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Correlation Effects in Hybrid Kohn–Sham Density Functionals: A Critical Evaluation of Existing Approximations and the New UMK26 Functional

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Abstract

This doctoral thesis examines the role of electron correlation in exchange–correlation (XC) approximations of Kohn–Sham (KS) Density Functional Theory (DFT). Since XC functionals have historically been evaluated almost exclusively on the basis of energy and energy-derived benchmarks, the thesis addresses this bias by benchmarking existing hybrid XC functionals, and by constructing a new one, against the KS XC potential, the electron density, and the ionization potentials, using highly accurate reference data obtained from wavefunction *ab initio* methods (FCI, CCSD(T), EOM CCSD).

To make such an assessment, we have tested the reliability of existing Kohn–Sham inversion schemes and developed strategies to overcome existing challenges in computing accurate KS XC potentials from hybrid KS and reference *ab initio* densities. Finally, the Wu–Yang inversion procedure was chosen and employed to compute the XC potentials.

We evaluated 155 hybrid density functionals from the LIBXC library, comparing the XC potentials obtained by inverting each hybrid’s self-consistent KS density against reference potentials obtained by inverting the FCI and CCSD(T) electron densities. A clear hierarchy in the error metrics emerged, with total energy errors being the smallest, followed by density errors, ionization potential errors, and, finally, XC potential errors, which were three to four orders of magnitude larger than the energy errors. The quality of the XC potential was found to be directly correlated with the accuracy of the ionization potentials, and the decomposition of the total energy error into density and functional-driven parts depicted a dominant functional-driven contribution.

Our key observation is that the main qualitative features of the correlation potential and the correlated density in hybrid functionals arise not from the semi-local correlation functional but from the difference between the semi-local and the exact (Hartree–Fock) exchange. Based on this insight and on the adiabatic connection formalism, we developed a new procedure to optimize the global hybrid functional. As a result, the UMK26 functional was defined, with its single parameter obtained by a line search that minimizes the ionization-potential discrepancy against the EOM-CCSD ionization potentials from a 16-system benchmark set.

Compared with conventional global hybrids, UMK26 improves the description of the correlation potential, the correlated density, the HOMO and valence ionization potentials (401 reference values over 63 systems), and the charge transfer excitation energies, reaching the level of dedicated range-separated hybrids; it also reduces the

self-interaction error, as demonstrated on the SIE4x4 test set and in the dissociation curves of charged species. Although UMK26 does not deliver a uniform gain across thermochemical benchmarks, its simple, physically transparent construction provides a route toward future XC functional design, including range-separated and machine learning variants.

The doctoral dissertation is based on two publications:

1. **Vignesh Balaji Kumar**, Szymon Śmiga, Ireneusz Grabowski; A Critical Evaluation of the Hybrid KS DFT Functionals Based on the KS Exchange-Correlation Potentials. *J. Phys. Chem. Lett.* 10 October 2024; 15 (40): 10219–10229.
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2. **Vignesh Balaji Kumar**, Szymon Śmiga, Rodrigo Araújo Mendes, Bogumiła Jezierska, Rodney Bartlett, and Ireneusz Grabowski, “On the Primary Role of Semi-Local and Exact-Exchange Difference in the Description of Correlation Effects in Hybrid Functionals” (*J. Chem. Theory Comput.* XXX, 2026),
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Streszczenie

Efekty korelacji w hybrydowych funkcjonalach gęstości Kohna–Shama: krytyczna ocena istniejących przybliżeń. Nowy funkcjonal UMK26.

Niniejsza rozprawa doktorska analizuje rolę korelacji elektronowej w przybliżonych wersjach funkcjonałów wymiennie-korelacyjnych (XC) w ramach teorii funkcjonału gęstości Kohna-Shama (KS) (DFT). Ponieważ funkcjonały XC historycznie ewaluowano niemal wyłącznie na podstawie benchmarków opartych na energii, w rozprawie opracowano nową procedurę oceny jakości funkcjonałów, opartą na potencjale wymiennie-korelacyjnym KS, gęstości elektronowej i potencjałach jonizacji, z wykorzystaniem bardzo dokładnych danych referencyjnych uzyskanych metodami *ab initio* (FCI, CCSD(T), EOM CCSD).

Aby efektywnie przeprowadzić taką ocenę, przetestowano niezawodność istniejących schematów inwersji Kohna-Shama i opracowano strategie przewyższania istniejących wyzwań w obliczaniu dokładnych potencjałów wymiennie-korelacyjnych KS z gęstości KS dla potencjałów hybrydowych oraz gęstości referencyjnych *ab initio*. W wyniku przeprowadzonej analizy wybrano procedurę inwersji Wu-Yanga i zastosowano ją do obliczenia potencjałów wymiennie-korelacyjnych uzyskanych z testowanych i referencyjnych gęstości elektronowych.

Wykorzystując opracowane narzędzia, przetestowano 155 funkcjonałów hybrydowych KS dostępnych w bibliotece LIBXC, porównując potencjały wymiennie-korelacyjne uzyskane z gęstości KS każdego funkcjonału hybrydowego z potencjałami referencyjnymi uzyskanymi z gęstości elektronowych metod FCI i CCSD(T). Analiza pokazała wyraźną hierarchię w obliczanych błędach analizowanych wielkości: błędy energii całkowitej były najmniejsze, następnie błędy gęstości, błędy potencjału jonizacji i wreszcie błędy potencjałów wymiennie-korelacyjnych, które były o trzy do czterech rzędów wielkości większe niż błędy energii całkowitej badanych funkcjonałów. Pokazano także, że jakość potencjału wymiennie-korelacyjnego KS jest bezpośrednio skorelowana z dokładnością potencjałów jonizacji, a rozkład całkowitego błędu energii całkowitej na części zależne od gęstości i funkcjonału, pokazał dominującą rolę części zależnej od postaci funkcjonału.

Kolejnym kluczowym rezultatem badań uzyskanym w ramach doktoratu było pokazanie, że główne cechy jakościowe potencjału korelacyjnego i gęstości korelacyjnej w funkcjonalach hybrydowych KS wynikają nie z półlokalnego funkcjonału korelacji, lecz z różnicy między półlokalną a dokładną wymianą Hartree-Focka. W oparciu o tę wiedzę i podejście adiabatic-connection opracowano nową procedurę optymalizacji globalnego funkcjonału hybrydowego. W rezultacie zdefiniowano jednoparametrowy

funkcjonał nazwany UMK26. Optymalną wartość parametru funkcyjonału UMK26 uzyskano poprzez minimalizację różnicy potencjałów jonizacji względem potencjałów jonizacji uzyskanych metodą EOM-CCSD dla zbioru wzorcowego złożonego z 16 układów. W porównaniu z konwencjonalnymi funkcyjonałami hybrydowymi KS, UMK26 poprawia jakość potencjału korelacyjnego, gęstości skorelowanej, potencjałów HOMO i potencjałów walencyjnych dla 401 wartości referencyjnych i 63 układów, oraz jakości energii wzbudzeń, osiągając poziom funkcyjonałów hybrydowych typu range-separated dedykowanych dla tego typu obliczeń. Przeprowadzono także krytyczną ocenę nowego funkcyjonału UMK26 analizując błąd samoodziaływania (na zbiorze testowym SIE4x4) i krzywych dysocjacji cząstek. Tu także zaobserwowano jednoznaczną poprawę jakości otrzymanych wyników. Pomimo, że w testach termochemicznych, nowy funkcjonał UMK26 nie zapewnia jednorodnej poprawy jakości, jego prosta, fizycznie transparentna konstrukcja jest podstawą efektywnej procedury do projektowania funkcyjonałów wymiennie-korelacyjnych, zarówno hybrydowych, typu range-separated jak i ich wariantów opartych o techniki uczenia maszynowego.

Rozprawa doktorska opiera się na dwóch publikacjach:

1. **Vignesh Balaji Kumar**, Szymon Śmiga, Ireneusz Grabowski; A Critical Evaluation of the Hybrid KS DFT Functionals Based on the KS Exchange-Correlation Potentials. *J. Phys. Chem. Lett.* 10 October 2024; 15 (40): 10219–10229.
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Dedication

Dedicated to my Father	N.Kumar
Mother	K.Amutha
Wife	V.Rakshana
Daughter	V.Sreshvika

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Structure of the Thesis

The Thesis is structured into four chapters, outlined below.

1. Introduction.

The chapter begins with an overview of the development of methods for solving the many-electron problem in quantum chemistry applications, presents the various approaches developed to date, and elaborates on the scientific quantities and concepts that form the core ingredients of the research presented in the thesis. The chapter presents a detailed state of the art of available exchange-correlation (XC) approximations. We present tools and techniques for computing XC potentials using non-local methods such as Hybrid DFT and wavefunction theories. We also elaborate on our efforts and strategies in overcoming challenges in inverse Kohn-Sham schemes.

2. Critical Evaluation of Hybrid XC Approximations.

This chapter elaborates on the primary findings of the state of the art of hybrid XC functionals in Density Functional Theory (DFT). We focus on the physical quantities such as the XC potential, electron densities, ionization potential, and total energy in our evaluation. The objective is to assess the abilities of XC approximations for diverse quantities against accurate reference data from the wavefunction theory. Since energy and energy-derived benchmarks have dominated XC functional development and testing, this diverse assessment is critical for identifying shortcomings and designing techniques to overcome various challenges in DFT.

3. UMK26: A New Global Hybrid XC Functional.

Based on our evaluation of the hybrid DFT functionals and our observation that the contribution to the correlation potential arises primarily from the exchange-only approximation, we develop the UMK26 global hybrid DFT functional. UMK26 is rooted in the Adiabatic Connection formalism; it is constructed via optimization with respect to the exchange differences between the Hartree-Fock and semilocal exchange. UMK26 addresses diverse properties such as the correlation potential, highest occupied molecular orbital (HOMO) energy, valence ionization potentials, electron self-interaction, and charge-transfer excitations.

4. Summary of Most Important Findings of the Thesis and Future Directions.

Finally, we summarize the scientific findings and future implications in the conclusion chapter. A list of other scientific publications outside the scope of the doctoral thesis and a list of conferences attended are presented.

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Chapter 1

Introduction

1.1 The Quantum Theory for Many-Electron Systems

1.1.1 Overview of quantum many-body theories

The discovery of the quantized energy exchange in black-body radiation by Max Planck in 1900, the observation of the photoelectric effect by Heinrich Hertz in 1887, and the unexplained discrete line spectra of hydrogen gas marked crucial scientific observations that set the stage for scientists to recognize the limits of classical physics at the atomic scale in favor of the quantum theory. Max Planck received the 1918 Nobel Prize for discovering the energy quanta, while the remarkable work of Albert Einstein in 1905 [2], which theoretically explained the photoelectric effect, earned him the 1921 Nobel Prize for Physics, and by the early 1930s, quantum theory had already matured and become an established part of modern science. These developments provided precise explanations for many enigmatic phenomena that emerged from the very beginning of the 20th century, culminating in the great scientific theory of quantum mechanics. Exactly a hundred years ago, in 1926, Erwin Schrödinger published a series of papers [3] that introduced the famous Schrödinger equation as an eigenvalue problem and accurately calculated the energy levels of the hydrogen atom. The Schrödinger equation, defined by equation 1.1 is a time-independent, linear, homogeneous partial differential equation.

$$\hat{H}\psi(\mathbf{x}_1, \mathbf{x}_2.. \mathbf{x}_N) = E\psi(\mathbf{x}_1, \mathbf{x}_2.. \mathbf{x}_N) \quad (1.1)$$

where $\psi(\mathbf{x}_1, \mathbf{x}_2.. \mathbf{x}_N)$ is the many-electron wavefunction, which is a function of spatial and spin coordinates $\mathbf{x}_i$. The Hamiltonian $\hat{H}$ within the Born-Oppenheimer

approximation[4] is defined as:

$$\hat{H} = \underbrace{-\frac{\hbar^2}{2m} \sum_{i=1}^N \nabla_i^2}_{\text{Electron Kinetic Energy}} - \underbrace{\frac{e^2}{4\pi\epsilon_0} \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{|\mathbf{r}_i - \mathbf{R}_A|}}_{\text{Electron-Nucleus Attraction}} + \underbrace{\frac{e^2}{4\pi\epsilon_0} \sum_{i=1}^{N-1} \sum_{j>i}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}}_{\text{Electron-Electron Repulsion}} + \underbrace{\frac{e^2}{4\pi\epsilon_0} \sum_{A=1}^{M-1} \sum_{B>A}^M \frac{Z_A Z_B}{|\mathbf{R}_A - \mathbf{R}_B|}}_{\text{Nuclear-Nuclear Repulsion}} \quad (1.2)$$

where $\mathbf{r}_i$ denotes the coordinate of the i^{th} electron, $\mathbf{R}_A$ corresponds to the coordinate of the A^{th} nucleus, e is the electronic charge, ϵ_0 is the permittivity of free space and Z represents the atomic number of the specific nucleus. Solving the Schrödinger equation, one can accurately calculate the states of any chemical system described by it, and this is of paramount importance for materials science research. The main challenge in solving the Schrödinger equation for a many-electron system is the exponential increase in computational cost with system size. Analytical solutions to the Schrödinger equation exist only for very simple cases, such as the hydrogen atom, and numerical approaches are the only practical option for real chemical systems. One needs four coordinates for each electron (3 for spatial and one for spin dimensions), and these coordinates are coupled with the coordinates of every other electron owing to the electron-electron Coulomb repulsion. This presents a computationally forbidden numerical problem which was quoted by P.A.M Dirac [5] as “The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble”, in his famous article entitled “Quantum mechanics of many-electron systems” in 1929. “It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex atomic systems without too much computation”, followed Dirac in the same article, acknowledging the vital role that approximate methods would play for the future of quantum theory to solve realistic many-electron systems.

The Thomas-Fermi model [6, 7], developed in 1927, was the first approximate formulation for constructing a computationally tractable equation to solve chemical systems based on the electron density, but was only applicable to the high-density limit, where electron homogeneity holds. The model assumes electrons as a perfect gas satisfying Fermi statistics in their lowest energy level of phase space, and later P.A.M Dirac proposed the inclusion of exchange effects in 1930[8].

The era of approximations within the Schrödinger equation began with Douglas Hartree, who proposed the Hartree method [9] in 1928, which replaced the Coulomb interaction with a common central potential field; it was also widely known as the

self-consistent field method, but it still lacked accounting for the proper distribution of electrons as warranted by quantum mechanical laws such as Pauli’s exclusion principle. A partial satisfaction of addressing it in the Hartree method was made by incorporating the exchange effects as developed by V. Fock[10] by Douglas Hartree and his father William Hartree in 1935 [11]. The still missing part is termed correlation, and various post-Hartree-Fock methods have been developed to compute it effectively. The configuration interaction approach, which relies on a linear combination of Slater determinants, explicitly introduces the electron correlation by construction. Though highly accurate, it requires more Slater determinants as the number of electrons increases. In fact, the computational bottleneck in solving the full configuration interaction and numerically solving the many-body Schrödinger equation is the same; hence, practical applications often involve a limited number of Slater determinant configurations. In 1934, C. Møller and M.S. Plesset proposed the Møller-Plesset theory[12, 13], based on the Rayleigh–Schrödinger perturbation theory, to account for the missing correlation effects of the Hartree-Fock theory. The method relies on a perturbation term; when expanded in a Taylor series, one obtains corrections to the Hartree-Fock wavefunction and energy. Here, too, the practicality involves truncating the expansion to certain orders for computational feasibility. The coupled cluster method[14, 15, 16] emerged in the latter half of the 20th century and relied on an exponential operator acting on the Hartree-Fock wavefunction to introduce missing correlation. It is also often truncated for practical real-world applications, and the Coupled Cluster with Singles, Doubles, and Perturbative Triplets (CCSD(T)) [17] method is considered the gold standard for quantum-chemical calculations. Reference [18] provides a comprehensive overview of the coupled-cluster theory.

A plethora of methods have been developed, including the Complete Active Space Self Consistent Field (CASSCF) [19], Complete Active Space Second Order Perturbation Theory (CASPT2)[20], Density Matrix Renormalization Group (DMRG)[21], and many others are still being developed. While most of these developments were wavefunction-based, Walter Kohn at the University of California, San Diego, California, was more fascinated by the Thomas-Fermi model and its computational simplicity. The idea of anchoring on density, which required only three coordinates rather than the electronic wavefunction, seemed computationally promising. In 1963, during his sabbatical at the École Normale Supérieure, Walter Kohn, along with his colleague, Pierre Hohenberg, provided a mathematical proof demonstrating the existence of a universal functional of electron density, such that the energy functional has a minimum corresponding to the true ground state density of the system [22]. This was a pioneering step that proved the equivalence between electron density and the electronic wavefunction in computational chemistry. In 1965,

Walter Kohn, along with L. Sham, formulated the Kohn-Sham equation, building on these previous findings [23]. This formally gave rise to the most widely used electron-structure method today, Density Functional Theory (DFT). Similar to the Hartree-Fock method, DFT is a self-consistent procedure with a single Slater determinant, and the exchange and correlation are accounted for by the Exchange-correlation (XC) term in the Kohn-Sham Hamiltonian.

Density functional theory is not an approximation in principle; in fact, the Local Density Approximation(LDA)[24] is an exact method for the homogeneous electron gas. The exact form of the exchange-correlation energy functional, in the KS formalism, is unknown; hence, it must be approximated for real chemical systems. Density functional theory is very successful across a wide range of computational simulations, from solid-state physics to surface science. DFT has made a pioneering contribution in tackling many chemical challenges. Many software packages have been developed over the past several decades and are widely employed in material science simulations worldwide. Similar to the Hartree-Fock method, many post-DFT methods have also been developed for advanced simulations, such as Time-Dependent Density Functional Theory (TDDFT) [25] and G_0W_0 [26], which are widely used to compute excitation properties. The next section elaborates on the Density Functional Theory.

1.1.2 Kohn-Sham Density Functional Theory

The Kohn-Sham (KS) Density Functional Theory is based on two theorems derived from the Hohenberg-Kohn paper in 1964 [22]. The First Hohenberg-Kohn theorem states that “*The ground-state energy from Schrödinger’s equation is a unique functional of the electron density*” [27].

While the direct relation between the many-body wavefunction and the total electron density is known from the very beginning of quantum theory via the Max Born’s interpretation of probability density in the equation 1.3, the first theorem of Hohenberg-Kohn, can be considered a profound and mathematically rigorous law that proves the importance of the ground-state density and provides equal status to the ground state electron density with the ground state wavefunction(Eq. 1.4). This enables computational chemists to circumvent the high-dimensional wavefunction and compute ground-state properties using a three-dimensional density.

$$\rho(\mathbf{r}) = N \int |\Psi(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N)|^2 d\mathbf{r}_2 \dots d\mathbf{r}_N. \quad (1.3)$$

$$\rho_{\text{gs}}(\mathbf{r}) \rightleftharpoons E_{\text{gs}} \rightleftharpoons \Psi_{\text{gs}} \quad (1.4)$$

Hereafter, we stick only to the spatial coordinate $\mathbf{r}$. $\rho(\mathbf{r})$ is the total electron density and $\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$ is the many body wavefunction. The second Hohenberg-Kohn theorem is stated as “*The electron density that minimizes the energy of the overall functional is the true electron density corresponding to the full solution of the Schrödinger equation*”[27].

The second Hohenberg-Kohn theorem is the main reason behind the self-consistent procedure in DFT. Today, all DFT calculations begin with an initial guess for the electron density, and molecular orbital coefficients are optimized until the electron density converges to its true ground-state value.

The Kohn-Sham equation is defined as

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V_{\text{ext}}(\mathbf{r}) + V_H(\mathbf{r}) + V_{\text{XC}}(\mathbf{r}) \right] \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r}). \quad (1.5)$$

where ε_i is the Kohn-Sham orbital eigenvalue and $\psi_i(\mathbf{r})$ is the single particle orbital. The first term of Eq. 1.5 is the non-interacting kinetic energy operator. Here, $V_{\text{ext}}(\mathbf{r})$ is the external potential arising from the interaction between the electron and the nucleus. The classical Coulomb repulsion $V_H(\mathbf{r})$ between the electron and the total electron density is defined as

$$V_H(\mathbf{r}) = \frac{e^2}{4\pi\varepsilon_0} \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3r' \quad (1.6)$$

The remaining potential arising from the actual electron-electron interaction and the interacting kinetic energy, owing to the fermionic nature of electrons and the actual quantum mechanical principles it has to obey, is modeled by the exchange-correlation(XC) term V_{XC} . In principle, the XC potential is mathematically defined as the functional derivative of the exchange-correlation energy functional with respect to the electron density. The V_{XC} term is defined by Equation 1.7 below.

$$V_{\text{XC}}(\mathbf{r}) = \frac{\delta E_{\text{XC}}[\rho(\mathbf{r})]}{\delta \rho(\mathbf{r})}. \quad (1.7)$$

1.1.3 Exchange-Correlation Functional Approximations in Density Functional Theory

The Kohn-Sham DFT is a complete quantum-mechanical theory that has been rigorously proven, but its inherent limitation lies in the lack of knowledge of the exact form of the universal functional of the electron density, the exchange-correlation energy term E_{XC} . Over the decades, many approximations have been introduced, which are broadly classified by the types of ingredients used. They are the Lo-

cal Density Approximation (LDA), Generalized Gradient Approximation (GGA), Meta-GGA, Hybrid, and Double-Hybrid XC approximations. The class of DFAs is arranged in a Jacob’s ladder (see Figure 1.1), with increasing accuracy and computational cost on the rungs [28]. The exchange-correlation energy (E_{xc}) functional is constructed as the sum of different exchange (E_x) and correlation energy (E_c) functionals developed to date as:

$$E_{xc} = E_x + E_c \quad (1.8)$$

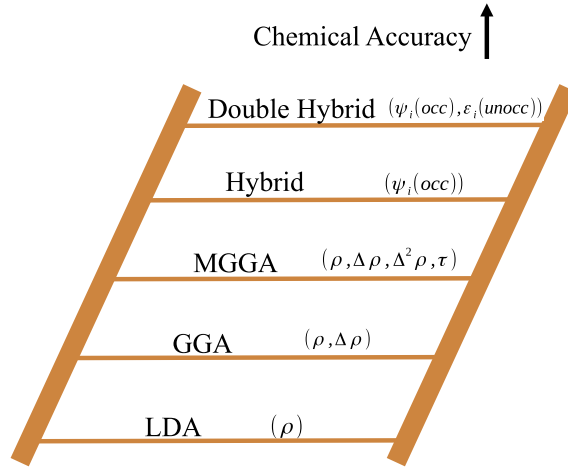


Figure 1.1: The Jacob’s ladder of density functional approximations

1.1.4 Local Density Approximation

The Local Density Approximation[23] is based on the homogeneous electron gas (HEG), which depends locally on the electron density and approximates the uniform and high-density limit of quantum-chemical systems. The XC functional form E_{xc}^{LDA} at the LDA level is defined by equation 1.9.

$$E_{xc}^{LDA} = \int d^3r \rho(\mathbf{r}) e_{xc}^{LDA}(\rho_{\uparrow}(\mathbf{r}), \rho_{\downarrow}(\mathbf{r})) \quad (1.9)$$

where e_{xc}^{LDA} is the exchange-correlation energy per electron, which is a function of up ($\rho_{\uparrow}(\mathbf{r})$) and down ($\rho_{\downarrow}(\mathbf{r})$) spin densities and is widely obtained from the HEG model. The most common form of LDA exchange is given by equation 1.10, derived by P.A.M. Dirac [8] in 1930.

$$e_x^{LDA}(\rho_{\uparrow}, \rho_{\downarrow}) = -C_x \frac{\rho_{\uparrow}^{4/3} + \rho_{\downarrow}^{4/3}}{\rho} \quad (1.10)$$

where $C_x = \frac{3}{2} \left(\frac{3}{4\pi} \right)^{1/3}$. Similarly, various approximations to $e_c^{LDA}(\rho_{\uparrow}, \rho_{\downarrow})$ exist, based

on fitting to correlation data from methods such as Monte Carlo and the Random Phase Approximation. One can readily note that equation 1.9 includes the self-interaction error by means of the functional definition itself. Though LDA sits at the bottom of the Jacob’s ladder, it is an integral part of all other rungs of the ladder, as all other types of approximation are built on top of the LDA. Although in its early stages, the LDA was employed to model solid-state systems, it lacked the capacity to treat atomic and molecular systems, which possess a discrete electronic structure that differs from that of the simple HEG model. LDA functionals such as VWN[29] are widely used, especially in the construction of Hybrid functionals.

