig. 8, E_c^{ccDF} indeed correlates with $E_{c,OS}^{CCSD}$ quite well. This indicates that the physics of opposite-spin correlation are essentially transferable between two- and many-electron system. However, neither this transferability nor the GGA approximation should be expected to be perfect. Future work will therefore focus on developing general correlation functionals based on CC. We consider the presented results to be very encouraging for this endeavour.

IV. CONCLUSIONS

In this paper, we have introduced a new approach to calculating CC correlation energy densities $\epsilon_c^{CC}(r)$ for atomic systems. These densities are derived from an AO-based formulation of CC and exactly integrate to the respective CC correlation energy. The properties of $\epsilon_c^{CC}(r)$ were discussed for a range of atomic two-electron systems.

As these energy densities are by construction topologically similar to the electron density, they are well suited to be approximated by DFAs. As a proof-of-principle, a CCSD based GGA functional was constructed for the He isoelectronic series. By analysis of the numerical CCSD functional, we find that a remarkably simple enhancement-factor formula can be fitted to yield highly

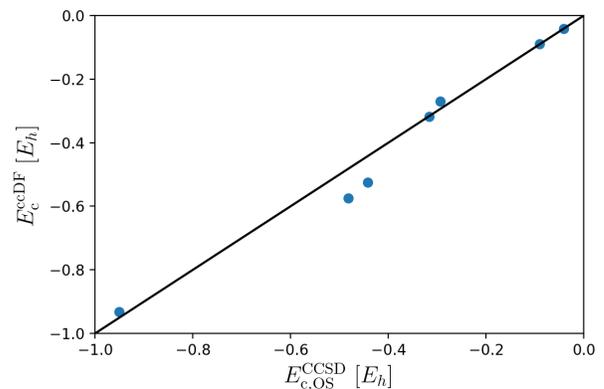


FIG. 8. ccDF vs. opposite-spin CCSD correlation energies for the closed-shell atoms He-Zn.

accurate correlation energies for these systems. Despite only being fitted to two-electron systems, we find that the ccDF functional also provides reasonable estimates of the opposite-spin correlation energies of many-electron atoms. This indicates that $\epsilon_c^{CC}(r)$ provides a robust physical basis for the design of DFAs, and that the He isoelectronics form an interesting set of model densities.

However, it should be emphasised that the proposed GGA functional is mainly intended as a proof-of-principle, and should not be applied to general systems as is. Most importantly, it should at least be augmented with a corresponding same-spin functional.⁸⁸

Furthermore, the proposed form of $\epsilon_c^{CC}(r)$ is only one possible choice. An expression based on the one- and two-particle density matrices may in fact be preferable, as it would allow using the “gold-standard” CCSD(T) method as reference, which includes perturbative triple contributions. In contrast, our current approach can only be used with full coupled cluster methods (CCSD, CCSDT, CCSDTQ, etc.), of which all but CCSD display prohibitive computational scaling for all but the simplest systems. Moving beyond CCSD is a prerequisite to obtain a good description of electron correlation from systems with more than two electrons.

Importantly, the present framework is general enough to be applied to more complex functional forms (e.g. truly non-local functionals), and this will be the subject of future work. An especially promising route lies in the use of CC energy densities to train “machine-learned” functionals.⁹⁴ The fact that $\epsilon_c^{CC}(r)$ can guide the design of a simple and accurate functional form like the GGA indicates that it contains the necessary information to this end.

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