1.1.5 Generalized Gradient Approximation

The need to develop XC functional beyond the uniform electron gas model was apparent[30, 31, 32], and the incorporation of density gradient on top of the LDA seemed the right direction[33]. As a first step toward improving the local density approximation, the Generalized Gradient Approximation (GGA) was developed to incorporate density-gradient information into the XC energy functional.

$$E_{xc}^{GGA} = \int d^3r \rho(\mathbf{r}) \times e_{xc}^{GGA}(\rho_{\uparrow}(\mathbf{r}), \rho_{\downarrow}(\mathbf{r}), \nabla\rho_{\uparrow}(\mathbf{r}), \nabla\rho_{\downarrow}(\mathbf{r})) \quad (1.11)$$

where e_{xc}^{GGA} is the GGA exchange-correlation energy per electron, which is a function of the up($\rho_{\uparrow}(\mathbf{r})$) and down($\rho_{\downarrow}(\mathbf{r})$) spin densities as well as their gradients($\nabla\rho_{\uparrow}(\mathbf{r}), \nabla\rho_{\downarrow}(\mathbf{r})$).

$$E_x^{GGA} = \int d^3r \rho(\mathbf{r}) \epsilon_x^{LDA}(\rho(\mathbf{r})) F_x(\mathbf{r}) \quad (1.12)$$

$F_x(\mathbf{r})$ is the enhancement factor which contains the gradient information. The PBE version of the GGA-type approximation proposed by John P. Perdew, Kieron Burke, and Matthias Ernzerhof, which improved and simplified the earlier PW91 GGA functional [34], is widely used. It relied on four conditions for exchange and three conditions for the correlation functional expression. The exchange conditions were

- The functional must obey the uniform density scaling and should correspond to LDA for HEG.
- The functional obeys the spin scaling relationship $E_X[\rho_{\uparrow}, \rho_{\downarrow}] = (E_X[2\rho_{\uparrow}] + E_X[2\rho_{\downarrow}])/2$.
- For small density variations, the linear response of density should correspond to that of LDA.
- It satisfies the Lieb-Oxford bound $E_X[\rho_{\uparrow}, \rho_{\downarrow}] \geq E_{XC}[\rho_{\uparrow}, \rho_{\downarrow}] \geq -1.679e^2 \int d^3r \rho^{4/3}$.

Based on these conditions, the PBE enhancement factor($F_X(s)$) is defined as:

$$F_X(s) = 1 + \kappa - \kappa/(1 + \mu s^2/\kappa) \quad (1.13)$$

where s is the reduced density gradient, κ and μ take constant values. The PBE correlation energy functional relies on the gradient-correction term H for the LDA correlation energy, which is based on the three conditions described below. PBE[35], B88[36], and PW91[34] are well-known GGA-type XC functionals.

- It obeys the second-order gradient expansion in the slowly varying density limit.
- The correlation energy vanishes in the rapidly varying density limit.
- The correlation energy must scale to a constant under uniform scaling in the high-density limit.

The development of the GGA-type XC approximation has enabled many reliable chemical predictions for molecular systems and greatly increased the popularity of DFT. Despite the gradient information, there is no mechanism in the LDA and GGA type approximations to overcome the self-interaction error[37], limiting their practical applications [38].

1.1.6 Meta-Generalized Gradient Approximation

Motivated by the superior performance achieved with gradient corrections, other functionals emerged to incorporate additional information, such as the Laplacian of the density, $\nabla^2\rho$, and the kinetic energy density, τ .

$$E_{xc}^{MGGA} = \int d^3r \rho(\mathbf{r}) \times e_{xc}^{MGGA}(\rho(\mathbf{r}), \nabla\rho(\mathbf{r}), \nabla^2\rho(\mathbf{r}), \tau(\mathbf{r})) \quad (1.14)$$

e_{xc}^{MGGA} is the Meta-GGA exchange-correlation energy per electron. Including these terms can help reduce self-interaction error. They are referred to as the Meta Generalized Gradient Approximation. MGGA-type functionals, such as TPSS [39] and SCAN [40], are well-known and widely used, and they heavily rely on obeying the exact constraints of XC functionals. The SCAN was developed to obey all 17 exact constraints. Though many studies [41] reported greater accuracy than GGA, their ability to describe magnetism remained at the same level as that of the GGA [42] type functionals.

1.1.7 Hybrid and Double Hybrid Approximation

Hartree-Fock theory is self-interaction-free. The exchange operator in the Hartree-Fock Hamiltonian exactly cancels the electron self-interaction in the Coulomb term. Being free of self-interaction error (SIE) is vital for describing one-electron systems, charge transfer, and the correct asymptotic behavior of the potential, etc. Unlike the HF theory, DFT has no systematic mechanism to eliminate the SIE. Nevertheless, the local nature of local and semi-local density functional approximations is efficient at describing dynamical correlation effects in many-electron systems. Mixing Hartree-Fock theory and DFT in a hybrid approach was envisaged to enhance accuracy [43, 44]. Hybrid DFT mixes a fraction of Hartree-Fock exchange with the DFT exchange, and the general construction of a hybrid functional is defined as:

$$E_{xc}^{\text{hybrid}} = aE_x^{\text{HF}} + (1 - a)E_x^{\text{DFT}} + E_c^{\text{DFT}} \quad (1.15)$$

The parameter a scales the fraction of Hartree-Fock and DFT exchanges. Eq. 1.15 includes a single exchange and correlation functional, whereas in reality multiple exchange and correlation functionals are incorporated in designing hybrid XC functionals. Many hybrid density functionals have been developed by mixing varying proportions of different exchange-correlation functionals with Hartree-Fock exchange and have become the most widely used and conventional functionals in day-to-day DFT simulations. The B3LYP hybrid functional is one of the most widely used approximations [45]. One main drawback of these global hybrid constructions with minimized HF component is that they miss the proper $-\frac{1}{r}$ shape of the potential since the fraction of HF coefficient scales the asymptotics of the potential as $-\frac{a}{r}$ ($a=0.2$ for B3LYP). This improper shape of the asymptotics leads to an inadequate description of Rydberg and charge-transfer excitations. To overcome this, range-separated hybrid functionals were developed that split the Coulomb term into long-range and short-range components [46], a widely recognized approach known as the Coulomb-Attenuated Method (CAM) [47].

$$\frac{1}{r_{12}} = \frac{1 - [\alpha + \beta \cdot \text{erf}(\mu r_{12})]}{r_{12}} + \frac{\alpha + \beta \cdot \text{erf}(\mu r_{12})}{r_{12}} \quad (1.16)$$

The first term of Eq. 1.16 is associated with the short-range component, and the latter part corresponds to the long-range component. μ is the range-separation parameter. α and β determine the ratio of exact exchange at short and long range. Based on this, the hybrid functionals are classified into range-separated hybrid and global hybrids. The superior performance of range-separated hybrids over global hybrids in many scenarios is evident from various studies [48, 49]. The Generalized

Kohn-Sham (GKS) scheme [50] scales as $\mathcal{O}(N^4)$, where N refers to the size of the system, an order higher compared to semi-local DFT (which scales as $\mathcal{O}(N^3)$) owing to the exchange operator in the GKS scheme.

The latest and topmost rung of the Jacob’s ladder is occupied by the Double-Hybrid (DH) functionals first developed by Grimme [51] admixing a fraction of correlation energy from the second order perturbation theory computed from KS orbitals, which makes DH calculations scale as $\mathcal{O}(N^5)$. The general construction of DH functionals is as follows:

$$E_{xc}^{\text{DH}} = \underbrace{a_x E_x^{\text{HF}} + (1 - a_x) E_x^{\text{DFT}}}_{\text{Hybrid Exchange}} + \underbrace{(1 - a_c) E_c^{\text{DFT}} + a_c E_c^{\text{MP2}}}_{\text{Hybrid Correlation}} \quad (1.17)$$

The superior accuracy of double hybrids across various scenarios has been rigorously established [52, 53]. Further augmentation in the form of Dispersion correction and spin-component scaling has improved double hybrids, and they are widely recognized as DSD-DFT (Dispersion Corrected and Spin component scaled Double Hybrid Density Functional Theory) [54, 55].

1.2 Exchange-Correlation Potential(v_{xc}) in Density Functional Theory

1.2.1 Direct evaluation of v_{xc} in KS-DFT

Computing the XC potential corresponding to local and semi-local functionals that explicitly depend on the electron density is straightforward using Eq. 1.7. However, the limitations of local and semi-local functionals in accurately predicting the exchange-correlation potential are well known[56, 57]. The Figure 1.2 depicts the XC potential computed via Eq. 1.7 for the Ne atom. The LDA potential clearly lacks a proper description of the shell structure in the core-valence region and exhibits incorrect asymptotic behavior relative to the CCSD(T) reference potential. Improving the description of XC potential is vital, and, in fact, a correct XC potential is a critical attribute of accurate density functional approximations. Many schemes have been developed to compute the XC potential via various routes, each with its own advantages and challenges. The subsequent sections elaborate on various existing methods for computing XC potentials. We also document the various challenges we faced with the methods we employed, and the practical procedures for employing them effectively.

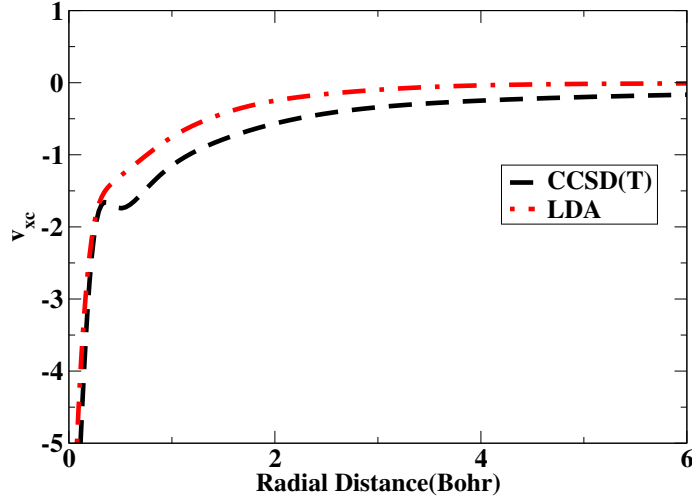


Figure 1.2: The LDA exchange-correlation potential computed using Eq. 1.7 for Ne. The reference CCSD(T) XC potential is computed using the Wu-Yang inverse method outlined in the subsequent sections. The uncontracted augmented cc-pVTZ basis set is employed

1.2.2 The Optimized Effective Potential(OEP) Method

In the case of orbital-dependent and implicit density-dependent energy functionals, Eq. 1.7 cannot be employed directly. The OEP method [58, 59, 60, 61, 62, 63, 64, 1] can be effectively applied in such scenarios because it computes the local multiplicative potential for orbitals that minimize the system’s total energy. The XC potential from the OEP method [58] is defined as :

$$V_{xc}^{\text{OEP}}(\mathbf{r}) = \sum_p \int \left\{ \frac{\delta E_{xc}^{\text{OEP}}[\{\phi_q\}]}{\delta \phi_p(\mathbf{r}')} \frac{1}{\phi_p^*(\mathbf{r}')} + \text{c.c.} \right\} X^{-1}(\mathbf{r}', \mathbf{r}) d\mathbf{r}' \quad (1.18)$$

$$X(\mathbf{r}, \mathbf{r}') = \frac{\delta \rho(\mathbf{r})}{\delta v(\mathbf{r}')} = \sum_i^N \sum_a \frac{\phi_i^*(\mathbf{r}) \phi_a(\mathbf{r}) \phi_a^*(\mathbf{r}') \phi_i(\mathbf{r}')}{\epsilon_i - \epsilon_a} + \text{c.c.} \quad (1.19)$$

where p corresponds to both occupied and virtual orbital indices. i and a correspond to occupied and virtual orbitals respectively, $v(\mathbf{r}')$ represent the effective Kohn-Sham potential, ϵ correspond to the Kohn-Sham eigenvalues and $X(\mathbf{r}, \mathbf{r}')$ is the static KS linear response function. More details on the OEP equations can be found in reference [58]. The presence of the inverse of $X(\mathbf{r}, \mathbf{r}')$ in Eq. 1.18, which is a first-kind Fredholm integral-type equation, presents computational challenges in finite Gaussian basis sets. Our work [65] outlines strategies for obtaining meaningful solutions in such scenarios, which require regularization procedures and a judicious choice of basis set.

1.2.3 The MRKS Method

The RKS method, introduced by Ryabinkin, Kohut, and Staroverov [66], is a scheme for computing the XC potential directly from the wavefunction. The RKS method relies on an exact condition, $\rho^{KS} = \rho^{WF}$, that the ideal Kohn-Sham electron density should match that of the wavefunction method for the same system. The RKS scheme begins with the construction of the total electronic energy as:

$$E = \sum_{ij} \gamma_{ij} \langle \psi_j | \hat{h} | \psi_i \rangle + \sum_{ikjl} \Gamma_{ikjl} \langle \psi_j \psi_l | r_{12}^{-1} | \psi_i \psi_k \rangle \quad (1.20)$$

$$\gamma_{ij} = \sum_{\sigma} \langle \Psi | \hat{a}_{j\sigma}^{\dagger} \hat{a}_{i\sigma} | \Psi \rangle \quad (1.21)$$

$$\Gamma_{ikjl} = \frac{1}{2} \sum_{\sigma\sigma'} \langle \Psi | \hat{a}_{j\sigma}^{\dagger} \hat{a}_{l\sigma'}^{\dagger} \hat{a}_{k\sigma'} \hat{a}_{i\sigma} | \Psi \rangle \quad (1.22)$$

where $\hat{h}$ is the one electron Hamiltonian and σ is the spin index. γ_{ij} and Γ_{ikjl} correspond to the matrix elements of the one-electron and two-electron Reduced Density Matrix (RDM), respectively. The Euler-Lagrange form of Eq. 1.20 is:

$$\begin{aligned} \hat{h}(\mathbf{r}) \sum_{ij} \gamma_{ij} \psi_i(\mathbf{r}) \psi_j^*(\mathbf{r}') + 2 \int \frac{\sum_{ikjl} \Gamma_{ikjl} \psi_i(\mathbf{r}) \psi_k(\mathbf{r}_2) \psi_j^*(\mathbf{r}') \psi_l^*(\mathbf{r}_2')}{|\mathbf{r} - \mathbf{r}_2|} d\mathbf{r}_2 \\ = \sum_{ij} \lambda_{ij} \psi_i(\mathbf{r}) \psi_j^*(\mathbf{r}') \end{aligned} \quad (1.23)$$

Considering only the $\mathbf{r} = \mathbf{r}'$ part and dividing by the electron density $\rho^{WF}(\mathbf{r})$ we obtain

$$\frac{\tau_L^{WF}(\mathbf{r})}{\rho^{WF}(\mathbf{r})} + v_{\text{ext}}(\mathbf{r}) + \frac{2}{\rho^{WF}(\mathbf{r})} \int \frac{P(\mathbf{r}, \mathbf{r}_2)}{|\mathbf{r} - \mathbf{r}_2|} d\mathbf{r}_2 = \bar{\epsilon}^{WF}(\mathbf{r}) \quad (1.24)$$

where $\tau_L^{WF}(\mathbf{r}) = -\frac{1}{2} \left[\nabla^2 \sum_{ij} \gamma_{ij} \psi_i(\mathbf{r}) \psi_j^*(\mathbf{r}') \right]_{\mathbf{r}'=\mathbf{r}}$ and the pair function $P(\mathbf{r}, \mathbf{r}_2)$ is $P(\mathbf{r}, \mathbf{r}_2) = \Gamma(\mathbf{r}, \mathbf{r}_2; \mathbf{r}, \mathbf{r}_2)$. The pair function can also be defined as:

$$P(\mathbf{r}, \mathbf{r}_2) = \frac{1}{2} \rho^{WF}(\mathbf{r}) [\rho^{WF}(\mathbf{r}_2) + \rho_{XC}^{WF}(\mathbf{r}, \mathbf{r}_2)], \quad (1.25)$$

Substituting Eq. 1.25 in 1.24, we get

$$\frac{\tau_L^{\text{WF}}(\mathbf{r})}{\rho^{\text{WF}}(\mathbf{r})} + v_{\text{ext}}(\mathbf{r}) + v_{\text{H}}^{\text{WF}}(\mathbf{r}) + v_{\text{S}}^{\text{WF}}(\mathbf{r}) = \bar{\epsilon}^{\text{WF}}(\mathbf{r}) \quad (1.26)$$

where v_{S}^{WF} is the Slater potential and we have the Kohn-Sham equations as:

$$\left[-\frac{1}{2}\nabla^2 + v_{\text{ext}}(\mathbf{r}) + v_{\text{H}}^{\text{KS}}(\mathbf{r}) + v_{\text{XC}}(\mathbf{r}) \right] \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r}) \quad (1.27)$$

subtracting Eq. 1.26 from 1.27 and using $\tau_L = \tau - \nabla^2 \rho / 4$, we get

$$v_{\text{XC}}(\mathbf{r}) = v_{\text{S}}^{\text{WF}}(\mathbf{r}) + \bar{\epsilon}^{\text{KS}}(\mathbf{r}) - \bar{\epsilon}^{\text{WF}}(\mathbf{r}) + \frac{\tau^{\text{WF}}(\mathbf{r})}{\rho^{\text{WF}}(\mathbf{r})} - \frac{\tau^{\text{KS}}(\mathbf{r})}{\rho^{\text{KS}}(\mathbf{r})} \quad (1.28)$$

where $\tau^{\text{KS}}(\mathbf{r}) = \frac{1}{2} \sum_i n_i |\nabla \phi_i(\mathbf{r})|^2$ and $\tau^{\text{WF}}(\mathbf{r}) = \frac{1}{2} [\nabla_{\mathbf{r}'} \nabla_{\mathbf{r}} \gamma(\mathbf{r}, \mathbf{r}')]_{\mathbf{r}'=\mathbf{r}}$. $\bar{\epsilon}^{\text{KS}}$ and $\tau^{\text{KS}}(\mathbf{r})$ are the only unknown terms in Eq. 1.28 which can be obtained self-consistently.

On a small basis, imposing the condition $\rho^{\text{KS}} = \rho^{\text{WF}}$ is not appropriate, considering the large errors from the minimal basis representation. This reduced the quality of the XC potential computed using the RKS method in a small basis set. Hence, the MRKS(Modified RKS) method was introduced. The MRKS uses $\tau^{\text{KS}} = \tau_{\text{W}}^{\text{KS}} + \tau_{\text{P}}^{\text{KS}}$ and $\tau^{\text{WF}} = \tau_{\text{W}}^{\text{WF}} + \tau_{\text{P}}^{\text{WF}}$ in Eq. 1.28 where $\tau_{\text{W}}^{\text{KS}} = |\nabla \rho^{\text{KS}}|^2 / 8 \rho^{\text{KS}}$ and $\tau_{\text{W}}^{\text{WF}} = |\nabla \rho^{\text{WF}}|^2 / 8 \rho^{\text{WF}}$ are von Weizsäcker noninteracting kinetic-energy density. The term $\frac{\tau_{\text{W}}^{\text{WF}}}{\rho^{\text{WF}}} - \frac{\tau_{\text{W}}^{\text{KS}}}{\rho^{\text{KS}}}$ approaches zero even in small basis set limits enhancing convergence to accurate XC potential and the v_{xc} expression in the MRKS scheme is :

$$v_{\text{XC}} = v_{\text{s}}^{\text{WF}} + \bar{\epsilon}^{\text{KS}} - \bar{\epsilon}^{\text{WF}} + \frac{\tau_{\text{P}}^{\text{WF}}}{\rho^{\text{WF}}} - \frac{\tau_{\text{P}}^{\text{KS}}}{\rho^{\text{KS}}} \quad (1.29)$$

The MRKS scheme follows the steps below to compute the XC potential corresponding to the given wavefunction.

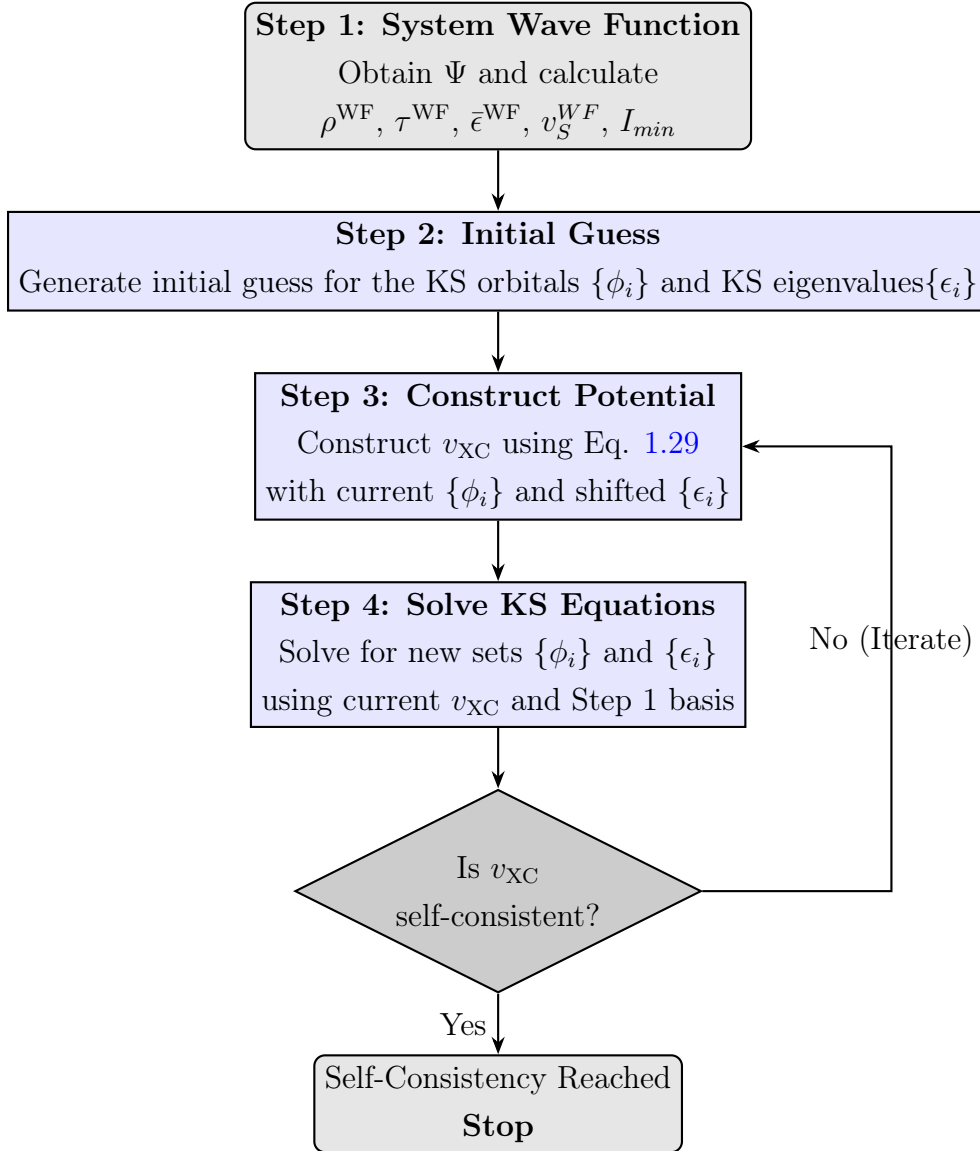


Figure 1.3: Flowchart of the MRKS scheme to compute the v_{XC} potential in a self-consistent cycle.

The MRKS method is not an inversion procedure in the sense of computing the XC potential corresponding to a target electron density. It relies on the wavefunction to compute the corresponding XC potential. This makes MRKS a rigorous approach for computing an accurate Kohn-Sham XC potential with wavefunction method accuracy. Nevertheless, MRKS also suffers from limitations in a finite Gaussian basis set [67]. Figure 1.4 compares the XC potential with and without diffuse basis functions. The presence of diffuse functions introduces spurious deviations in the asymptotic region. El-Samman and Staroverov observed that the average local ionization energy (ALIE)[67] directly entering the MRKS Eq. 1.29 is affected by the non-zero coefficients for low-lying molecular orbitals, which is mostly caused when diffuse functions are utilized. In such a scenario, the asymptotics, which are

highly dominated by the slowly varying HOMO orbital, include contributions from low-lying orbitals. As a result, the inclusion of these diffuse basis functions affects the quality of the XC potential in the MRKS method’s asymptotic regime. With a judicious choice of the basis set, the MRKS method stands as one of the most rigorous ways to obtain accurate XC potentials directly from the wavefunction.

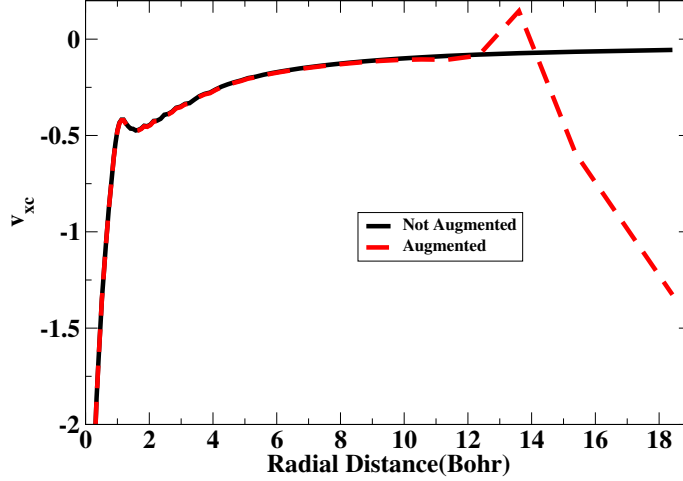


Figure 1.4: The XC potential computed using the MRKS method for the Be atom. The black curve is computed using an uncontracted cc-pVTZ basis, while the red dashed curve uses the same basis but with the inclusion of augmented basis functions.

1.2.4 The Wu-Yang Method

Qin Wu and Weitao Yang proposed an inverse procedure to compute the Kohn–Sham XC potential from target electron densities[68]. The method relies on Levy’s constrained search formalism[69].

$$T_s[\rho_{\text{in}}] = \min_{\Psi_{\text{det}} \rightarrow \rho_{\text{in}}} T[\Psi_{\text{det}}] \quad (1.30)$$

where $T[\Psi_{\text{det}}] = \langle \Psi_{\text{det}} | \hat{T}^N | \Psi_{\text{det}} \rangle = 2 \sum_i^{N/2} \langle \phi_i | \hat{T} | \phi_i \rangle$ is minimized under the constraint on the orbitals to compute the electron density as $\rho(\mathbf{r}) = 2 \sum_i^{N/2} |\phi_i(\mathbf{r})|^2$ equal to an input density $\rho_{\text{in}}(\mathbf{r})$

The kinetic energy term in Eq. 1.30 is modified with an added Lagrange multiplier function as:

$$W_s[\Psi_{\text{det}}, v(\mathbf{r})] = 2 \sum_i^{N/2} \langle \phi_i | \hat{T} | \phi_i \rangle + \int d\mathbf{r} v(\mathbf{r}) \{ \rho(\mathbf{r}) - \rho_{\text{in}}(\mathbf{r}) \} \quad (1.31)$$

The effective KS potential can be constructed as [70]:

$$v(\mathbf{r}) = v_{\text{ext}}(\mathbf{r}) + v_0(\mathbf{r}) + \sum_t b_t g_t(\mathbf{r}) \quad (1.32)$$

where $v_{\text{ext}}(\mathbf{r})$ is the external potential, $v_0(\mathbf{r})$ is the guide potential, such as Fermi-Amaldi, and the last term is the linear combination of basis functions with b_t as basis set expansion coefficients.

substituting Eq. 1.32 in 1.31, we obtain

$$\begin{aligned} W_s[\Psi_{\text{det}}, v(\mathbf{r})] = & 2 \sum_i^{N/2} \langle \phi_i | \hat{T} | \phi_i \rangle + \int d\mathbf{r} \{ v_{\text{ext}}(\mathbf{r}) \\ & + v_0(\mathbf{r}) \} \{ \rho(\mathbf{r}) - \rho_{\text{in}}(\mathbf{r}) \} + \int d\mathbf{r} \sum_t b_t g_t(\mathbf{r}) \{ \rho(\mathbf{r}) - \rho_{\text{in}}(\mathbf{r}) \} \end{aligned} \quad (1.33)$$

Where the motivation is to find the optimized basis coefficients b_t corresponding to the effective KS potential through the unconstrained maximization of the $W_s[\Psi_{\text{det}}, v(\mathbf{r})]$ with respect to b_t .

The Wu-Yang method requires representing both orbitals and the potential in a Gaussian basis set. It also suffers from oscillations in the core region due to basis-set imbalance(see Figure 1.5). We observed that using the same basis for both orbitals and the potential helps minimize the imbalance. Nevertheless, further regularization procedures are necessary.

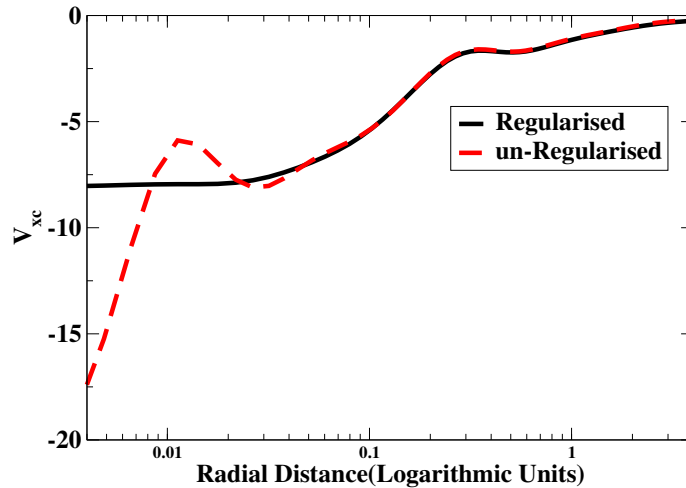


Figure 1.5: The XC potential for Ne in uncontracted augmented cc-pVTZ basis with (Black) and without (Red Dashed) regularization mechanism. The black curve uses the L-curve regularization parameter of 1×10^{-5} .

Regularization mechanisms, such as the Truncated Singular Value Decomposition,

are commonly used to alleviate numerical instabilities in finite-basis-set calculations [65]. Bulat, Heaton-Burgess, Cohen, and Yang proposed the L-Curve regularization procedure for the Wu–Yang inversion method[71].

$$\bar{W}_s[\Psi_{\text{det}}, v(\mathbf{r})] = W_s[\Psi_{\text{det}}, v(\mathbf{r})] - \lambda \|\nabla v_b(\mathbf{r})\|^2, \quad (1.34)$$

where λ is the regularization parameter, $\|\nabla v_b(\mathbf{r})\|^2 = \sum_t \sum_u b_t b_u \langle g_t(\mathbf{r}) | -\nabla^2 | g_u(\mathbf{r}) \rangle$. The optimal λ is chosen at the minimum slope on the log-log plot of the $W_s^0 - W_s^\lambda$ versus the $\|\nabla v_b(\mathbf{r})\|$ (L-Curve). With a proper choice of basis set and regularization, the Wu–Yang method provides a reliable XC potential(see Figure 1.6) from the target density computed at various levels of theory.

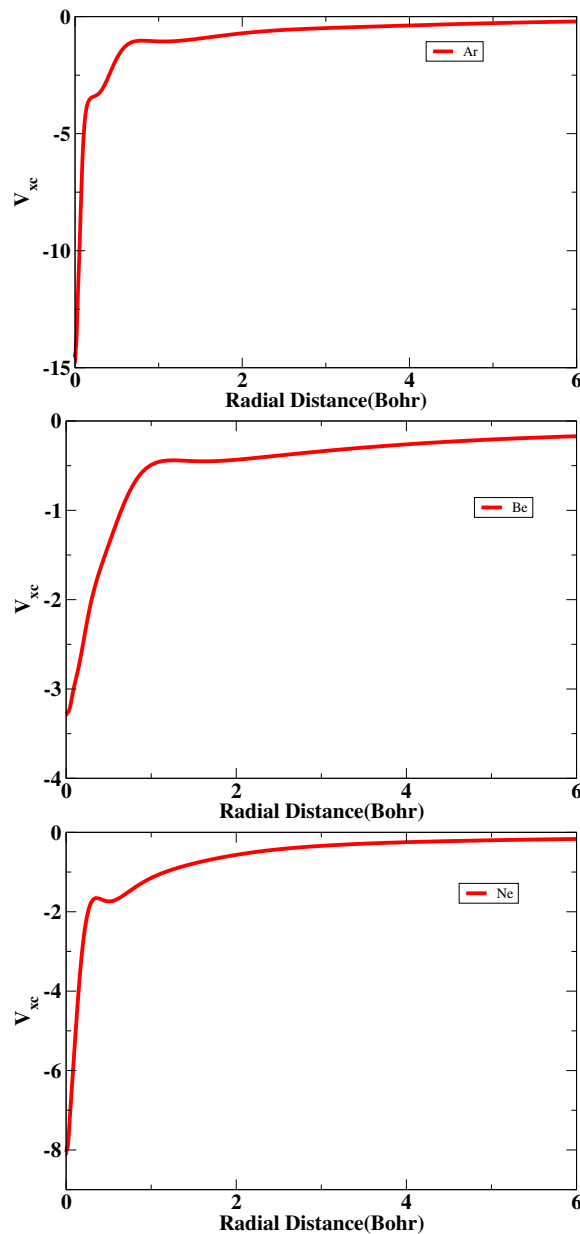


Figure 1.6: The XC potential computed for Ar, Be, and Ne atoms with CCSD(T) target electron densities using the Wu-Yang inversion procedure with a regularization parameter of 1×10^{-5} .

1.2.5 More Procedures to compute the KS XC potential

In addition to the methods described above, a few other methods for evaluating the XC potential exist that are not employed in this work and are listed below.

- Zhao, Morrison and Parr(ZMP) method [72].
- PDE-Constrained Optimization [73].
- Numerically Stable Inversion Approach [74].
- SlaterRKS [75].

1.2.6 Our Efforts in Obtaining Accurate XC Potentials

Obtaining the XC potential using the various methods discussed above, such as the MRKS and Wu-Yang methods, presents practical challenges [76]. Overcoming such challenges and facilitating the seamless computation of accurate XC potentials are active areas of research.

In the early stages of the doctoral program, we evaluated inverse procedures to develop techniques for tackling these challenges and computing robust XC potentials. In this section, we document our efforts and the challenges we encountered in this direction, which are described below to aid future work in this area.

- A Scheme to find an optimal regularization parameter for the Wu-Yang method in a straightforward way was conceptualized.

Regularization parameters are crucial for the optimum utility of the different Kohn-Sham inverse procedures. We designed an automatic scheme to obtain the regularization parameter for the Wu-Yang method, employing Eq. 1.35 and the MRKS reference potential.

$$\Delta\lambda = |v_{MRKS} - v_{wy}\{\lambda\}| \quad (1.35)$$

Python code using n2v (a quantum chemistry package to compute Kohn-Sham XC potentials from various methods) [77] was developed to perform the routine.

The main challenge in this scheme was the deviation from the asymptotic in the MRKS scheme, as elaborated in section 1.2.3. The deviation in the asymptotic behavior of the MRKS potential would contribute to the actual difference arising from oscillations in the core region, posing a practical challenge in

employing Eq. 1.35 in an automated scheme.

- **Basis Set Artifact Profiling.** In cases where the unphysical oscillation emanates purely from the basis set, basis set profiling [78] is a straightforward solution. In direct inversion procedures[78], the oscillations profile can be separated[78] as:

$$\Delta v_{\text{osc}}(\mathbf{r}) = v_{\text{computed}}(\mathbf{r}) - v_{\text{analytical}}(\mathbf{r}) \quad (1.36)$$

where v_{computed} is the XC potential computed from the Kohn-Sham orbitals and density using equations 2 and 3 in reference [78] and $v_{\text{analytical}}$ is the potential computed using analytical expression as $v_{\text{X}}^{\text{LDA}}(\mathbf{r}) = -\left(\frac{3}{\pi}\right)^{1/3} \rho^{1/3}(\mathbf{r})$. This oscillation profile can then be used to correct the unphysical oscillations in the XC potential in the same basis set.

We performed a detailed analysis on methods such as MRKS and Wu-Yang to check whether the oscillation profiles are basis-set-specific. In such a scenario, one can readily employ the oscillation profile computed from the low-level theory to obtain an artifact-free potential from the higher level of theory through a simple subtraction. In our analysis, we observed that even within the same basis set, the oscillation profiles differ across levels of theory. Hence, basis set profiling does not apply to procedures like the Wu-Yang or the MRKS.

- We chose the Wu-Yang procedure because it can readily be used to generate XC potentials from target wavefunction-theory densities, which is crucial for obtaining accurate reference data for our evaluations. Also, the Wu-Yang potentials matched the quality of those computed via the OEP procedure, attesting to the procedure’s robustness. From our evaluations, using the same basis set for both orbitals and potentials helped minimize oscillations. Hence, throughout the study, we employed the same basis set for both the orbital and potentials.

1.3 Correlation Potential and Correlated Density in Density Functional Theory

The correlation energy contributes only a small fraction to the exchange-correlation energy; however, it is paramount for the accurate prediction of quantum-chemical properties, and the same applies to the XC potential, too. The correlation potential and correlated density are crucial quantities that capture correlation effects missing in pure exchange-only theories, such as Hartree-Fock. In KS-DFT, they also serve as critical quantities to evaluate the efficiency of correlation functional approximations.

Unlike energy, which is a unique real number for a given system and method, these quantities are represented on a three-dimensional real-space grid. To evaluate the correlated density, ρ_c , from the total electron density computed via a post-Hartree-Fock method or DFT(ρ^{method}), one subtracts the total electron density from the electron density computed at the exchange-only level, such as Hartree-Fock.

$$\rho_c(r) = \rho^{\text{method}}(r) - \rho^{\text{HF}}(r) \quad (1.37)$$

For atomic systems, it is the standard procedure to consider(ρ_c) as the Difference Radial Distribution as:

$$\rho_c(r) = 4\pi r^2(\rho^{\text{method}}(r) - \rho^{\text{HF}}(r)) \quad (1.38)$$

Computing ρ_c is straightforward, as electron densities can be readily computed from wavefunctions or density matrices, whereas computing the correlation potential requires procedures discussed in previous sections. Given the total electron density from the post-Hartree-Fock method or DFT, the corresponding exchange correlation potential(v_{xc}^{method}) can be computed through inverting ρ^{method} . Similarly, the exchange potential(v_x) can be computed by inverting electron densities computed at the Hartree-Fock level. Then the correlation potential v_c can be computed as:

$$v_c(r) = v_{xc}^{\text{method}}(r)[\rho^{\text{method}}] - v_x^{\text{HF}}(r)[\rho^{\text{HF}}] \quad (1.39)$$

Throughout the thesis, we employ the Wu-Yang procedure to compute the potentials corresponding to the target electron densities. The correlation potentials computed from the Wu-Yang method inverting the target electron densities at the CCSD(T) level for different atomic systems are depicted in Figure 1.7. The computed potentials match the Quantum Monte Carlo reference[1], indicating the quality of the generated XC potentials. Similarly, the correlated densities(Eq. 1.38) are depicted in figure 1.8

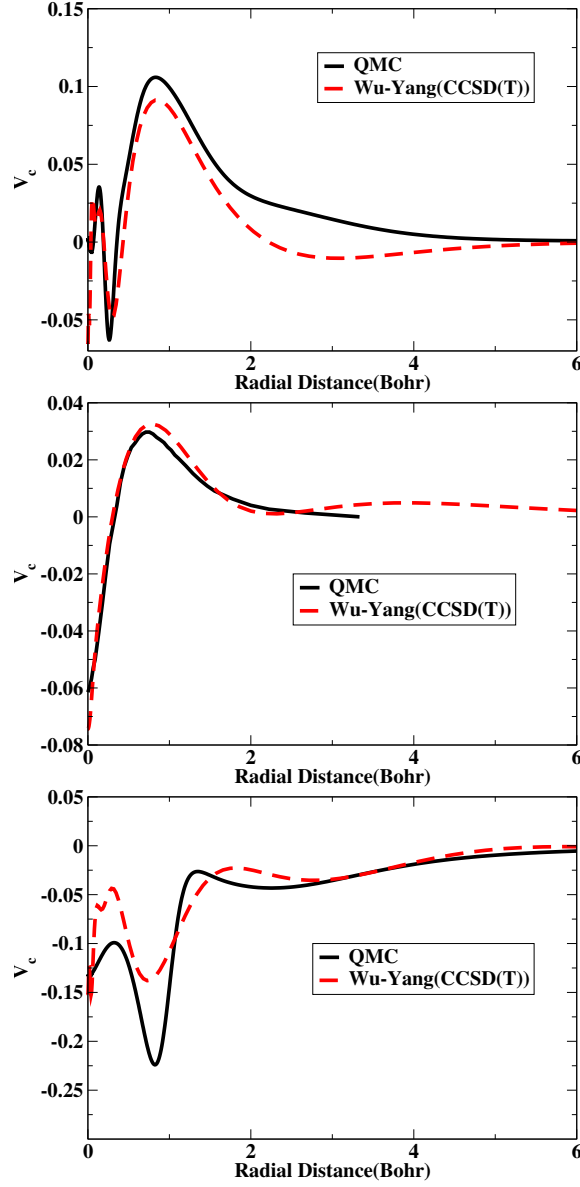


Figure 1.7: The correlation potential computed for Ne (Top), He (Middle), and Be (Bottom) atoms with CCSD(T) target electron densities using the Wu-Yang inversion procedure and utilizing Eq. 1.39. The Exact potentials computed at the level of Quantum Monte Carlo (QMC)[1] in the black curve are used as a reference

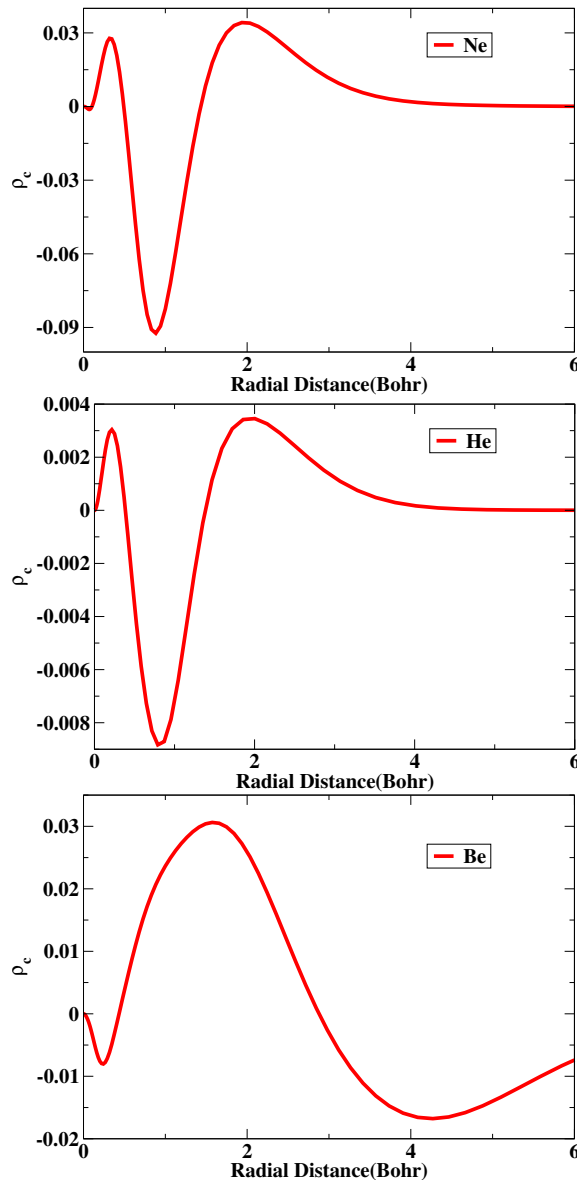


Figure 1.8: The correlated densities computed for Ne (top), He (middle), and Be (bottom) atoms from CCSD(T) and HF densities utilizing Eq. 1.38.

1.3.1 Correlated Orbital Theory

Our evaluation highly relies on HOMO and valence ionization potential obtained from the Kohn–Sham orbital energies, as well as the XC potentials. The Correlated Orbital Theory proposed by Bartlett[79] highlights the importance of ionization potentials (IPs) and electron affinities (EAs) in the one-particle picture. It validates the I-A exact conditions, that is, the accuracy of IPs and EAs in depicting electron removal and addition in chemical systems, as a necessary exact condition in the one particle eigenvalues problem. Many critical challenges in Density Functional Theory, such as the Self-Interaction Error, inefficient description of the integer-discontinuity upon addition or removal of electrons, long-range charge transfer, and

Rydberg states, arise from an inappropriate description of the XC potential. The XC potential is also crucial for describing orbital energies. The COT uses a single-reference coupled-cluster ansatz:

$$\Psi_{\text{CC}} = \exp(T)\Phi_0 \quad (1.40)$$

where Φ_0 is a single determinant. Then the ground state energy can be computed as:

$$E_{\text{CC}} = \langle \Phi_0 | \overline{H} | \Phi_0 \rangle \quad (1.41)$$

where $\overline{H} = e^{-T} \hat{H} e^T$ and $T = T_1 + T_2 + \dots$ is the coupled cluster operator.

The COT[79] proves the existence of one-particle frequency-independent non-hermitian operator $\hat{g}(1)$ such that:

$$\hat{g}(1)\overline{\varphi}_i(1) = \omega_i\overline{\varphi}_i(1), \quad \omega_i = I(i) \quad (1.42)$$

$$\hat{g}(1)\overline{\varphi}_a(1) = \omega^a\overline{\varphi}_a(1), \quad \omega^a = A(a) \quad (1.43)$$

where $I(i)$ and $A(a)$ denote the principal ionization potential and electron affinities respectively. Hence, the Correlated Orbital Theory recognizes the crucial role of orbital energies in validating single-determinant theories, such as Kohn-Sham DFT.

1.3.2 Ionization Potentials in KS-DFT

The Koopmans' theorem [80] defines the negative of the HOMO orbital energy of a closed shell system described by the Hartree-Fock theory as the ionization potential of the system. Correspondingly, Bartlett's IP theorem[81] establishes the same in the context of KS-DFT. Hence, the HOMO and valence orbital energies become indispensable tools for evaluating the quality and robustness of XC approximations. In fact, inspired by Bartlett's IP conditions, several global and range-separated hybrid functionals were developed by fitting to orbital and valence IPs, forming the well-known QTP family of functionals. There are two main routes to compute the ionization potential of the system in KS-DFT. The first one is directly from the Kohn-Sham orbital energies. The negative of the KS orbital energies can be directly interpreted as the system's ionization potential. The IPs computed in this manner are termed the vertical ionization potential. The second route is from the difference between the total energy of the neutral atom and its positively charged cation (ΔSCF method). Prof Bartlett, with his team, also pioneered benchmarks [82] for evaluating XC functionals based on IPs. These benchmarks are used to evaluate our new global hybrid functional proposed in the thesis. The quality of the

IPs is vital to Time-Dependent Density Functional Theory.

1.4 Objectives of this thesis

The exchange–correlation term in the Kohn–Sham equation is the sole approximation keeping Kohn–Sham DFT from being an exact theory to real chemical systems, and finding the exact XC functional is still an open research problem. The various rungs of approximate functionals have been built with predominant focus on total-energy and energy-derived benchmarks. A functional’s quality is directly reflected in the XC potential, electron density, and observables such as the ionization potential. The available tools for accessing these quantities, i.e., RKS/MRKS, and Wu–Yang inversion, suffer from numerical instabilities, and no systematic study to date has used the inverted potentials as a benchmark metric to evaluate the vast number of hybrid functionals. Equally, the physical origin of the "correlation" contribution in a hybrid functional, the correlation potential and correlated density, has never been analyzed systematically, especially in the context of the presence of correlation effects at the exchange-only level.

The objectives of this thesis are therefore to:

1. Analyze existing tools for computing KS exchange–correlation potentials and thereby correlation potentials and correlated densities, from various levels of theories. This comprises developing tools and strategies, such as an automated strategy for selecting the regularization parameter with reference to the MRKS reference potential, and evaluating basis-set effects in inverse Kohn–Sham schemes.
2. Carry out the first of its kind comprehensive evaluation of 155 hybrid functionals available in the libxc library against wavefunction-theory reference data (FCI, CCSD(T), EOM-CCSD), benchmarking the exchange–correlation potentials, the electron density, the correlated density, and the ionization potentials, and thereby exposing the limitations resistant to sole energy-based benchmarks.
3. Evaluate the correlation potential and correlated density of global hybrids, showing that their dominant features do not arise from the semi-local correlation functional but from the difference between the semi-local and the exact (Hartree–Fock) exchange.
4. On this basis, construct a new global hybrid functional, the UMK26 family, based on the adiabatic connection, in which a single parameter(γ) is optimized by minimizing the ΔIP error against the EOM-CCSD reference IPs.

5. Test and Validate the resulting UMK26 functional (and its exchange-only variant UMK26x) across a wide range of quantum chemical properties such as the HOMO and valence ionization potentials (401 reference values from 63 systems)[[82](#)], charge-transfer excitation energies, self-interaction error, integer-discontinuity, and dissociation curves of charged species, and thermochemistry.

Chapter 2

Critical Evaluation of Hybrid XC Approximations

Vignesh Balaji Kumar, Szymon Śmiga, Ireneusz Grabowski; *A Critical Evaluation of the Hybrid KS DFT Functionals Based on the KS Exchange-Correlation Potentials*. J. Phys. Chem. Lett. 10 October 2024; 15 (40): 10219–10229. <https://doi.org/10.1021/acs.jpcllett.4c01979>

2.1 Introduction

Developing and evaluating XC functionals is an active area of research aimed at overcoming various limitations of Density Functional Theory and enabling wider, more accurate applications across diverse chemical systems and scenarios. One straightforward way to assess an XC functional is through the energy and its derived quantities, such as atomization and isomerization energies, barrier heights, etc. Various benchmarks have been developed and grouped into well-known large benchmark sets such as GMTKN55[83] and MGCDB84[84]. A large number of large-scale XC evaluations have been conducted using these benchmark sets, and these tests aid the proper choice of XC functional for computational studies and shed light on their construction and scope for XC functional development. An important observation is the dominance of energy and energy-derived evaluation criteria for XC approximations, and the lack of focus on other crucial quantities, such as electron densities, XC potentials, exchange-only and correlation potentials, correlated densities, HOMO, and valence ionization potentials.

The main challenge in such evaluations is that, unlike energy, which is straightforward to obtain, these quantities, such as XC KS potentials and electron densities, are represented on a 3D grid, which requires specialized evaluation procedures.

Our primary objective is to define reliable and effective evaluation and conduct a comprehensive assessment of hybrid XC functionals across the diverse physical quantities specified above to gain a broad understanding of the advantages and limitations of different hybrid DFT approximations. This is our primary step in developing a new XC approximation to improve DFT.

Both Hartree-Fock theory and Density Functional Theory individually have their own merits and limitations. There are certain aspects in which both theories are complementary. HF theory is self-interaction-free; it can effectively describe one-electron systems, which is a serious drawback in DFT, where there is no systematic mechanism to cancel electron self-interaction. Hence, HF theory possesses the correct shape of the potential in the asymptotic region, an attribute that is not possessed by local and semilocal approximations in DFT. The mixing of HF theory and DFT was conceived [44, 85], and its success in establishing DFT as a workhorse for computational chemistry simulations is crucial. Hence, we especially focus on hybrid DFT approximations for this analysis.

The non-local nature of Generalized Kohn-Sham (GKS) [50] forbids the direct evaluation of the XC potential in Hybrid DFT. The Inverse Kohn-Sham (IKS) method, such as the Wu-Yang method discussed in 1.2.4, can be used to compute the XC potential using a converged electron density obtained from a Hybrid DFT calculation. As a preliminary step to assess the quality of different hybrid approximations developed to date, we evaluated 155 hybrid approximations obtained from the libxc [86] library. Apart from energy, we also emphasize evaluation on diverse crucial quantities such as the electron density, XC potential, ionization potential, correlation potential, and correlated density. Since energy and energy-derived quantities are widely used in XC functional development and benchmarking, this analysis would reveal their efficiency across different computational properties and their robustness. We employ CCSD(T) and FCI to generate the reference data. The reference XC potentials are obtained by target FCI and CCSD(T) densities through the same Wu-Yang procedure. We use an augmented cc-pVTZ basis set with uncontracted functions for this evaluation, which is standard in such XC evaluations. Nevertheless, we properly scrutinized the basis set effect and grid size effects in the end results.

We also classify the functionals by the ingredients used in their construction, such as LDA, GGA, and MGGA, for both global and range-separated XC functionals.

Density- and Functional-driven errors[87] are other vital metrics for decomposing the origin of total energy errors into density- or functional-expression-driven effects, which we employ to evaluate the 155 hybrid DFT approximations. Most crucially,

we also present a comparison with respect to wavefunction methods, such as HF, MP2, MP3, and CCSD, to evaluate the hybrid functional expression relative to well-established wavefunction methods.

2.2 The most important findings of the study

The primary observation of the study is a hierarchy among the errors[88] computed with these hybrid functionals, with errors in total energy(ΔE_t) and density($\Delta\rho$) being the smallest, and larger errors for other quantities, such as the ionization potential(ΔIP) and XC potential(Δv_{xc})[89]. We observed that range-separated hybrid functionals possessing 100% long-range Hartree-Fock potentials show superior performance in describing the XC potential. We also rely on $\Delta\rho^{ref}v_{xc}$ error[89] in which the rapidly decaying density along the radial distance truncates the asymptotics of the XC potentials and presents the behavior and core and valence region. The hierarchy in the error magnitudes is illustrated in Eq. 2.1

$$\Delta v_{xc} > \Delta IP > \Delta\rho^{ref}v_{xc} > \Delta\rho > \Delta E_t \quad (2.1)$$

The second crucial finding of the study is the direct correlation between the quality of the exchange-correlation potential and the ionization potential, and the crucial role of the long-range Hartree-Fock coefficient in shaping both the exchange-correlation potential and the ionization potential. Bartlett’s IP theorem and correlated orbital theory highlight the importance of IPs computed from the orbital eigenvalues. We observed that a full long-range Hartree-Fock coefficient is required to describe the XC potential and ionization accurately.

The analysis revealed the efficiency of hybrid KS-DFT compared with well-studied wavefunction-theory methods. Though most hybrid DFT approximations performed better than Hartree-Fock for energy, and a few functionals outperformed MP2, no functional could outperform MP2 in the case of electron density. The wavefunction-based methods were clearly superior across other metrics, such as ΔIP , Δv_{xc} , and $\Delta\rho^{ref}v_{xc}$ errors.

The study also presents a list of the best- and worst-performing functionals across all error metrics considered.

The analysis based on density- and functional-driven errors indicated that most errors in the total energy arise from the functional expression rather than the electron density. It highlights the necessity of focusing on the robust construction of functional expressions with reduced functional-driven error to tackle the challenges in

DFT.

2.3 Conclusions

The study is the first of its kind to comprehensively evaluate a large number of density functionals with respect to diverse physical quantities, such as the XC potential, electron densities, ionization potentials, etc. The work identifies existing deficiencies in hybrid DFT approximations, necessitating consideration of critical physical quantities, such as the exchange-correlation potential, when evaluating and developing XC functionals.

A superior accuracy in energy, followed by density, is clearly due to the fact that these quantities were given utmost importance in the historical development of XC approximations. Other quantities, such as the XC potentials and IPs, are seldom considered. This is also because obtaining XC potentials from non-local methods, such as Hybrid DFT, requires alternative approaches, and recent developments in inverse Kohn-Sham schemes have facilitated such evaluations.

Bartlett’s IP theorem and correlated orbital theory highlight the importance of IPs computed from the orbital eigenvalues. The study clearly shows the elevated error in IPs compared to energy and density. The study underscores the necessity to consider critical physical quantities, such as the exchange-correlation potential and ionization potentials, when evaluating and developing XC functionals.

A Critical Evaluation of the Hybrid KS DFT Functionals Based on the KS Exchange-Correlation Potentials

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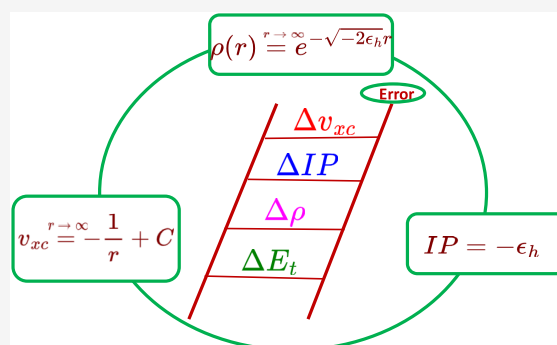
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ABSTRACT: We have developed a critical methodology for the evaluation of the quality of hybrid exchange-correlation (XC) density functional approximations (DFAs) based on very fundamental quantities, i.e., Kohn–Sham (KS) XC potentials, self-consistent electron densities, first ionization potentials (IPs), and total energies. Since the XC potentials, the primary objects in the current study, are not directly accessible for the hybrids, we calculate them by inverting the KS electron densities. Utilizing this methodology, we tested 155 hybrid DFAs available in the LIBXC library using FCI and CCSD(T) methods as a reference. We have found that a group of functionals produces very decent XC potentials, mainly those with a large mixture of Hartree–Fock exchange. Moreover, the value of IP strongly depends on the XC potential quality. On the other hand, we show that the XC energy is dominated by functional-driven error, which in some cases leads to substantial errors in electronic densities. The study shows new directions for constructing more accurate XC functionals within the KS-DFT framework.



Density functional theory (DFT)¹ is one of the most popular computational methods extensively applied in chemistry, physics, and materials science calculations. In principle, DFT is an exact theory; however, in practice, for the implementation of Kohn–Sham’s (KS) approach,² it requires an approximation for the exchange–correlation (XC) energy functional. Hundreds of nonempirical and semi-empirical density functional approximations (DFAs) have been developed in the past six decades, presenting different levels of complexity and quality.³ Among them, so-called hybrid functionals are common in standard DFT applications and have proven practical in KS-DFT calculations,⁴ being the best compromise between accuracy and efficiency. In general, hybrid XC functionals (E_{xc}^{HYB}) are a mixture of a fraction of the Hartree–Fock (HF) exact exchange energy (E_x^{EXX}) with some parts of semilocal exchange and correlation functionals, usually at LDA, GGA, and meta-GGA levels.⁵ DFT hybrids introduced by Axel Becke in 1993⁶ can be theoretically justified with the adiabatic connection formula^{7–10} and generalized KS (GKS) framework.^{11–13} The popularity of hybrid functionals reflects their essential features, i.e., systematically higher predictive accuracy for several properties,^{3,14} reduction of the self-interaction errors (SIE), and approaches to address the KS derivative discontinuity¹⁵ allowing to overcome the bandgap partially or the charge transfer excitation problem.^{16–18} In addition, to ensure the proper behavior of the exchange potential at the long-distance limit, the range-separated (RS) class of hybrids¹⁹ was successfully developed.

By definition, the KS XC potential (v_{xc}) is obtained as the functional derivative of the XC energy functional (E_{xc}) with respect to the density (ρ)

$$v_{xc} = \frac{\delta E_{xc}[\rho]}{\delta \rho} \quad (1)$$

We note that the hybrid class of KS functionals depends directly on KS orbitals via the nonlocal HF (exact) exchange energy term and kinetic energy density²⁰ utilized by meta-GGA hybrids to define these functionals. For this reason, to remain entirely in the KS framework, one needs to employ the optimized effective potential (OEP) method^{21–23} to compute the XC potential in eq 1. In practice, however, to avoid difficulties related to the OEP method,^{24–26} the hybrid functionals are realized within the GKS framework^{11–13} with nonlocal XC potential. Nonetheless, as pointed out in many studies,^{27–30} the GKS and full KS realizations of hybrids give practically the same accuracy for ground-state properties, differing only for quantities involving excited states.³¹

For this reason, the KS XC and correlation potentials are not usually the objects of study in the process of developing new

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XC functional approximations. We remark, however, that these potentials are well-defined quantities that directly enter the KS equations. As was pointed out in a recent study,^{30,32} the hybrid functionals can provide reasonably accurate local XC³² potentials and densities³⁰ obtained within the KS scheme realized via the OEP method³⁰ and the inverse procedures.³² Moreover, it was shown in ref 30 that the correlation functionals (E_c^{HYB}), which can be defined for any hybrid XC approximation as $E_c^{\text{HYB}} = E_{xc}^{\text{HYB}} - E_x^{\text{EXX}}$, give very physical correlation potentials, capable of describing the quantum shell oscillations of the high-level reference data for atoms and molecules correctly.

The present study is devoted to a generalized assessment of the most popular hybrid XC functionals available in the LIBXC library.³³ To this end, we have tested 155 hybrid functionals, mainly focusing on their XC and correlation potentials, which are usually underestimated and even ignored in DFT functional development. Certainly, there are some exceptions, e.g., *ab initio* DFT,^{26,34–36} correlated orbital theory (COT),³⁷ and Handy and co-workers' work.^{38–40} Here, we show how significant and influential the KS XC potential is for investigating the properties and quality of existing XC functionals and developing new DFT functionals. In addition, our evaluation also focuses on the fundamental KS-DFT features: total energies, electron densities, and ionization potentials, which are the standard quantities used in the KS-DFT assessment process. This allows us to reveal and confirm some essential relations, e.g., the correlation between the quality of the XC potential and the accuracy of ionization potentials for a given hybrid XC DFT approximation (DFA). We also analyze density- and functional-driven errors for all hybrid functionals. This work paves the way for further functional development of these types of DFAs by significantly increasing their predictive power.

In our assessment, we have considered 155 hybrid functionals currently available in the LIBXC library³³ (version 6.1.0.), representing the most important and most frequently used hybrid approximations in practical DFT calculations. All functionals are listed and numbered in Table ST1 in the Supporting Information (SI) file, with the original names kept as indicated in the LIBXC library. To make our overview of hybrids more systematic, within Table ST1, the functionals are organized using three main factors: (i) they are divided into the global and RS classes of hybrids; (ii) within each class, they are grouped according to standard DFT approximations classification, i.e., LDA, GGA, and meta-GGA (MGGA); (iii) and finally, within these groups, the functionals are arranged in ascending order according to a fraction of the nonlocal HF exchange energy contribution in the XC approximation. In the case of global hybrid DFAs, the HF fraction is described by the value of the HF coefficient itself, whereas, in the RS hybrids, it is described by the long-range HF coefficient. Both coefficients are taken directly from the LIBXC library. The same ordering of DFAs is utilized in Figure 2 and Figure 3.

Our primary object in the current study is XC potential, which is computed from a given self-consistently obtained hybrid GKS density matrix, employing the Wu–Yang⁴¹ (WY) inversion procedure (for more details, see Section 2 in the SI file).

We also calculate the correlation potential as $v_c = v_{xc} - v_{\text{HF}}$ where v_{HF} is the local, exchange-only potential obtained from the self-consistently obtained HF density. Additionally, in our assessment, we have also considered a few quantities that are

directly accessible from standard self-consistent GKS realization of hybrids, i.e., total energies, electron densities, and ionization potentials computed from the highest occupied molecular orbital (HOMO) energy ($IP = -\epsilon_{\text{HOMO}}$). The comparison of densities, XC potentials, and IPs is critical from the conceptual point of view of KS-DFT theory and the development of new XC approximations. We recall that the asymptotic behavior of the XC potential governs the quality of the first IP, which also impacts the behavior of electron density in the asymptotic tail. The density, in turn, is connected by one-to-one mapping of the Hohenberg–Kohn theorems with XC potential.^{1,2} Thus, all of these quantities are related, as depicted in Figure 1.

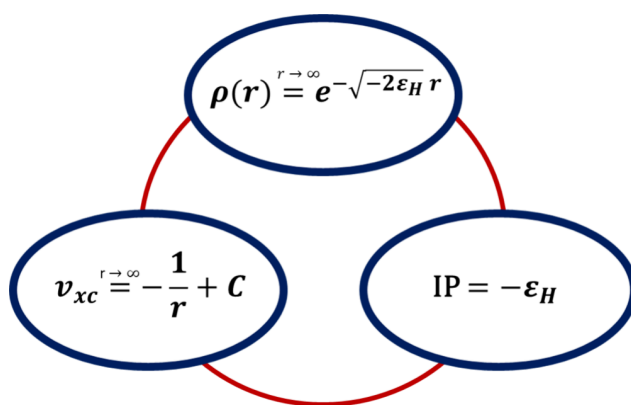


Figure 1. Graphical representation of relations between ρ , v_{xc} and IP in KS-DFT ($\epsilon_H = \epsilon_{\text{HOMO}}$).

To quantify the hybrid DFA comparison, we use a few error measurements,³² namely,

$$\Delta v_{xc} = \frac{\|\delta v_{xc}\|_{L_2}}{\|v_{xc}^{\text{ref}}\|_{L_2}} \quad (2)$$

$$\Delta \rho = \frac{\|\delta \rho\|_{L_2}}{\|\rho^{\text{ref}}\|_{L_2}} \quad (3)$$

where Δv_{xc} and $\Delta \rho$ are the relative errors of the hybrid XC potential (v_{xc}) and electron density ρ , respectively, defined using the standard L_2 norm, so, e.g., $\|\delta A\|_{L_2} = (\int d\mathbf{r} (A^{\text{ref}}(\mathbf{r}) - A(\mathbf{r}))^2)^{1/2}$, where for a given quantity $\delta v_{xc} = v_{xc}^{\text{ref}} - v_{xc}$ and $\delta \rho = \rho^{\text{ref}} - \rho$ are computed at every grid point. Because of that, the Δv_{xc} can give rise to significant errors for hybrids that exhibit differently than $-1/r$ asymptotic behavior in the tail of the XC potential.³⁰ Section 3 in the SI discusses this issue in more detail. Hence, we consider the Δv_{xc} error as a good indicator of the quality of XC potentials, mainly in the asymptotic limit. We recall that asymptotic behavior of the XC potential has a significant impact on the quality of the first ionization potential, as well as excitation energies.^{19,42,43} We also calculate the error of the correlation potential Δv_c in analogy to Δv_{xc} (see eq 2). In addition, to get some insight into how XC potentials behave in the core and valence regions, we define another useful error indicator:

$$\Delta \rho^{\text{ref}} v_{xc} = \frac{\|\rho^{\text{ref}} \delta v_{xc}\|_{L_2}}{\|\rho^{\text{ref}} v_{xc}^{\text{ref}}\|_{L_2}} \quad (4)$$

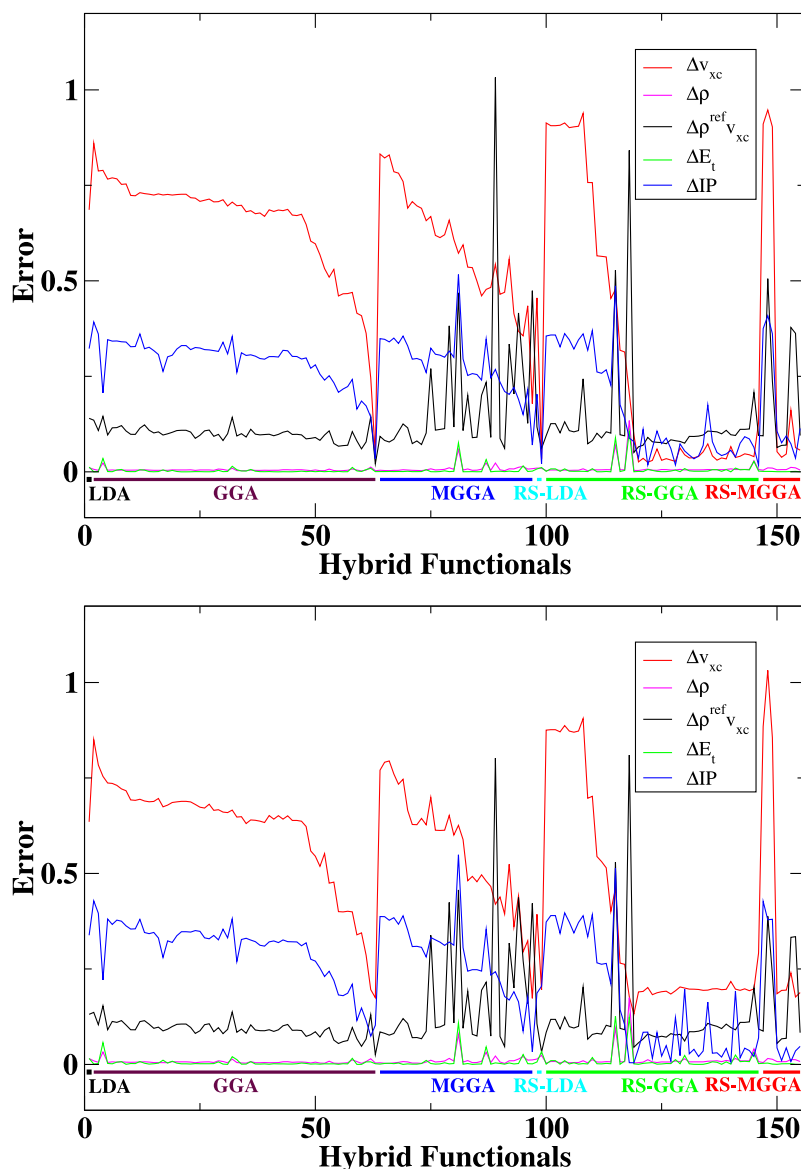


Figure 2. Errors defined by eqs 2–6 for the Be (top) atom and LiH (bottom) molecule with the FCI reference. The IP EOM-CCSD method is used as a reference to calculate IP error. The X-axis corresponds to various hybrid functionals numbered and grouped according to Table ST1.

Because ρ^{ref} decays much faster than v_{xc} as we move away from the center of the nuclei, we eliminate from $\Delta\rho^{\text{ref}}v_{\text{xc}}$ error a large contribution coming from the asymptotic tail and focus on the behavior of v_{xc} in more energetically important (the core and valence) regions.³²

Because the total energy and IPs are the single values corresponding to the system, we use the absolute relative error (ARE) in their error evaluation ΔE_t and ΔIP

$$\Delta E_t = \frac{|E^{\text{ref}} - E|}{|E^{\text{ref}}|} \quad (5)$$

$$\Delta IP = \frac{|IP^{\text{ref}} - IP|}{|IP^{\text{ref}}|} \quad (6)$$

where E^{ref} and IP^{ref} denote the reference total energy and IP, respectively, whereas E and IP correspond to their hybrid counterparts. The errors given by eqs 2–6 are computed separately for each system and hybrid functional.

The reference energies E^{ref} and densities ρ^{ref} have been calculated at the FCI and CCSD(T) level of theory depending on the considered benchmark set (see below), whereas the very accurate IP-EOM-CCSD^{44,45} method was used as a reference for a first vertical IP. In turn, in the case of reference XC potentials $v_{\text{xc}}^{\text{ref}}$, the WY inverse procedure is employed to obtain the potentials from the FCI or CCSD(T) relaxed density matrixes, depending on the benchmark set.

In our consideration, we use two benchmark sets: (i) FCI benchmark set consisting of systems up to four electrons, i.e., He, H₂, He₂, Be, and LiH for which reference data have been obtained at the FCI level of theory; (ii) CCSD(T) benchmark set consisting 16 atomic and molecular systems listed in Table 1 in ref 46 for which reference data have been obtained at the CCSD(T) level of theory. The geometries for molecular systems are taken from ref 46.

As in similar studies^{32,47} utilizing the WY method, the triple ζ quality basis set was used (uncontracted aug-cc-pVTZ⁴⁸) in all calculations, in order to make a comparison on the same

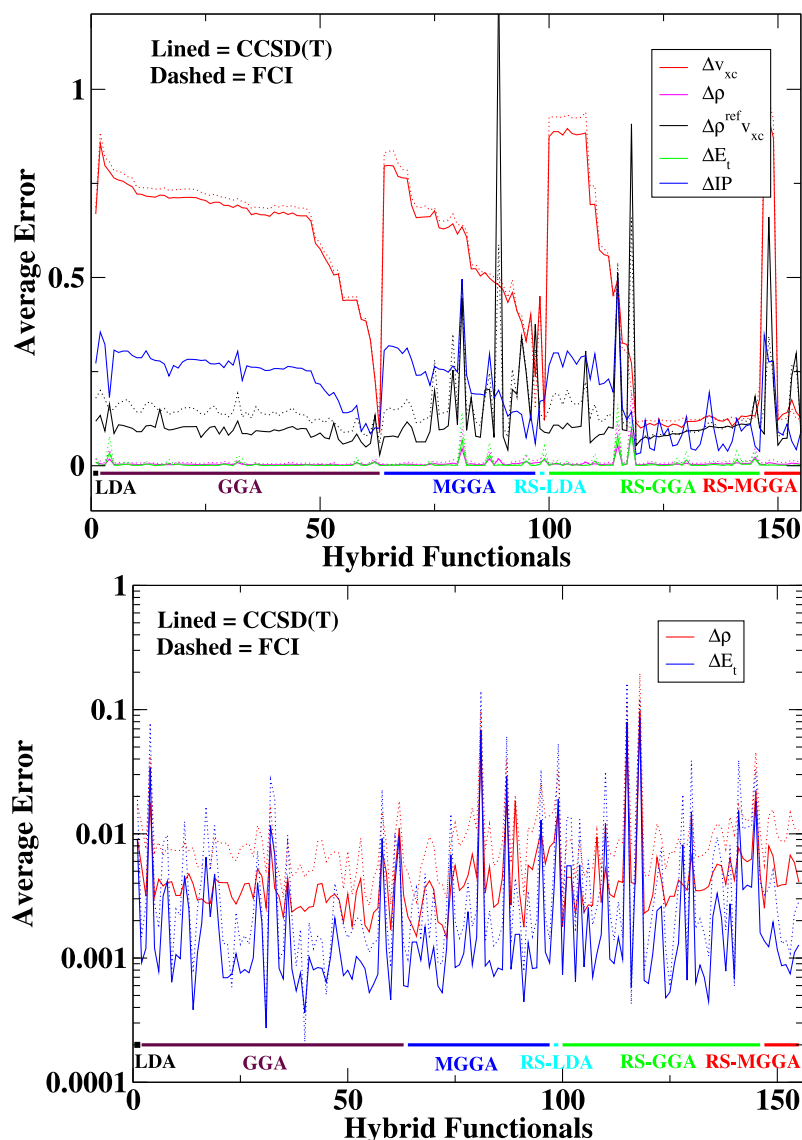


Figure 3. Top panel: Average errors (see the text) were calculated for the FCI and CCSD(T) benchmark sets. The IP EOM-CCSD method is used as a reference to calculate IP error. Bottom panel: As in the top panel but scaled up for total energy and density errors. Please note the logarithmic scale on the Y-axis at bottom panel. The X-axis corresponds to various hybrid functionals numbered and grouped according to Table ST1.

footing and to reduce basis set related errors. The same basis set is used for potential expansion to ensure a smooth, balanced solution with the WY inverse method. We underline that the same qualitative behavior is obtained by using the larger basis set, namely, uncontracted aug-cc-pV5Z^{48–50} (see Figure S2 in the SI file). Thus, at this point we conclude that a triple ζ quality basis set is sufficient for the present investigation.

The FCI and CCSD(T) reference electron densities and total energies are computed using the Psi4⁵¹ program. The reference XC potentials are calculated via the WY scheme using the $n2v$ package of the same software.^{51,52} The hybrid XC potentials, in turn, are computed using the same WY inversion procedure with the $n2v$ package and PySCF^{53,54} program. We refer the reader to Section 2.1 in the SI file for more information regarding the WY method. The reference IPs are obtained with the IP-EOM module from the PySCF package.

In all GKS DFT calculations, we have employed a Lebedev and Laiko quadrature formula for DFT grid construction^{55,56} that corresponds to level 5 as implemented in the PySCF package. We underline that errors defined by eqs 2–4 have been evaluated on the same DFT grid as used for KS-DFT calculations. We also note that the convergence of these errors has been tested concerning grid size, and the level 5 constructed in PySCF package is sufficiently large for this assessment (see Section 2.2 and Figure S1 in the SI file).

We start our analysis by directly comparing errors defined by eqs 2–6 computed separately for the Be atom and LiH molecule, w.r.t. FCI references for all 155 hybrid DFAs. We report these in Figure 2. The X-axis corresponds to various hybrid functionals numbered and grouped as Table ST1 indicates. To make the analysis easier, we highlight the main groups of DFAs by using color coding.

One can note that the error behaviors are almost identical for both systems, qualitatively and quantitatively, and among all of the functional groups. This is also the case for other

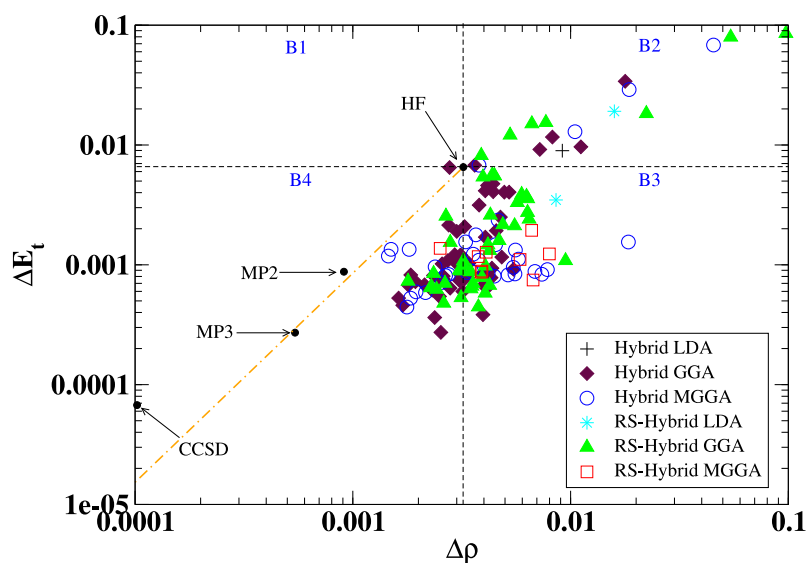


Figure 4. Average $\Delta\rho$ error vs average ΔE_t error for the CCSD(T) benchmark set. Note the logarithmic scale used for both axes. The orange (dash-dotted) line in block B4 indicates the ideal error decrease trend.

systems analyzed in our research. For credibility purposes, we also report, in Figure S3 in the SI, the error plots for the Ar atom and HCl molecule calculated with respect to the CCSD(T) reference. This is the first important finding of the present study.

Similar behavior can also be noted for averaged errors computed separately for the whole FCI and CCSD(T) benchmark sets, as presented in Figure 3. Here, we see that the qualitative behavior of average errors is very similar, despite the size of the benchmark set and reference data. Therefore, in further analysis, we will focus only on average errors calculated concerning the CCSD(T) reference data (CCSD(T) benchmark set) to describe the main trends in the hybrid DFAs performance. These data are collected for all hybrid functionals in the external repository (10.18150/V4XZSF),⁵⁷ together with the HF fraction coefficients. This can be useful to the reader for checking, e.g., different types of errors for individual functionals and for making their additional analyses.

By analyzing the error plots in Figure 2 and Figure 3, one can note a considerable deviation between the sizes of the different types of errors (Δv_{xc} , $\Delta\rho$, $\Delta\rho^{ref}v_{xc}$, ΔE_t , ΔIP). In most cases, the total energy error (ΔE_t) is the most minor, usually three or four orders smaller than the XC potential error. This is not surprising, because good performance for energetics is usually the primary concern of XC functional developers. We note that most functionals have been parametrized regarding several types of energy qualities or physical constraints related to energetics (e.g., second-order gradient expansion,⁵⁸ Lieb–Oxford bound,^{59,60} etc.), and only very few of them have been developed to have correct XC potentials⁶¹ or IPs.^{62,63}

We also observe that the density error ($\Delta\rho$) is very similar in magnitude to the total energy error (ΔE_t) for all hybrids. Therefore, we present total energy and density errors on an additional separate plot (bottom panel of Figure 3). This can also be observed in Figure 4, where we analyze ΔE_t and $\Delta\rho$ errors together. One can note that for both errors many hybrid DFAs yield accuracy between HF and MP2 methods. It confirms the well-known behavior of the KS DFT hybrids versus the *ab initio* methods. In particular, none of the hybrid

DFAs exceeds the MP2 method for the averaged $\Delta\rho$ error, which agrees with the findings from ref 64 (see Table 1).

Table 1. Three Hybrid XC DFAs with the Largest Average Errors Calculated for the CCSD(T) Benchmark Set

Error Type	XC Functional	Type	Error
ΔE_t	CAM-O3LYP	RS-GGA	0.0854
	WHPBE0	RS-GGA	0.0795
	X1B95	MGGA	0.0683
$\Delta\rho$	CAM-O3LYP	RS-GGA	0.0974
	WHPBE0	RS-GGA	0.0543
	X1B95	MGGA	0.0453
Δv_{xc}	MN12-SX	RS-MGGA	0.9206
	HJS-B97X	RS-GGA	0.8959
	HJS-PBE-SOL	RS-GGA	0.8875
$\Delta\rho^{ref}v_{xc}$	MN15	MGGA	1.2917
	CAM-O3LYP	RS-GGA	0.9080
	MN12_SX	RS-MGGA	0.6605
Δv_c	MN12-SX	RS-MGGA	13.4627
	HJS-B97X	RS-GGA	13.2353
	HJS-PBE-SOL	RS-GGA	13.1643
ΔIP	WHPBE0	RS-GGA	0.4959
	X1B95	MGGA	0.4957
	MPWLYP1M	GGA	0.3552

On the other hand, a large group of hybrids yield much worse densities than those given by the HF method. In particular, one can divide the Figure 4 area into four interesting regions by taking the HF results as a reference point ($\Delta\rho^{HF} = 0.0032$, $\Delta E_t^{HF} = 0.0065$). In the B1 part for which $\Delta\rho < \Delta\rho^{HF}$ and $\Delta E_t > \Delta E_t^{HF}$ we do not register any functionals, which indicates that none of the existing hybrid XC DFAs can generate a simultaneously good quality of densities (better than the HF one) with poorer performance for total energies

(worse than the HF method). In the B2 region ($\Delta\rho > \Delta\rho^{\text{HF}}$ and $\Delta E_t > \Delta E_t^{\text{HF}}$), in turn, one can note quite a few DFAs (18 cases). In particular, in this block, we can find the group of energetically (ΔE_t) worse-performing hybrid functionals, namely, the CAM-O3LYP, WHPBE0, and X1B95 (see also Table 1), which are placed in the right top corner of Figure 4. Interestingly, these three functionals also yield the largest density error values $\Delta\rho$ (see also Table 1), indicating the possible correlation between ΔE_t and $\Delta\rho$ errors for worse-performing functionals. This can be related to a large self-interaction error build-in in these DFAs, which is then transferred to the electron density via a self-consistent DFT procedure. In other words, this shows that, if the functional is very bad for energetics, it will also most probably lead to large density errors. The third block (B3) contains a large number of functionals (82 cases) for which $\Delta\rho > \Delta\rho^{\text{HF}}$ and $\Delta E_t < \Delta E_t^{\text{HF}}$. Here we can find, e.g., popular B3LYP,⁶⁵ HSEsol,⁶⁶ or QTP17⁶³ DFAs. Energetically, these hybrid DFAs, by definition, should include correlation effects that are beyond the HF picture. On the other hand, the same functionals produce electron densities that perform worse than the HF method. To analyze that in more detail, we have decomposed the total energy error into the density-driven (DD) and functional-driven (FD) parts⁴⁷ computing the absolute relative DD and FD errors separately as

$$\Delta E_t^{\text{DD}} = \frac{|E[\rho^{\text{ref}}] - E[\rho]|}{|E^{\text{ref}}|} \quad (7)$$

and

$$\Delta E_t^{\text{FD}} = \frac{|E^{\text{ref}}[\rho^{\text{ref}}] - E[\rho^{\text{ref}}]|}{|E^{\text{ref}}|} \quad (8)$$

respectively, for the CCSD(T) set. Figure S4 and S5 in the SI file depict the correlation between ΔE_t and ΔE_t^{FD} and ΔE_t^{DD} errors, respectively. Figure S4 shows an almost perfect correlation between ΔE_t and ΔE_t^{FD} , confirming the dominant role of FD error for all hybrid DFAs. We recall that the FD error depends on only ρ^{ref} , thus showing solely the impact related to the analytical form of DFA. Figure S5, in turn, shows that DD errors produced by GKS hybrid realization are always 2–3 orders of magnitude smaller than FD counterparts. This is not surprising, since, in most cases, the electronic density enters the XC energy expressions nonlinearly, making it less sensitive to the choice of input density. This is depicted in Figure S6 in the SI file, where we correlate averaged ΔE_t^{DD} and $\Delta\rho$ errors for a given hybrid DFA. One can note that the DD error is usually 1–2 orders smaller than $\Delta\rho$. This most probably suggests that the FD errors in the functionals are transferred via the SCF procedure to the electron density visible in block B3.

The final block B4 is dominated by functionals (55 cases) for which $\Delta\rho < \Delta\rho^{\text{HF}}$ and $\Delta E_t < \Delta E_t^{\text{HF}}$. In this region, we also note all tested *ab initio* post-HF methods, which are close to the “ideal” error-decreasing trend indicated by the diagonal dash-dotted line. Here, we can find, e.g., PBE0,⁶⁷ r²SCAN0,⁶⁸ CAM-QTP-00,⁶² or ω B97X-V⁶⁹ DFAs. For total energy error, one can note that some DFAs (mostly GGA and RS-GGA hybrids) perform better than MP2 and usually do not exceed MP3 performance. The only exception is found for the smallest ΔE_t reported by three global hybrid GGAs, APF, MPW1PBE, and REV3LYP, also shown in Table 2. In these cases, the accuracy is comparable to that of the MP3 results. In the same

Table 2. Three Hybrid XC DFAs with the Lowest Average Errors Calculated for the CCSD(T) Benchmark Set

Error Type	XC Functional	Type	Error
ΔE_t	APF	GGA	0.0003
	MPW1PBE	GGA	0.0004
	REV3LYP	GGA	0.0004
	HF	<i>ab initio</i>	0.0065
	MP2	<i>ab initio</i>	0.0009
	MP3	<i>ab initio</i>	0.0003
	CCSD	<i>ab initio</i>	0.0001
$\Delta\rho$	TPSS0	MGGA	0.0015
	REVTPSSH	MGGA	0.0015
	PBE50	GGA	0.0016
	HF	<i>ab initio</i>	0.0032
	MP2	<i>ab initio</i>	0.0009
	MP3	<i>ab initio</i>	0.0005
	CCSD	<i>ab initio</i>	0.0001
Δv_{xc}	HFLYP	GGA	0.0884
	LC-WPBEH-WHS	RS-GGA	0.1002
	WB97X	RS-GGA	0.1015
	HF	<i>ab initio</i>	0.0922
	MP2	<i>ab initio</i>	0.0401
	MP3	<i>ab initio</i>	0.0359
	CCSD	<i>ab initio</i>	0.0205
$\Delta\rho^{\text{ref}}v_{\text{xc}}$	HFLYP	GGA	0.0285
	R2SCAN50	MGGA	0.0419
	PBE-2X	GGA	0.0497
	HF	<i>ab initio</i>	0.0173
	MP2	<i>ab initio</i>	0.0090
	MP3	<i>ab initio</i>	0.0053
	CCSD	<i>ab initio</i>	0.0019
Δv_{c}	HFLYP	GGA	1.2657
	LC-WPBEH-WHS	RS-GGA	1.5593
	WB97X	RS-GGA	1.6344
	HF	<i>ab initio</i>	1.0
	MP2	<i>ab initio</i>	0.4621
	MP3	<i>ab initio</i>	0.4435
	CCSD	<i>ab initio</i>	0.3736
ΔIP	CAM-QTP-00	RS-GGA	0.0301
	LC-WPBEH-WHS	RS-GGA	0.0343
	RCAM-B3LYP	RS-GGA	0.0382
	HF	<i>ab initio</i>	0.0614
	MP2	<i>ab initio</i>	0.0348
	MP3	<i>ab initio</i>	0.0247
	CCSD	<i>ab initio</i>	0.0000

table, we also report the three smallest errors for $\Delta\rho$, which are yielded by TPSS0,⁷⁰ revTPSSH,⁷¹ and PBE50⁷² hybrid DFAs. Also, here the best hybrids do not exceed the MP2 performance. Additional inspection of Figures S4 and S5 in the SI file indicates that all functionals in the B4 segment of Figure 4 are characterized by small FD and DD errors. Because of that and noting small errors in electronic density, one can conclude that the functionals in the B4 block, due to various physical constraints built into the XC formula, provide accurate results for good reasons.

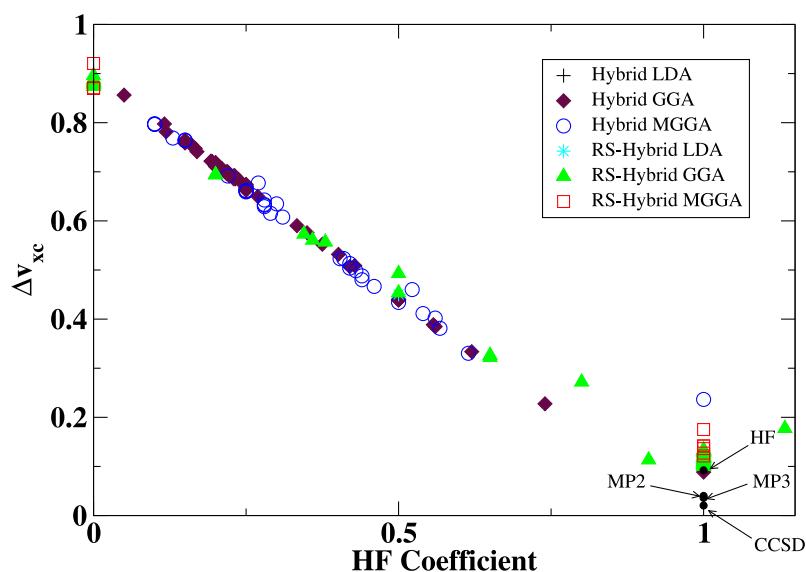


Figure 5. Average Δv_{xc} errors versus the HF coefficients (global hybrids) and long-range HF coefficients (range-separated hybrids).

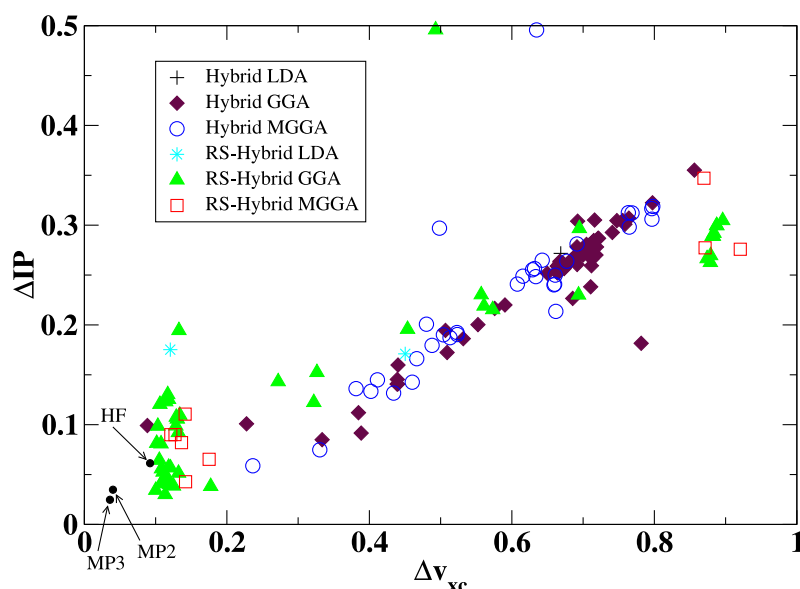


Figure 6. Average IP errors vs average errors of the exchange-correlation potential calculated for the CCSD(T) benchmark set. The IP EOM-CCSD method is used as a reference to calculate IP error.

Now we turn our attention to Δv_{xc} , $\Delta \rho^{ref} v_{xc}$, and ΔIP errors reported in Figure 3 to analyze the behavior of XC potentials and IPs generated by all hybrid functionals. As mentioned, the XC potential is a well-defined quantity entering the KS scheme. It is often overlooked in the DFA development process, but it tremendously impacts the quality of the orbitals and eigenvalues (e.g., first IP). One can note that $\Delta \rho^{ref} v_{xc}$ error is generally 1–2 orders larger than density and total energy errors. The Δv_{xc} error, in turn, gives much larger values for most DFAs (3–4 orders larger than $\Delta \rho$ errors). This confirms the findings from ref 32, where authors observe similar behavior for a few of the most popular global hybrids. However, the present analysis further reveals that this difference is much smaller for long-range corrected hybrids. This is due to the large HF contribution in the XC functional, which, in turn, recovers the proper asymptotic behavior of v_{xc} and thus reduces the Δv_{xc} error for these species (see also

Section 3 in the SI file). This is depicted in Figure 5 where we report the value of Δv_{xc} as a function of HF contribution. One can note that the error is relatively large for most global hybrids compared to long-range corrected DFAs and *ab initio* methods. The same feature also significantly impacts the quality of the first IP obtained from all hybrid DFAs. An evident direct quality dependence between the first IP and the XC potential exists, as seen in Figure 6. The best IPs are yielded by the CAM-QTP-00 functional (see Table 2), which was constructed to provide the smallest IP error,⁶² which agrees with our findings. That indicates the ultimate necessity in DFT calculations to care for the high quality of the XC potential to provide better IPs, which also results directly from the structure of the KS equations. This offers alternative confirmation of previous findings.^{30,73–76} From Figure 3, we can see that the region with lower v_{xc} and IP error starts from the 119 functional, and it is highly dominated by RS-GGA and

RS-MGGA XC functionals. In general, those functionals have long-range HF coefficients equal to 1, which results in a correct $-1/r$ behavior of the XC potential in the asymptotic tail. On the other hand, the results displayed in Table 1 show that all functionals with the largest v_{xc} errors are mostly yielded by short-range corrected hybrids for which the long-range HF coefficients equal zero. Thus, except for some individual cases, the RS hybrids better describe v_{xc} effectively and hence have a lower error for IPs.

The $\Delta\rho^{ref}v_{xc}$ error, in turn, yields generally (for global and RS hybrids) an error varying between 0.02 and 1.29. This is presented in Figure S7 in the SI file on which we show the $\Delta\rho^{ref}v_{xc}$ and density $\Delta\rho$ errors together with the *ab initio* results. As we see, the $\Delta\rho^{ref}v_{xc}$ error is bigger for all hybrid functionals than the HF one and certainly MP2, MP3, and CCSD. Generally the $\Delta\rho^{ref}v_{xc}$ error is notably smaller in almost all cases than the Δv_{xc} counterpart. This is an outcome of removing large contributions in the latter coming from the asymptotic tail observed for global hybrids. For this reason, $\Delta\rho^{ref}v_{xc}$ error provides us more insight into the quality of the XC potential in the core and valence regions.

An inspection of Table 2 shows that the smallest Δv_{xc} error is provided by the HFLYP^{77,78} functional, which is a simple combination of 100% HF contribution and 100% of LYP^{77,78} correlation functional. It provides very good Δv_{xc} , $\Delta\rho^{ref}v_{xc}$, and even the correlation-only potentials (Δv_c). This is closely followed by LC-WPBEH-WHS^{79,80} and WB97X,⁸¹ which yield similar errors. We note that the quality of the XC potentials can also be effectively examined by a direct visual comparison. This is done in Figures S8 and S9 (top row) in the SI file, where we report the XC potential obtained with HFLYP, LC-WPBEH-WHS, and CAM-QTP-00 DFAs for the Be atom and LiH molecule compared with FCI reference data. One can note that the hybrid potentials almost match the reference data in all cases. However, this can be misleading. Closer inspection of Δv_{xc} errors reveals that practically none of the existing hybrid DFAs can give a smaller error for v_{xc} than the one obtained for the HF method ($\Delta v_{xc}^{HF} = 0.0922$). This is an astonishing result since HF density provides the exchange-only potential (without any correlation). This indicates that the correlation potential (v_c) obtained for a given hybrid DFA possesses significant errors. In Table 2, we also report the smallest correlation potential error (Δv_c). In this case, errors are larger than those of HF. This is confirmed by the inspection of correlation potentials depicted in Figures S8 and S9 (bottom row) of the SI file. The deviations are far more visible in this case, especially in the core and valence regions, which indicate that accurate v_c potentials are the main drawback of present day hybrid DFAs. Nevertheless, these v_c are very physical, being in phase with and having the shape of the reference FCI counterpart, which extends and confirms the finding from ref 30.

In conclusion, the study evaluates the quality of 155 hybrid functionals available in the LIBXC library with the main focus on their XC and correlation KS potentials, electron densities, ionization potentials, and total energies by direct comparison with the *ab initio* FCI and CCSD(T) reference data.

The analysis of total energies and electron densities revealed a group of approximations (mostly global hybrid GGAs and MGGA) that mutually yield small errors for both quantities. Further analysis in terms of the DD and FD clearly indicates that the hybrid energy expression is mainly dominated by the FD error, which is related to the analytical form of DFA.

Therefore, in order to find a better hybrid functional, one should focus on the maximal reduction of the FD error given by the analytical formula.

Because the XC potentials are not directly accessible for the DFT hybrids and *ab initio* references, we calculated them by inverting their electron densities. The first important finding from this analysis is that most global and RS hybrids produce similar shell structure oscillations in v_{xc} potentials that are comparable qualitatively with reference data. Further improvement can be seen for long-range corrected RS-GGA and RS-MGGA hybrids for which v_{xc} decays as $-1/r$ in the asymptotic tail, providing the best overall performance of XC and correlation potentials. This explains the dramatic improvement upon global hybrids in the calculation of many properties.^{82,83} The same feature also impacts the quality of the first IPs, which benefit from the correct $-1/r$ asymptotic behavior of v_{xc} incorporated by the HF long-range component. Increasing the contribution of the HF exchange term results in smaller errors for XC and IPs, for which we observe mutual direct and systematic dependence.

The closer inspection of Δv_{xc} and Δv_c errors reveals that practically none of the existing hybrid DFAs can give a smaller error than the one obtained for the HF method. This indicates that the correlation potential obtained for a given hybrid DFA possesses significant errors. Therefore, this finding emphasizes the ultimate need to inspect FD errors and XC and correlation KS potentials as a decisive criterion in constructing new and improved hybrid functionals.

We have provided the individual values of all averaged errors for all hybrid functionals via 10.18150/V4XZSF,⁵⁷ which allows the reader to perform an additional assessment in the context of the applications and DFT functional development. It must be stressed here that hybrids with the highest errors should be avoided in actual DFT applications. We think that the present analysis can help overcome current limitations and face essential challenges in constructing new XC DFAs within the KS-DFT framework.

■ ASSOCIATED CONTENT

Data Availability Statement

The data that support the findings are published within this study.

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpclett.4c01979>.

The table with the list of all hybrid functionals, additional figures showing error correlations, figures with XC, and correlation potentials (PDF)

Transparent Peer Review report available (PDF)

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Notes

The authors declare no competing financial interest.

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Supplementary Materials for "A Critical Evaluation of the Hybrid KS DFT Functionals Based on the KS Exchange-Correlation Potentials"

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1 List of hybrid functionals

Table ST1: The list of 155 hybrid functionals used in the assessment. They are numbered according to the order described in the main manuscript and used in the figures. The names of the functionals are taken from the LIBXC library.

S.No	Hybrid Functional	Functional Type
1	HYB.LDA_XC.LDA0	Hybrid-LDA
2	HYB.GGA_XC_MPWLYP1M	Hybrid-GGA
3	HYB.GGA_XC_O3LYP	Hybrid-GGA
4	HYB.GGA_XC_WP04	Hybrid-GGA
5	HYB.GGA_XC_B97_1P	Hybrid-GGA
6	HYB.GGA_XC_B3LYPS	Hybrid-GGA
7	HYB.GGA_XC_B1WC	Hybrid-GGA
8	HYB.GGA_XC_HPBEINT	Hybrid-GGA
9	HYB.GGA_XC_EDF2	Hybrid-GGA
10	HYB.GGA_XC_SB98_1C	Hybrid-GGA
11	HYB.GGA_XC_B97	Hybrid-GGA
12	HYB.GGA_XC_B3LYP_MCM1	Hybrid-GGA
13	HYB.GGA_XC_SB98_1B	Hybrid-GGA
14	HYB.GGA_XC_REVB3LYP	Hybrid-GGA
15	HYB.GGA_XC_B3PW91	Hybrid-GGA
16	HYB.GGA_XC_MPW3PW	Hybrid-GGA
17	HYB.GGA_XC_B3P86_NWCHEM	Hybrid-GGA
18	HYB.GGA_XC_B3P86	Hybrid-GGA
19	HYB.GGA_XC_MB3LYP_RC04	Hybrid-GGA
20	HYB.GGA_XC_B3LYP	Hybrid-GGA

Continuation of Table S1

S.No	Hybrid Functional	Functional Type
21	HYB_GGA_XC_B3LYP3	Hybrid-GGA
22	HYB_GGA_XC_B3LYP5	Hybrid-GGA
23	HYB_GGA_XC_HAPBE	Hybrid-GGA
24	HYB_GGA_XC_B97_2	Hybrid-GGA
25	HYB_GGA_XC_B97_1	Hybrid-GGA
26	HYB_GGA_XC_X3LYP	Hybrid-GGA
27	HYB_GGA_XC_MPW3LYP	Hybrid-GGA
28	HYB_GGA_XC_SB98_2C	Hybrid-GGA
29	HYB_GGA_XC_B3LYP_MCM2	Hybrid-GGA
30	HYB_GGA_XC_SB98_1A	Hybrid-GGA
31	HYB_GGA_XC_APF	Hybrid-GGA
32	HYB_GGA_XC_RELPE0	Hybrid-GGA
33	HYB_GGA_XC_SB98_2A	Hybrid-GGA
34	HYB_GGA_XC_SB98_2B	Hybrid-GGA
35	HYB_GGA_XC_CAP0	Hybrid-GGA
36	HYB_GGA_XC_PBE_SOL0	Hybrid-GGA
37	HYB_GGA_XC_PBEH	Hybrid-GGA
38	HYB_GGA_XC_PBE0	Hybrid-GGA
39	HYB_GGA_XC_CASE21	Hybrid-GGA
40	HYB_GGA_XC_MPW1PBE	Hybrid-GGA
41	HYB_GGA_XC_B1PW91	Hybrid-GGA
42	HYB_GGA_XC_MPW1PW	Hybrid-GGA
43	HYB_GGA_XC_B1LYP	Hybrid-GGA
44	HYB_GGA_XC_MPW1LYP	Hybrid-GGA
45	HYB_GGA_XC_APBE0	Hybrid-GGA
46	HYB_GGA_XC_PBE_MOL0	Hybrid-GGA
47	HYB_GGA_XC_PBE_MOLB0	Hybrid-GGA
48	HYB_GGA_XC_B97_3	Hybrid-GGA
49	HYB_GGA_XC_PBE0_13	Hybrid-GGA
50	HYB_GGA_XC_BLYP35	Hybrid-GGA
51	HYB_GGA_XC_PBE38	Hybrid-GGA
52	HYB_GGA_X_SOGGA11_X,GGA_C_SOGGA11_X	Hybrid-GGA
53	HYB_GGA_XC_B97_K	Hybrid-GGA
54	HYB_GGA_XC_MPW1K	Hybrid-GGA
55	HYB_GGA_XC_PBE50	Hybrid-GGA
56	HYB_GGA_XC_B5050LYP	Hybrid-GGA
57	HYB_GGA_XC_BHANDHLYP	Hybrid-GGA
58	HYB_GGA_XC_BHANDH	Hybrid-GGA
59	HYB_GGA_XC_KMLYP	Hybrid-GGA
60	HYB_GGA_XC_PBE_2X	Hybrid-GGA

Continuation of Table S1

S.No	Hybrid Functional	Functional Type
61	HYB_GGA_XC_QTP17	Hybrid-GGA
62	HYB_GGA_XC_WC04	Hybrid-GGA
63	HYB_GGA_XC_HFLYP	Hybrid-GGA
64	HYB_MGGA_XC_R2SCANH	Hybrid-MGGA
65	HYB_MGGA_XC_TPSSH	Hybrid-MGGA
66	HYB_MGGA_XC_REVTPSSH	Hybrid-MGGA
67	HYB_MGGA_XC_TPSS1KCIS	Hybrid-MGGA
68	HYB_MGGA_X_TAU_HCTH,GGA_C_HYB_TAU_HCTH	Hybrid-MGGA
69	HYB_MGGA_XC_MPW1KCIS	Hybrid-MGGA
70	HYB_MGGA_XC_PBE1KCIS	Hybrid-MGGA
71	HYB_MGGA_X_SCAN0,MGGA_C_SCAN	Hybrid-MGGA
72	HYB_MGGA_XC_R2SCAN0	Hybrid-MGGA
73	HYB_MGGA_XC_TPSS0	Hybrid-MGGA
74	HYB_MGGA_XC_B0KCIS	Hybrid-MGGA
75	HYB_MGGA_X_M06,MGGA_C_M06	Hybrid-MGGA
76	HYB_MGGA_XC_B88B95	Hybrid-MGGA
77	HYB_MGGA_XC_B86B95	Hybrid-MGGA
78	HYB_MGGA_XC_PW6B95	Hybrid-MGGA
79	HYB_MGGA_X_M05,MGGA_C_M05	Hybrid-MGGA
80	HYB_MGGA_XC_PW86B95	Hybrid-MGGA
81	HYB_MGGA_XC_X1B95	Hybrid-MGGA
82	HYB_MGGA_XC_MPW1B95	Hybrid-MGGA
83	HYB_MGGA_X_REVM06,MGGA_C_REVM06	Hybrid-MGGA
84	HYB_MGGA_XC_MPWKICIS1K	Hybrid-MGGA
85	HYB_MGGA_XC_BB1K	Hybrid-MGGA
86	HYB_MGGA_X_BMK,GGA_C_BMK	Hybrid-MGGA
87	HYB_MGGA_XC_XB1K	Hybrid-MGGA
88	HYB_MGGA_XC_MPWB1K	Hybrid-MGGA
89	HYB_MGGA_X_MN15,MGGA_C_MN15	Hybrid-MGGA
90	HYB_MGGA_XC_PWB6K	Hybrid-MGGA
91	HYB_MGGA_XC_R2SCAN50	Hybrid-MGGA
92	HYB_MGGA_X_M08_HX,MGGA_C_M08_HX	Hybrid-MGGA
93	HYB_MGGA_X_M06_2X,MGGA_C_M06_2X	Hybrid-MGGA
94	HYB_MGGA_X_M08_SO,MGGA_C_M08_SO	Hybrid-MGGA
95	HYB_MGGA_X_DLDF,MGGA_C_DLDF	Hybrid-MGGA
96	HYB_MGGA_X_M05_2X,MGGA_C_M05_2X	Hybrid-MGGA
97	HYB_MGGA_X_M06_HF,MGGA_C_M06_HF	Hybrid-MGGA
98	HYB_LDA_XC_CAM_LDA0	RS-Hybrid-LDA
99	HYB_LDA_XC_BN05	RS-Hybrid-LDA
100	HYB_GGA_XC_HSE12S	RS-Hybrid-GGA

Continuation of Table S1

S.No	Hybrid Functional	Functional Type
101	HYB_GGA_XC_HSE_SOL	RS-Hybrid-GGA
102	HYB_GGA_XC_HJS_PBE_SOL	RS-Hybrid-GGA
103	HYB_GGA_XC_HSE12	RS-Hybrid-GGA
104	HYB_GGA_XC_HJS_B97X	RS-Hybrid-GGA
105	HYB_GGA_XC_HJS_PBE	RS-Hybrid-GGA
106	HYB_GGA_XC_HSE03	RS-Hybrid-GGA
107	HYB_GGA_XC_HSE06	RS-Hybrid-GGA
108	HYB_GGA_X_N12_SX,GGA_C_N12_SX	RS-Hybrid-GGA
109	HYB_GGA_XC_CAM_PBEH	RS-Hybrid-GGA
110	HYB_GGA_XC_CAMY_PBEH	RS-Hybrid-GGA
111	HYB_GGA_X_CAM_S12G,GGA_C_PBE	RS-Hybrid-GGA
112	HYB_GGA_X_CAM_S12H,GGA_C_PBE	RS-Hybrid-GGA
113	HYB_GGA_XC_MCAM_B3LYP	RS-Hybrid-GGA
114	HYB_GGA_XC_CAMH_B3LYP	RS-Hybrid-GGA
115	HYB_GGA_XC_WHPBE0	RS-Hybrid-GGA
116	HYB_GGA_XC_CAM_B3LYP	RS-Hybrid-GGA
117	HYB_GGA_XC_CAMY_B3LYP	RS-Hybrid-GGA
118	HYB_GGA_XC_CAM_O3LYP	RS-Hybrid-GGA
119	HYB_GGA_XC_CAM_QTP_00	RS-Hybrid-GGA
120	HYB_GGA_XC_LC_WPBEH_WHS	RS-Hybrid-GGA
121	HYB_GGA_XC_WB97X_D	RS-Hybrid-GGA
122	HYB_GGA_XC_LC_WPBESOL_WHS	RS-Hybrid-GGA
123	HYB_GGA_XC_CAM_QTP_02	RS-Hybrid-GGA
124	HYB_GGA_XC_LRC_WPBEH	RS-Hybrid-GGA
125	HYB_GGA_XC_WB97X_V	RS-Hybrid-GGA
126	HYB_GGA_XC_WB97X_D3	RS-Hybrid-GGA
127	HYB_GGA_XC_CAM_QTP_01	RS-Hybrid-GGA
128	HYB_GGA_XC_CAMY_BLYP	RS-Hybrid-GGA
129	HYB_GGA_XC_WB97X	RS-Hybrid-GGA
130	HYB_GGA_XC_LCY_PBE	RS-Hybrid-GGA
131	HYB_GGA_XC_LC_VV10	RS-Hybrid-GGA
132	HYB_GGA_XC_LC_WPBE08_WHS	RS-Hybrid-GGA
133	HYB_GGA_XC_LC_WPBE_WHS	RS-Hybrid-GGA
134	HYB_GGA_XC_LRC_WPBE	RS-Hybrid-GGA
135	HYB_GGA_XC_TUNED_CAM_B3LYP	RS-Hybrid-GGA
136	HYB_GGA_XC_LC_PBEOP	RS-Hybrid-GGA
137	HYB_GGA_XC_LC_BOP	RS-Hybrid-GGA
138	HYB_GGA_XC_LC_WPBE	RS-Hybrid-GGA
139	HYB_GGA_XC_LC_QTP	RS-Hybrid-GGA
140	HYB_GGA_XC_WB97	RS-Hybrid-GGA

Continuation of Table S1

141	HYB_GGA_XC_LCY_BLYP	RS-Hybrid-GGA
142	HYB_GGA_XC_LC_BLYP	RS-Hybrid-GGA
143	HYB_GGA_XC_LC_BLYPR	RS-Hybrid-GGA
144	HYB_GGA_XC_LC_BLYP_EA	RS-Hybrid-GGA
145	HYB_GGA_XC_LB07	RS-Hybrid-GGA
146	HYB_GGA_XC_RCAM_B3LYP	RS-Hybrid-GGA
147	HYB_MGGA_X_JS18,MGGA_C_TPSS	RS-Hybrid-MGGA
148	HYB_MGGA_X_MN12_SX,MGGA_C_MN12_SX	RS-Hybrid-MGGA
149	HYB_MGGA_X_M06_SX,MGGA_C_M06_SX	RS-Hybrid-MGGA
150	HYB_MGGA_XC_WB97M_V	RS-Hybrid-MGGA
151	HYB_MGGA_X_PJS18,GGA_C_LYP	RS-Hybrid-MGGA
152	HYB_MGGA_XC_LC_TMLYP	RS-Hybrid-MGGA
153	HYB_MGGA_X_M11,MGGA_C_M11	RS-Hybrid-MGGA
154	HYB_MGGA_X_REVM11,MGGA_C_REVM11	RS-Hybrid-MGGA
155	HYB_MGGA_XC_GAS22	RS-Hybrid-MGGA

2 Computational details

2.1 Wu-Yang method

We employ the Wu-Yang (WY) inverse Kohn-Sham (KS) method [5, 4, 3] to compute the KS exchange-correlation (XC) potential corresponding to a given input density. The input densities (ρ_{in}) are obtained from the *ab initio* FCI, CCSD(T), MP3, MP2, HF methods, and the hybrid GKS calculations. The inverse method is based on the unconstrained maximization of the WY functional $W_s[\psi_{det}, v(\mathbf{r})]$ which is defined as

$$W_s[\psi_{det}, v(\mathbf{r})] = 2 \sum_i^{N/2} \langle \phi_i | \hat{T} | \phi_i \rangle + \int d\mathbf{r} v_s(\mathbf{r}) [\rho(\mathbf{r}) - \rho_{in}(\mathbf{r})], \quad (1)$$

where ψ_{det} is the system's wavefunction, and ϕ_i are the KS orbitals. v_s is the effective KS potential constructed as

$$v_s(\mathbf{r}) = v_{ext}(\mathbf{r}) + v_0(\mathbf{r}) + v_{pbs}(\mathbf{r}), \quad (2)$$

where v_{ext} is the external potential, v_0 is the guide potential usually fixed as the Fermi-Amaldi potential, and v_{pbs} is the rest of the potential expanded in the auxiliary finite potential basis set. Once $v_s(\mathbf{r})$ is obtained, the XC potential can be computed in a straightforward way, such as

$$v_{xc}(\mathbf{r}) = v_0(\mathbf{r}) + v_{pbs}(\mathbf{r}) - v_h(\mathbf{r}) \quad (3)$$

where v_h is the Hartree potential.

In our calculations, the FCI and CCSD(T) reference electron densities are obtained using the Psi4 [6] routines. Their corresponding reference XC potentials, in turn, are calculated via the WY scheme using the *n2v* package with Psi4[6, 7] as the engine. The hybrid XC potentials are computed using the same WY inversion with the *n2v* and PySCF[8, 10] program package. In all the WY calculations, the lambda regularization parameter[4], which prevents nonphysical v_{xc} oscillations near the core, is set to 10^{-5} . In addition, the Trust-Exact optimization method with a convergence tolerance of 10^{-6} and the Fermi-Amaldi guide potential is employed to correct the asymptotic behavior of the XC potentials.

2.2 Grid and basis set convergence

To ensure that our results do not depend on the DFT grid and basis set used in the calculations, we have performed an extended analysis of such dependence. In our calculations, we use the DFT grid described by the Lebedev-Laiko quadrature formula as implemented in the PySCF package. The standard PySCF calculations used a predefined grid corresponding to level 5. To check how the results depend on the choice of the DFT grid, we also perform calculations using a larger DFT grid constructed with 131 radial and 4334 angular grid points (He_2 molecule). In Figure S1, we present the convergence of various errors concerning DFT grid size calculated for the He_2 molecule with the FCI reference. The qualitative behavior of all errors is almost identical. Thus, we conclude that the errors are well-converged w.r.t. grid size. A similar test was performed to check the basis set convergence of all errors. This is reported in Figure S2 for the case of He_2 molecule with the FCI reference, using an uncontracted aug-cc-pVTZ basis set [2] and a much larger uncontracted aug-cc-pV5Z basis set [1]. Also, here, the qualitative behavior of all errors is very similar despite the size of the basis set used in the calculations.

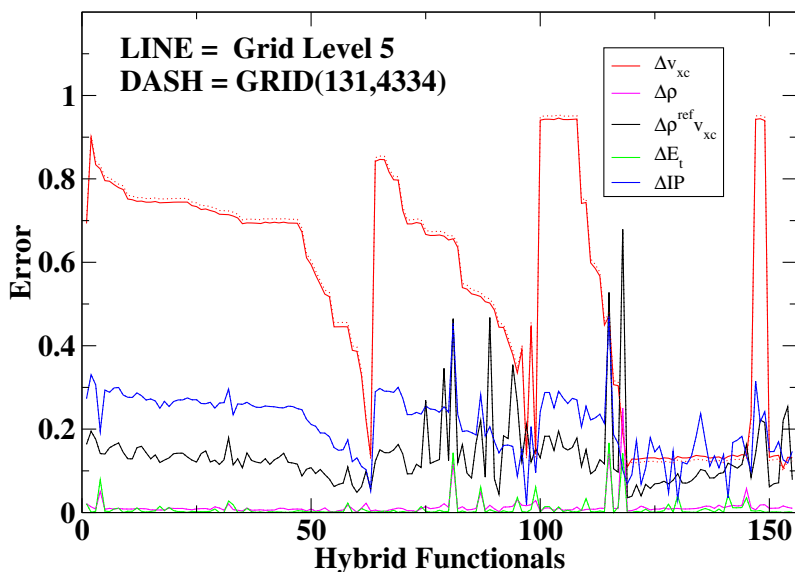


Figure S1: Errors calculated for two different DFT grid levels, 5 (Line) and (131,4334) (Dash), for He_2 and FCI reference. The IP-EOM-CCSD method is used as a reference to calculate IP error.

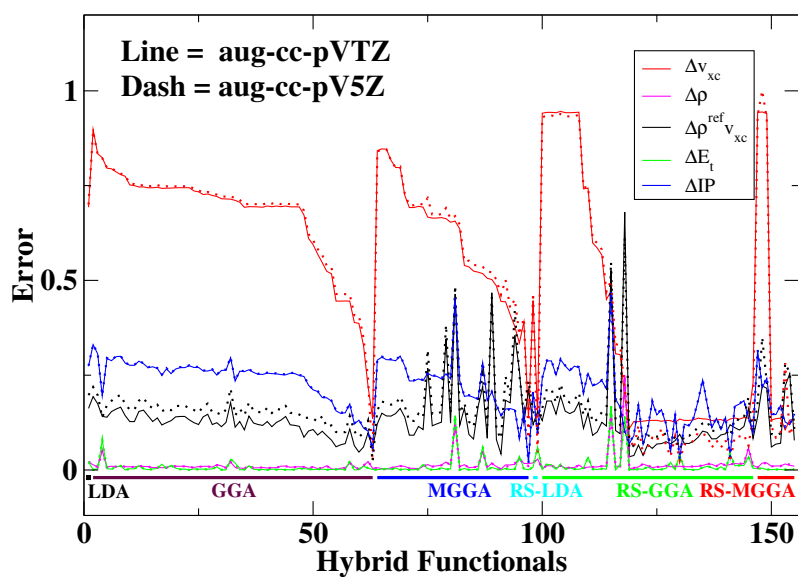


Figure S2: Errors calculated for He_2 molecule with FCI reference, using two different basis sets: uncontracted aug-cc-pVTZ (Line) and uncontracted aug-cc-pV5Z (Dash). The IP-EOM-CCSD method is used as a reference to calculate IP error.

3 The asymptotic behavior of Δv_{xc} error

Let us consider an atom with the reference v_{xc}^{ref} potential generated from the WY method. When $r \rightarrow \infty$, it behaves as $v_{xc}^{ref} \approx -\frac{1}{r} + C$ where C is a constant which emerges from the fact that XC WY potential can be computed up to a constant. On the other hand, the hybrid asymptotic behavior is governed by mutual semilocal and Hartree-Fock exchange contributions in the full XC energy expression as discussed in Ref. [9]. This could be in general written as $v_{xc} \approx -\frac{\alpha}{r} + (1 - \alpha)f(r) + C'$ where $f(r)$ denotes the asymptotic decay of the semilocal exchange potential (e.g., $f(r) = -\frac{1}{r^2}$ and $f(r) = e^{-r}$, for B88 and PBE exchange, respectively) and C' is the constant. Thus, the asymptotic behavior of $\delta v_{xc} = v_{xc}^{ref} - v_{xc}$ error is given by

$$\delta v_{xc} \approx \frac{\alpha - 1}{r} - (1 - \alpha)f(r) + C - C' . \quad (4)$$

If $\alpha = 1$ (100% HF contribution in the hybrid functional), then $\delta v_{xc} \approx C - C'$. Thus, a small (non-zero) systematic error still contributes to all integration grid points. This indicates, in turn, that δv_{xc} can take zero value only for the case when $v_{xc} = v_{xc}^{ref}$. On the other hand, if $\alpha = 0$, we have $\delta v_{xc} \approx -\frac{1}{r} - f(r) + C - C'$. Therefore, the Δv_{xc} error has a significant contribution from the asymptotic region, which governs the behavior of the error. This is also the case for all intermediate values of $\alpha \in (0, 1)$.

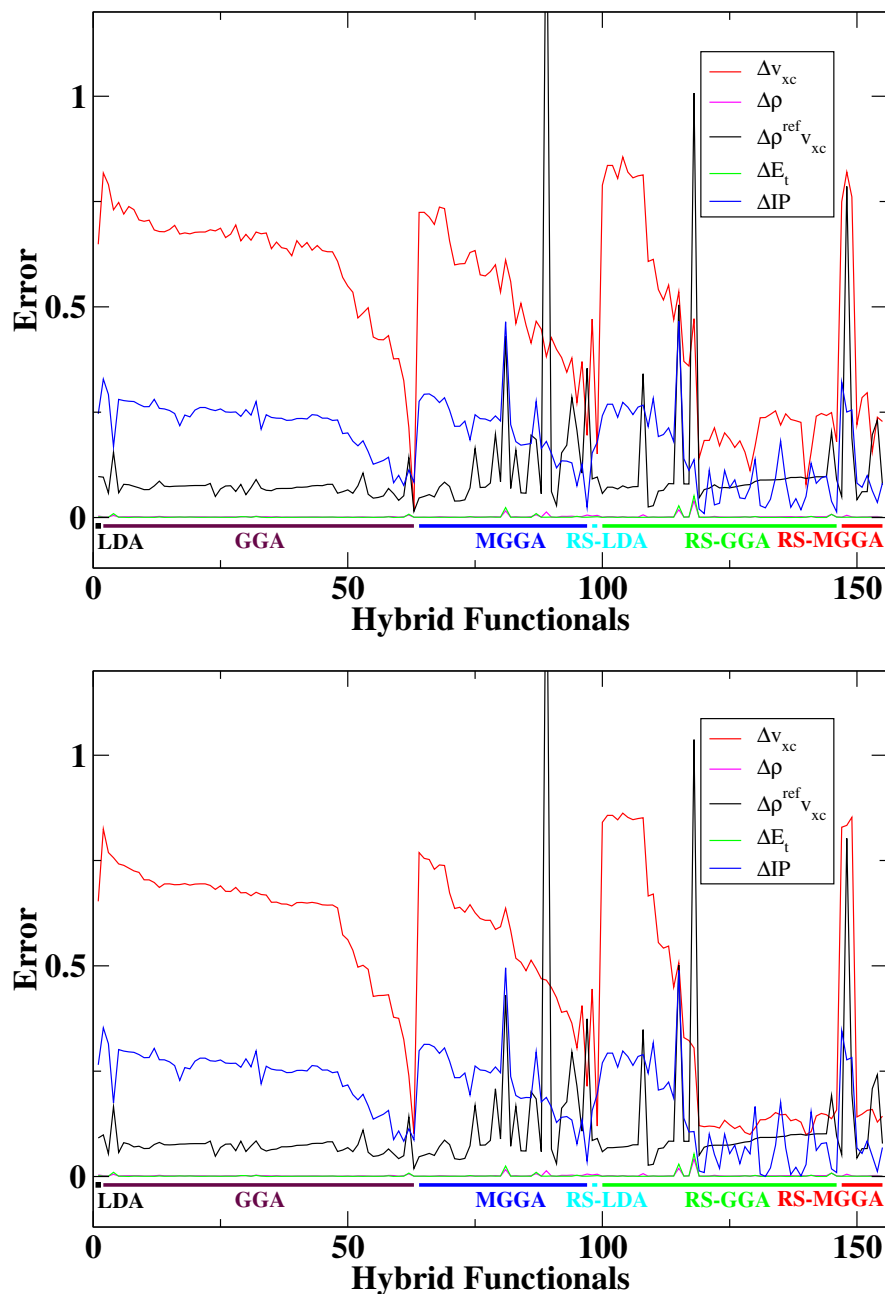


Figure S3: Errors defined by Eqs.(2)-(6) in the main manuscript calculated for Ar (top) atom and HCl (bottom) molecule with the CCSD(T) reference. The IP-EOM-CCSD method is used as a reference to calculate IP error. The X-axis corresponds to various hybrid functionals numbered and grouped according to the Tab. ST1.

S10

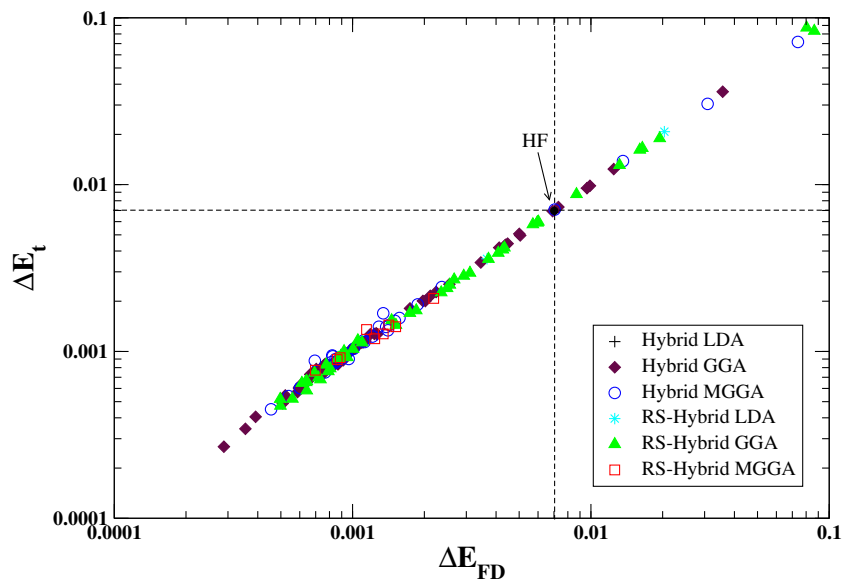


Figure S4: Average total energy error (ΔE_t) vs average functional-driven error (ΔE_{FD}) obtained for the CCSD(T) benchmark set. In both axes, the logarithmic scale is used.

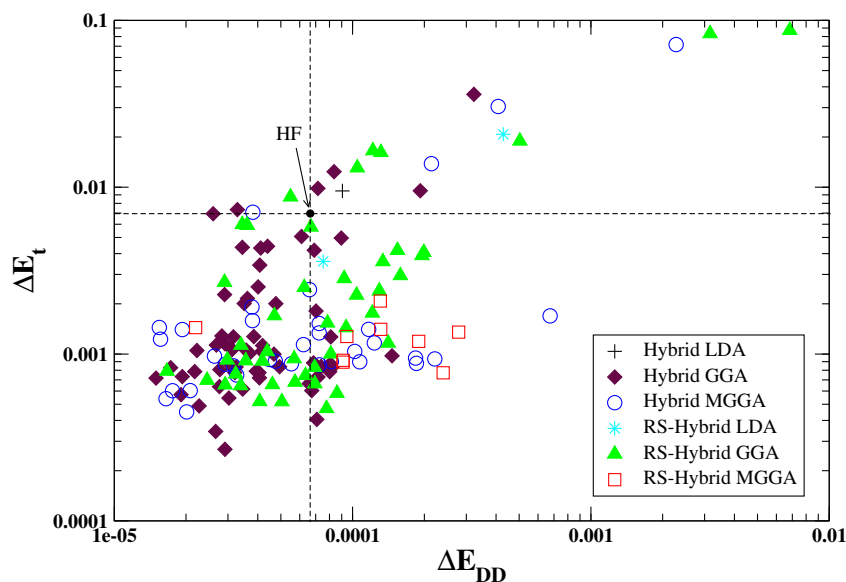


Figure S5: Average total energy error (ΔE_t) vs average density driven error (ΔE_{DD}) calculated for the CCSD(T) benchmark set. In both axes, the logarithmic scale is used.

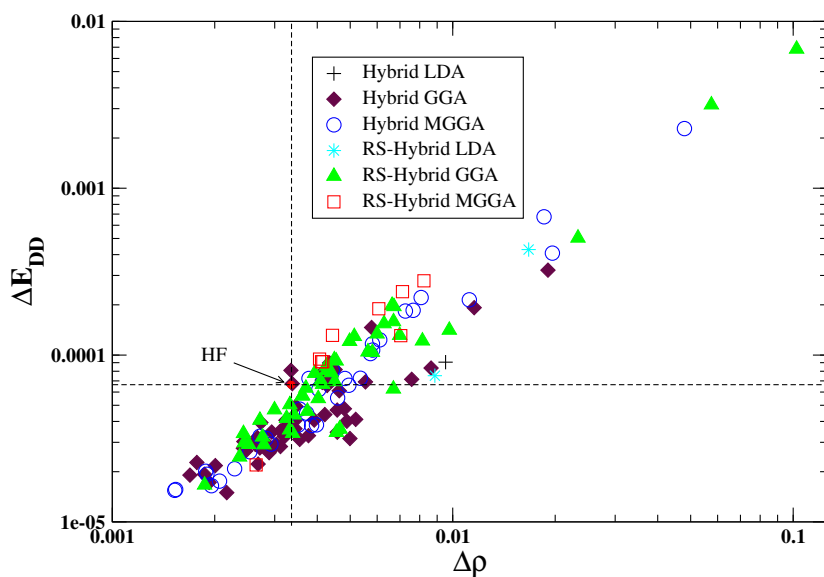


Figure S6: Average density-driven error (ΔE_{DD}) vs an average density error ($\Delta\rho$) obtained for CCSD(T) benchmark set. In both axes, the logarithmic scale is used.

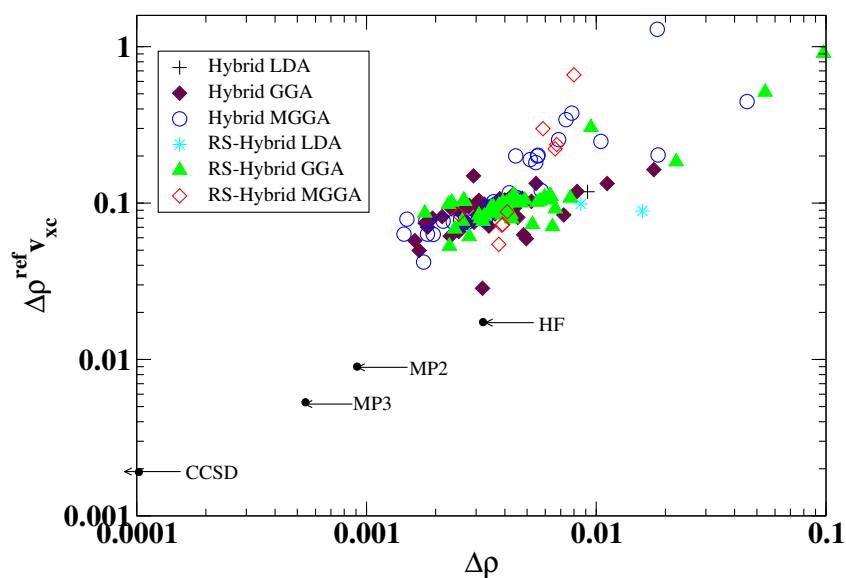


Figure S7: Average $\Delta\rho^{ref}_{v_{xc}}$ error vs average density $\Delta\rho$ error calculated for the CCSD(T) benchmark set. In both axes, the logarithmic scale is used.

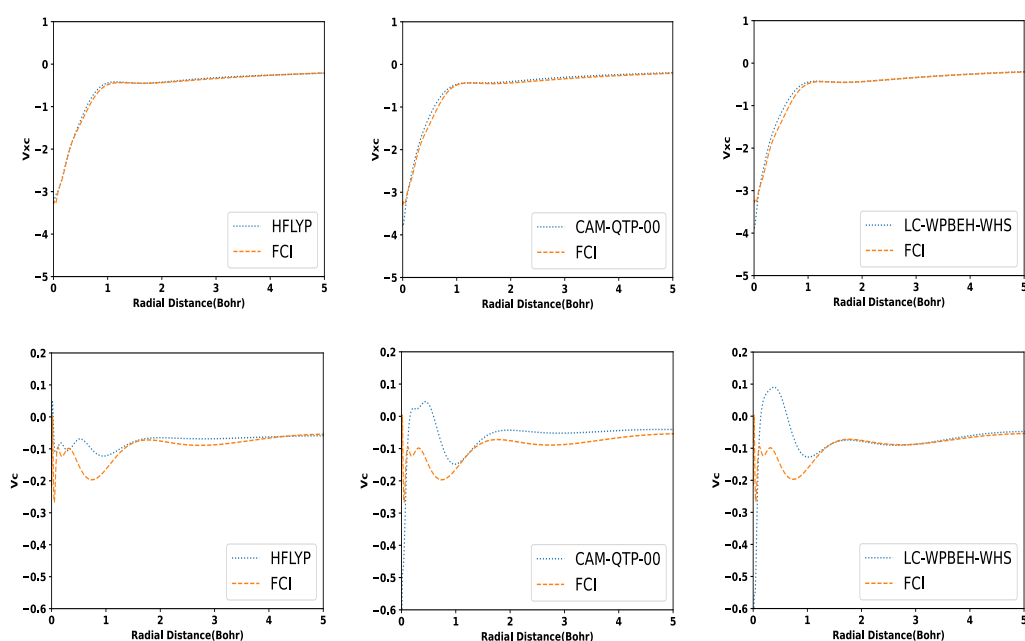


Figure S8: Exchange-Correlation potentials (Top Row) and correlation potentials (Bottom Row) computed using the Wu-Yang inverse method for Be atom for different functionals. The reference potentials are obtained from the FCI density.

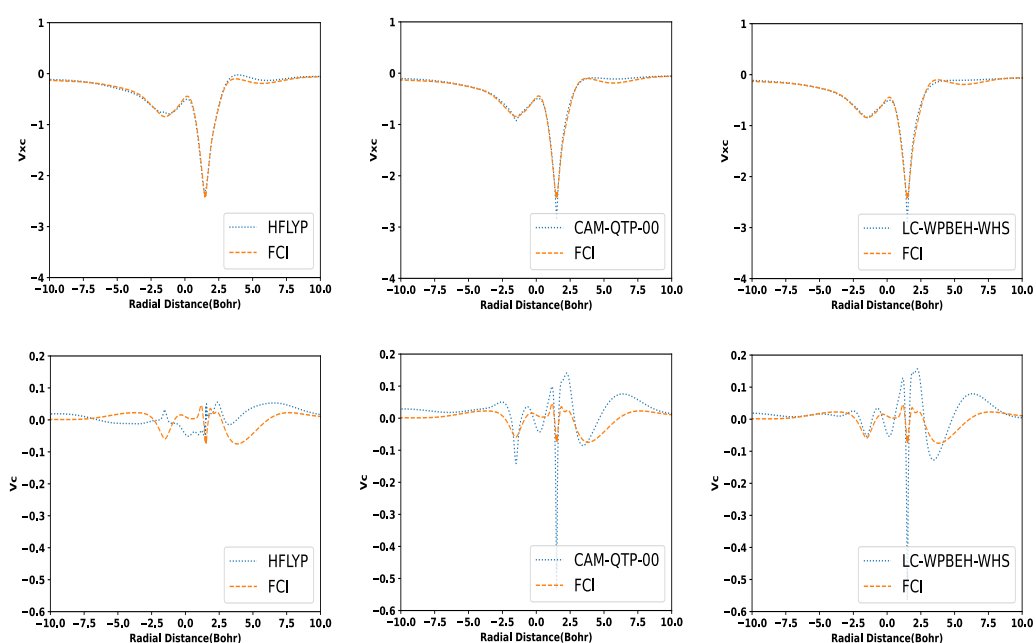


Figure S9: Exchange-Correlation potentials (Top Row) and correlation potentials (Bottom Row) computed using the Wu-Yang inverse procedure for LiH molecule for different functionals. The reference potentials are obtained from the FCI density.

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Chapter 3

UMK26: A New Global Hybrid XC Functional.

Vignesh Balaji Kumar, Szymon Śmiga, Rodrigo Araújo Mendes, Bogumiła Jezierska, Rodney Bartlett, and Ireneusz Grabowski, *On the Primary Role of Semi-Local and Exact-Exchange Difference in the Description of Correlation Effects in Hybrid Functionals*. (J. Chem. Theory Comput. XXX, 2026),
<https://doi.org/10.1021/acs.jctc.6c00843>

3.1 Introduction

To address the shortcomings of the Hybrid DFT approximations discussed in the previous chapter, we develop an effective procedure to develop hybrid functionals and propose the UMK26 global hybrid functional, which accounts for correlation effects present at the exchange-only level. The work addresses the authors’ observation that the vast contribution to physical quantities, such as the correlation potential and correlated densities, arises predominantly from the exchange approximation rather than from the correlation functionals. To explore this phenomenon, we investigate the effects of exchange-correlation (XC) differences between the Hartree-Fock and semi-local exchange, and their optimal tuning for accurate ionization potentials, a quantity directly related to the quality of the XC potential. The work is based on the Adiabatic Connection (AC)[90, 91, 92, 93, 94] formalism, which provides a rigorous mathematical foundation for the exchange-correlation approximation in KS-DFT.

The XC energy expression(Eq. 3.1) backed by the AC formalism can be expressed as:

$$E_{xc}^{\text{HYB}}[\rho] = E_{xc}^{\text{DFA}}[\rho] - \frac{1}{n}(E_x^{\text{DFA}}[\rho] - E_x^{\text{EXX}}) \quad (3.1)$$

Where E_{xc}^{HYB} is the exchange-correlation energy from the hybrid DFT functional. E_x^{EXX} is the exact exchange energy and E_x^{DFA} is the exchange energy from the exchange functional.

Eq. 3.1 is significant and formed the rationale behind the construction of Hybrid Density Functional Theory[85], and the role of n can be scientifically explained through the perturbation theory[85].

Reformulating Eq. 3.1 We arrive at Eq. 3.2 as:

$$E_{xc}^{\text{HYB}}[\rho] = E_x^{\text{EXX}} + \frac{n-1}{n}(E_x^{\text{DFA}}[\rho] - E_x^{\text{EXX}}) + E_c^{\text{DFA}}[\rho] . \quad (3.2)$$

Eq. 3.2 is then expressed as Eq. 3.3, with $\gamma = \frac{n-1}{n}$

$$E_{xc}^{\text{UMK}}[\rho] = E_x^{\text{EXX}} + \gamma(E_x^{\text{DFA}}[\rho] - E_x^{\text{EXX}}) + E_c^{\text{DFA}}[\rho] , \quad (3.3)$$

Eq. 3.3 defines the new effective procedure for constructing a hybrid functional. We use B88[36] for the semi-local exchange and LYP[95] for the correlation part. We rely on ΔIP error introduced in the previous chapter 2 to optimize the γ underpinning the importance of IPs as established by Bartlett’s IP theorem and Correlated Orbital Theory(COT)[79]. The tuning resulted in an optimum γ value of 0.25. We name the new hybrid functional UMK26 (Uniwersytet Mikołaja Kopernika w Toruniu).

The resulting UMK26 global hybrid functional is:

$$\text{UMK26} = 0.75\text{HF} + 0.25\text{B88} + \text{LYP} \quad (3.4)$$

To check the generality of the construction defined in Eq. 3.3, we also develop a pure exchange-only functional UMK26x, and following the same optimization procedure we obtained new UMK26x functional:

$$\text{UMK26x} = 0.9\text{HF} + 0.1\text{B88} \quad (3.5)$$

We base our evaluation on various quantities, including the correlation potential, correlated densities, and error metrics discussed in Chapter 2, HOMO and valence ionization potentials, TDDFT excitation energies, electron-integer discontinuity, the GMTKN55[83], SLIM20[96] benchmark set, and dissociation curves of charged species.

3.2 The Most Important Findings of the Study

As a preliminary step, the work compares the correlation potentials and correlated densities computed from the full-hybrid and exchange-only (X-only) parts of the same hybrid functional. One can readily observe that most contributions to these quantities arise from the pure exchange component, indicating the significant role of the exchange part in the correlation effects of the hybrid functional.

The analysis on the error metric from chapter 2 for full and X-only hybrid approximations revealed that error in potential and density barely change, whereas one can clearly observe a significant change for total energy error ΔE_t .

The correlation energy analysis between the correlation energy computed via two schemes: 1) From the difference between the KS total energy and HF energy (computed using KS orbitals), and 2) The correlation energy from the correlation energy expression of the hybrid approximation, was analyzed for popular hybrid functionals such as the B3LYP[97], and LC- ω PBE.[49] The analysis clearly indicated that the error in the correlation energy computed via the correlation functional expression is larger than the KS-HF difference. This is another indicator supporting the exploration of exchange differences to improve hybrid DFT.

We show that a large contribution to the qualitative features of correlation in hybrid DFAs does not originate primarily from the semilocal correlation functional, but instead from the difference between the semilocal exchange and exact-exchange contributions.

The UMK26 global hybrid functional, developed using exchange-difference tuning, demonstrated significant improvement over the well-known and conventional hybrid functionals considered. UMK26 possesses superior efficiency in describing correlation potential and correlated density compared to other known hybrid functionals studied.

The evaluation of HOMO and valence ionization potentials revealed the clear edge UMK26 possesses compared to other global hybrid functionals. This test set contains 401 reference ionization potentials from 63 molecular systems. The G_0W_0 evaluation also revealed a similar enhancement in IPs. This is a direct demonstration of improving orbital energies through improved description of the XC potential.

An evaluation for predicting accurate charge-transfer excitations in TDDFT was performed, and UMK26 showed a clear edge in accuracy over other global hybrid functionals and performed on par with range-separated hybrid functionals such as the QTP family of functionals, which were developed based on ionization potentials.

UMK26 demonstrates greater efficiency in overcoming self-interaction errors, describing correlation potential, correlated densities, and charge-transfer excitations. Although UMK26 does not show a general improvement across thermochemical benchmarks, its simple construction highlights the crucial need to address this exchange-level correlation effect when constructing XC functionals.

Most importantly, the work presents a decomposed analysis of the exchange-correlation components in Hybrid DFAs for diverse quantum-chemical properties.

3.3 Conclusions

The study centers on the findings of chapter 2 and further observations of correlation effects from the exchange components of the hybrid functional approximation, and addresses them by developing a new global hybrid XC functional, UMK26, presenting its implications for diverse quantum chemical properties.

We have shown that the dominant qualitative features of correlation in hybrid DFAs do not arise primarily from the semilocal correlation functional itself, but instead from the difference between the semilocal exchange and exact-exchange contributions.

Based on this analysis, we propose an interpretable construction principle for hybrid functionals in which the difference between semilocal and exact-exchange is scaled in a controlled way.

One can note a straightforward improvement in quantities such as correlation potential and correlated densities for UMK26. An appropriate shape of the correlation potential and the correlated density is essential for the accurate prediction of chemical properties. Here, we show how an IP-based fitting procedure can enhance the topological features of v_c and ρ_c . Further enhancement in HOMO and valence ionization potentials is demonstrated employing KS orbital energies and G_0W_0 .

The ability to accurately describe charge-transfer excitations, which are crucial in studies involving excited states and photoinduced applications, was evaluated using TDDFT. UMK26 demonstrated significant accuracy on par with well-known range-separated functionals and outperformed conventional global hybrid functionals considered.

It was observed that UMK26 has a much lower error on the SIE4x4 data set, which quantifies electron self-interaction error. This is further confirmed by the dissociation curve analysis of charged systems, in which UMK26 outperforms well-known hybrid functionals. It was also observed from the GMTKN55 SLIM20 benchmark test

analysis that, though UMK26 performs on par with other well-known global hybrid approximations in terms of the WTMAD-2 metric, it does not demonstrate general improvement across different thermochemical sets.

While the accurate asymptotic of the potential has the $-\frac{1}{r}$ form, UMK26’s asymptotics possess $-\frac{0.75}{r}$ form. This can be addressed within the range-separated formalism, which provides additional flexibility through long- and short-range Hartree-Fock coefficients. Further improvement is possible in the range-separated formalism and incorporating AI/ML tools in XC functional development, which is gaining wide popularity in the current era.

The proposed procedure opens a perspective for the rational development of future hybrid approximations, including improved global hybrids, range-separated ones, and double-hybrid functionals built on the same physical principles.

Primary Role of Semi-Local and Exact-Exchange Difference in the Description of Correlation Effects in Hybrid Functionals

Published as part of Journal of Chemical Theory and Computation special issue "100 Years of Quantum Mechanics - All About Molecules".

Vignesh Balaji Kumar, Szymon Śmiga,* Rodrigo Araújo Mendes, Bogumiła Jezierska, Rodney Bartlett, and Ireneusz Grabowski*



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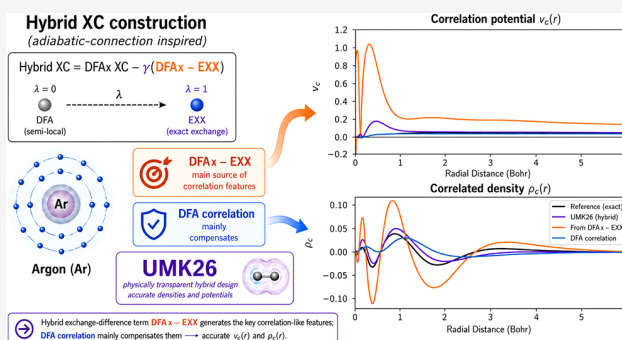
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ABSTRACT: Hybrid density functional approximations are among the most widely used electronic-structure methods, yet the physical origin of their representation of correlation effects remains incompletely understood. In this work, we analyze correlation in hybrid functionals from the perspectives of Kohn–Sham exchange–correlation potentials, correlated densities, and energy-related observables. We show that the dominant qualitative features of correlation in hybrid DFAs do not arise primarily from the semilocal correlation functional itself, but instead from the difference between the semilocal exchange and exact-exchange contributions. This exchange-difference term is essential for restoring the physically correct structure of the correlation component of the exchange–correlation potential and the corresponding correlated density, whereas the semilocal correlation part acts mainly as a compensating contribution in the core and valence regions. Based on this analysis, we propose an interpretable construction principle for hybrid functionals in which the semilocal/exact-exchange difference is scaled in a controlled way. As a proof of concept, this methodology yields the simple global hybrid UMK26 functional. Despite its uncomplicated global-hybrid form, the functional produces correlation potentials and correlated densities in good agreement with CCSD(T) references, delivers accurate ionization potentials from orbital energies, and yields very good charge-transfer excitation energies, performing on a comparable footing with several recently proposed range-separated hybrids. Although UMK26 is not uniformly optimal across all thermochemical benchmarks, it performs particularly well for self-interaction-sensitive systems and provides a physically transparent route for the rational design of future hybrid density functionals.



1. INTRODUCTION

The Kohn–Sham density functional theory (KS-DFT)¹ is one of the most popular computational methods, offering a cheaper and faster alternative to traditional *ab initio* wave function approaches. The key element of this methodology is the exchange–correlation (XC) energy functional, which accounts for many-body effects beyond the Hartree approximation and the noninteracting kinetic energy. Of course, the correct formula for XC functionals remains unknown and will likely remain so, despite the enormous effort put into their development. However, to date, many practical classes of density functional approximations (DFAs) have been developed.^{2,3} Among them, the so-called hybrid (HYB) class of DFAs⁴ are common in standard KS-DFT applications, offering the best compromise between accuracy and efficiency.^{5–10} In general, HYB XC functionals (E_{xc}^{HYB}) are defined as a mixture of a fraction of the Hartree–Fock (HF) exact-exchange (EXX)

energy (E_x^{EXX}) with additional amounts of semilocal exchange and correlation functionals, usually defined at LDA, GGA, and meta-GGA levels.¹¹ Formally, they can be defined using the density-fixed adiabatic connection (AC) formalism.^{4,12,13} To recall, the AC XC functional definition is based on the coupling constant ($\alpha \geq 0$) integral formula^{14–19}

$$E_{xc}[\rho] = \int_0^1 d\alpha W_{xc}^\alpha[\rho] \quad (1)$$

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with integrand defined as $W_{xc}^\alpha[\rho] = \langle \Psi^\alpha[\rho] | \hat{V}_{ee} | \Psi^\alpha[\rho] \rangle - U[\rho]$, where $\hat{V}_{ee}$ is the Coulomb operator, $U[\rho]$ is the Hartree energy, and $\Psi^\alpha[\rho]$ is the α -dependent ground state electronic wave function, which yields for any value of α the density $\rho(\mathbf{r})$. eq 1 connects a noninteracting KS single particle determinant ($\alpha = 0$) with a real, fully interacting one ($\alpha = 1$). This provides the exact and formal definition of the XC functional. Two limiting cases of the $W_{xc}^\alpha[\rho]$ expansion are essential for the HYB DFA construction, namely the $\alpha \rightarrow 0$ and the full interacting limit at $\alpha \rightarrow 1$. Using those, one can construct the general approximate integrand formula, which defines the HYB class of DFAs

$$W_{xc,\alpha}^{\text{HYB}}[\rho] = W_{xc,\alpha}^{\text{DFA}}[\rho] - (E_x^{\text{DFA}}[\rho] - E_x^{\text{EXX}})(1 - \alpha)^{(n-1)} \quad (2)$$

where $E_x^{\text{DFA}}[\rho]$ is the semilocal DFA exchange energy, and $W_{xc,\alpha}^{\text{DFA}}[\rho]$ the semilocal DFA coupling-constant integrand derived from the Levy-Perdew scaling relation²⁰

$$W_{xc,\alpha}^{\text{DFA}}[\rho] = E_x^{\text{DFA}}[\rho] + 2E_c^{\text{DFA}}[\rho_{1/\alpha}]\alpha + \frac{\partial E_c^{\text{DFA}}[\rho_{1/\alpha}]}{\partial \alpha} \alpha^2 \quad (3)$$

with $\rho_{1/\alpha}(\mathbf{r}) = \alpha^{-3}\rho(\mathbf{r}/\alpha)$ being the coordinate-scaled density. Equation 2 correctly reduces to the E_x^{EXX} energy expression when $\alpha = 0$ and to $W_{xc,\alpha}^{\text{DFA}}[\rho]$ at $\alpha = 1$, where this approximation is most trustworthy.¹³ The parameter $n \in \langle 0, \infty \rangle$ is the curvature parameter which controls the shape of the approximate AC integrand.

Using eq 1 and taking into account that close to the upper limit ($\alpha = 1$) eq 3 can be approximated by $W_{xc}^1[\rho] \approx E_x^{\text{DFA}}[\rho] + 2E_c^{\text{DFA}}[\rho]$, one obtains¹³

$$E_{xc}^{\text{HYB}}[\rho] = E_{xc}^{\text{DFA}}[\rho] - \frac{1}{n}(E_x^{\text{DFA}}[\rho] - E_x^{\text{EXX}}) \quad (4)$$

which gives the general HYB XC energy expression, where the $1/n$ factor controls the semilocal and HF-exchange difference contributions in the HYB DFA. For instance, PBE0,²³ with 25% exact exchange, corresponds to $n = 4$, while B3LYP,²⁴ with 20% exact exchange, corresponds to $n = 5$. The role of the exact-exchange mixing coefficient has recently been explored in the context of machine-learning (ML) assisted HYB DFA construction²⁵ showing that the adaptive system-dependent exact-exchange fraction can lead to improved quality of HYB DFA predictions.

Conceptually this, is illustrated in Figure 1 where the gray area corresponds to the AC XC functional eq 1, whereas the orange dashed one represents the HYB XC energy defined via

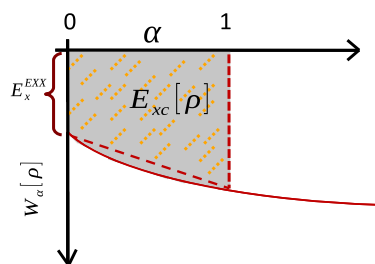


Figure 1. Graphical representation of the adiabatic connection formula.¹⁸ The gray area corresponds to AC XC energy (see eq 1). The red dashed line represents the approximated integrand formula given by eq 2, whereas the orange dashed area represents the HYB DFA XC energy defined by eq 4.

eq 4. It is important to stress that the exchange energy difference term appearing in eq 4 is not system-specific, but follows directly from the AC construction of hybrid functionals.

Although the HYB DFAs are developed solely within the KS framework, their practical implementation is performed within the generalized KS (GKS) framework,^{26–28} where the XC potential remains nonlocal. This is due to the orbital dependence of the nonlocal HF exact-exchange energy term. This is also one of the reasons why the KS HYB XC potentials are not typically investigated during functional development. We recall, however, that these local XC potentials are well-defined quantities entering the KS equations directly.^{29,30} In addition to many other necessary features, an XC functional approximation should exhibit an accurate description of the KS XC potential. The good performance of an XC functional for some property, e.g., the total energy, without a correct XC potential, is artificial. Applications of such XC approximations are subject to numerous practical if-else conditions, which are among the present and long-term challenges faced by DFT.^{17,31–33}

As shown in a recent study,^{29,30,34} hybrid functionals can provide reasonably accurate local XC potentials within the KS scheme via inverse procedures.²⁹ Moreover, it was shown^{30,34} that the correlation functionals (E_c^{HYB}), which can be defined for any HYB XC approximation as

$$E_c^{\text{HYB}}[\rho] = E_{xc}^{\text{HYB}}[\rho] - E_x^{\text{EXX}} \quad (5)$$

give very physical correlation potentials, capable of correctly describing the quantum shell oscillations in the high-level reference data for atoms and molecules, unlike other semilocal functionals.^{35,36} Thus, we have recently developed a critical methodology for evaluating the quality of HYB XC DFA, where the KS XC potentials, together with other quantities,³⁰ serve as a comprehensive tool to assess the quality of existing and new HYB approximations.

We also note that the local XC potential v_{xc} in DFT can be viewed as a local counterpart of the optical potential, namely, the self-energy $\Sigma(E)$ entering the Dyson equation for the one-particle Green's function.^{37,38} Unlike v_{xc} , $\Sigma(E)$ is generally nonlocal and energy dependent. The two descriptions are formally connected through the Sham–Schlüter equation,³⁹ which determines a local potential reproducing the Green's-function density.³⁸ In the correlated-orbital formulation discussed by Bartlett,⁴⁰ incorporating coupled-cluster theory, removes the explicit frequency dependence and leads to the IP- and EA-EOM-CC one-particle picture. Projection of this correlated-orbital theory onto DFT yields QTP functionals satisfying the corresponding correlated-orbital conditions.^{40,41} The present work concerns the static local KS/GKS representation of correlation and does not calculate the full energy-dependent self-energy.

In the present study, we examine how correlation effects are represented in the XC, exchange-only, and semilocal correlation parts of the KS potentials and energies within the HYB class of functionals, and how these representations affect other key quantities, including correlated densities and ionization potentials (IPs). We show that the semilocal and HF-like exchange-energy difference terms appearing in eqs 2 and 4 play a central role in accurately describing correlation effects in HYB functionals, at both the potential and electron-density levels.

Table 1. Correlation Energies (in E_h) for Several Systems Computed for PBE0 HYB Functional Using Eq 7 (Third Column) and PBE Semi-Local Correlation Energy Expression (Fourth Column) using Self-Consistent PBE0 Reference^a

systems	CCSD(T)	eq 7	$E_c^{\text{PBE}}[\rho]$	$E_c^{\text{XDiff}}[\rho]$
He	−0.0411819	−0.0341513	−0.041400	0.0072487
H ₂	−0.0404878	−0.0358609	−0.0432167	0.0073558
Be	−0.088351	−0.0649265	−0.0856687	0.0207422
He ₂	−0.082365	−0.0683034	−0.0827999	0.0144965
Ne	−0.3621118	−0.3295189	−0.3484019	0.018883
H ₂ O	−0.3509719	−0.3253928	−0.3260439	0.000651
HF	−0.3644942	−0.3359948	−0.3363827	0.000388
NH ₃	−0.3222876	−0.3004125	−0.3154617	0.0150492
Mg	−0.2189615	−0.3607493	−0.4098516	0.0491023
CO	−0.5025411	−0.4583556	−0.4494995	−0.008856
N ₂	−0.5173779	−0.4699707	−0.4525074	−0.017463
Ar	−0.4433619	−0.5764346	−0.7055727	0.1291381
C ₂ H ₆	−0.534443	−0.5040304	−0.5605092	0.056479
HCl	−0.4369698	−0.5748036	−0.6873607	0.1125571
Ne ₂	−0.7244349	−0.6593054	−0.6968715	0.037566
Cl ₂	−0.8398284	−1.1247353	−1.3285813	0.203846
MAE		0.065	0.090	
MARE[%]		18.49	20.32	

^aThe last column presents the scaled energy difference. The MAE (in E_h) and MARE are calculated with respect to CCSD(T) reference data (second column). All calculations have been performed in the uncontracted aug-cc-pVQZ basis set.

Building on this insight, we then propose a methodology for the interpretable construction of XC DFAs, which we use to develop a global hybrid XC functional that performs remarkably well for the IPs and charge transfer (CT) excitation energies of a wide range of species.

2. METHODOLOGY

We start from reformulating eq 4 into the following form

$$E_c^{\text{HYB}}[\rho] = E_c^{\text{EXX}} + \frac{n-1}{n}(E_c^{\text{DFA}}[\rho] - E_c^{\text{EXX}}) + E_c^{\text{DFA}}[\rho] \quad (6)$$

The above representation, together with eq 5, allows the correlation HYB functional to be written as

$$E_c^{\text{HYB}}[\rho] = \frac{n-1}{n}(E_c^{\text{DFA}}[\rho] - E_c^{\text{EXX}}) + E_c^{\text{DFA}}[\rho] = E_c^{\text{XDiff}}[\rho] + E_c^{\text{DFA}}[\rho] \quad (7)$$

where $E_c^{\text{XDiff}}[\rho]$ explicitly stands for the difference of the exchange-only DFA functional and HF-like one, scaled by $(n-1)/n$ factor. For a global hybrid, the fraction of exact exchange (a_{EXX}) is connected with the scaling prefactor of the exchange-difference contribution as $(n-1)/n = 1 - a_{\text{EXX}}$. Thus, increasing the amount of exact exchange directly reduces the E_c^{XDiff} contribution, which vanishes in the limit of 100% exact exchange. A similar construction can also be applied to the range-separated^{42,43} (RS) hybrid DFAs.

In the present study, we can consider two key cases of eq 6:

- for the $n \neq 1$ case, we see that the HYB correlation functional $E_c^{\text{HYB}}[\rho]$ consists of two separable contributions: one, which depends solely on exchange-only terms ($E_c^{\text{XDiff}}[\rho]$), and the standard semilocal correlation functional ($E_c^{\text{DFA}}[\rho]$).
- for $n = 1$, eq 6 reduces to $E_c^{\text{HYB}}[\rho] = E_c^{\text{EXX}} + E_c^{\text{DFA}}[\rho]$ which incorporates 100% of EXX energy, whereas the correlation term is represented solely by the semilocal approximation ($E_c^{\text{DFA}}[\rho]$). In some cases, this con-

struction can outperform the HF/EXX method's predictions.^{44–46} However, from a broader perspective, it suffers from a lack of compatibility between exact-exchange and semilocal correlation. This aspect will be discussed in more detail later.

In both cases, we investigate the effects of electron correlation by examining KS correlation potentials and correlated densities calculated for several HYB DFAs. The correlated density is defined as^{35,36,47}

$$\rho_c(r) = \rho^{\text{method}}(r) - \rho^{\text{xref}}(r) \quad (8)$$

where ρ^{xref} is the density obtained from the exact-exchange (xref = EXX) and HF (xref = HF) calculations for KS-DFT and conventional WFT methods, respectively. In the case of atoms, we consider difference radial-density (DRD)^{35,48} distributions defined as $\text{DRD}(r) = 4\pi r^2 \rho_c(r)$. In turn, correlation potentials in our considerations are defined as

$$v_c(r) = v_{xc}^{\text{method}}(r)[\rho^{\text{method}}] - v_x^{\text{HF}}(r)[\rho^{\text{HF}}] \quad (9)$$

i.e., the difference between the XC potential obtained for a given method and that obtained from HF density. Both potentials are computed using the Wu-Yang (WY)⁴⁹ inverse method. All calculations have been performed using an identical computational setup as in ref 30. for the (coupled cluster singles-doubles with perturbative triples) CCSD(T)⁵⁰ benchmark set.

We note that full analytical analysis of the corresponding local potentials is highly challenging, because the exact-exchange contribution is orbital-dependent and the associated local KS potential must be obtained through the optimized-effective-potential formalism or by inverse procedures such as the Wu-Yang method. The present numerical analysis, therefore, relies on high-quality reference densities and accurate inversion techniques, while the formal origin of the exchange-difference in eq 7 follows directly from the hybrid AC expression.

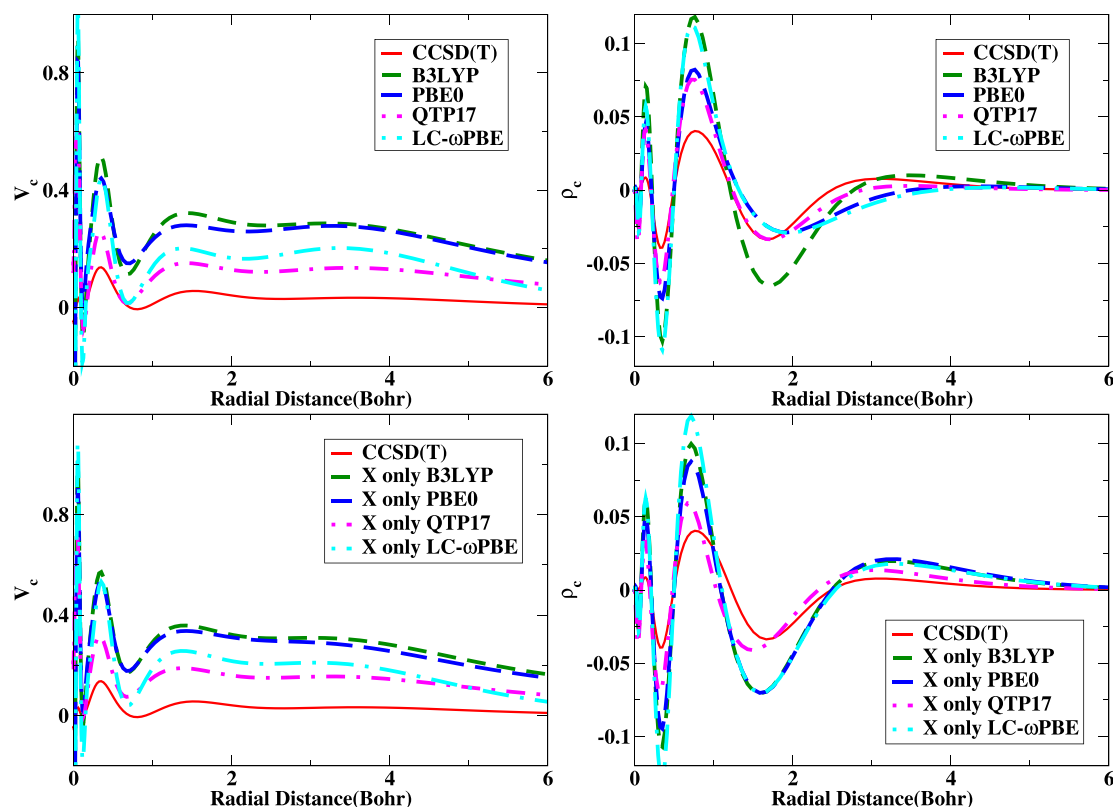


Figure 2. Correlation potentials (eq 9) and correlated densities (eq 8) of the Ar atom, calculated for several popular HYB DFAs with (top panel) and without (bottom panel) semilocal DFA correlation functional ($E_c^{\text{DFA}}[\rho]$) in eq 6.

3. RESULTS

We begin our considerations with the construction for $n \neq 1$ in eq 6. To this end, we have assessed four commonly applied global HYB DFAs, namely PBE0,²³ B3LYP,²⁴ QTP17,⁵¹ and one RS HYB LC- ω PBE⁵² variant. First, we turn our attention to the correlation energies calculated using eq 7, which usually provide more accurate results than those obtained from the semilocal DFA formula. This trend is illustrated in Table 1, where we report the correlation energies for several systems computed using the representative PBE0 hybrid DFA. As can be observed, the semilocal component typically overestimates the correlation energy (MAE = 0.090 E_h , MARE = 20.32%). In contrast, the $E_c^{\text{XDiff}}[\rho]$ contribution, generally positive in value, mitigates this overestimation, resulting in improved hybrid correlation energies (MAE = 0.065 E_h , MARE = 18.49%). Therefore, this term should not be interpreted as an uncontrolled double counting of correlation, but rather as a compensating contribution. Similar trends are observed for the other two functionals tested, i.e., B3LYP and LC- ω PBE, reported in the Supporting Information (SI) (see Tables S2–S3).

Next, in Figure 2, we report the correlation potentials and correlated densities of the Ar atom, obtained with and without the semilocal correlation functional $E_c^{\text{DFA}}[\rho]$ in eq 6, presented in the top and bottom panels, respectively. Similar plots for a few other systems (Be, Ne, CO, and H₂O) are shown in the SI file (see Figures S1–S4). Inspecting the fully correlated case (top panel) in Figure 2, one can note that all the investigated functionals yield correlation potentials that are qualitatively comparable to the CCSD(T) reference data.³⁰ On the other hand, the potentials are overestimated, leading to significant

errors in the asymptotic region. The only exception is observed for LC- ω PBE DFA, where we note improved behavior due to its correct long-range description, i.e., 100% nonlocal HF exchange. This was also reported in reference.^{30,34} Similar observations apply to the correlated densities, which are obtained from fully self-consistent KS-DFT GKS calculations. All correlated densities are in phase with the reference CCSD(T) data, although the quantitative agreement varies for all DFAs. The same behavior is visible for other atomic systems reported in SI. Slightly worse behavior is observed in molecular systems, with a more significant deviation in the core regions, consistent with other studies.^{34,36,53}

In the bottom panel of Figure 2, we present the correlation potentials and correlated densities obtained from the self-consistent, exchange-only (X-only) HYB DFA calculations i.e., the semilocal DFA ($E_c^{\text{DFA}}[\rho]$) term is fully neglected in eq 6. Inspection of Figure 2 reveals that

- (i) the correlation potentials and correlated densities obtained from the X-only case are qualitatively comparable to the reference data and to the full XC counterpart. This indicates that the $E_c^{\text{XDiff}}[\rho]$ term in eq 7, which is mostly positive and formally depends on the X-only terms, carries a large portion of the correlation effects. It is evident that it plays a crucial role in restoring the correct shape and qualitative behavior of the correlation potential and correlated densities in the HYB DFAs
- (ii) in principle, for the true exact density dependent exchange DFT functional, the $E_c^{\text{XDiff}}[\rho]$ term as well as its functional derivative should be exactly zero. This is, for example, the case for the *ab initio* OEP DFT^{54–56}

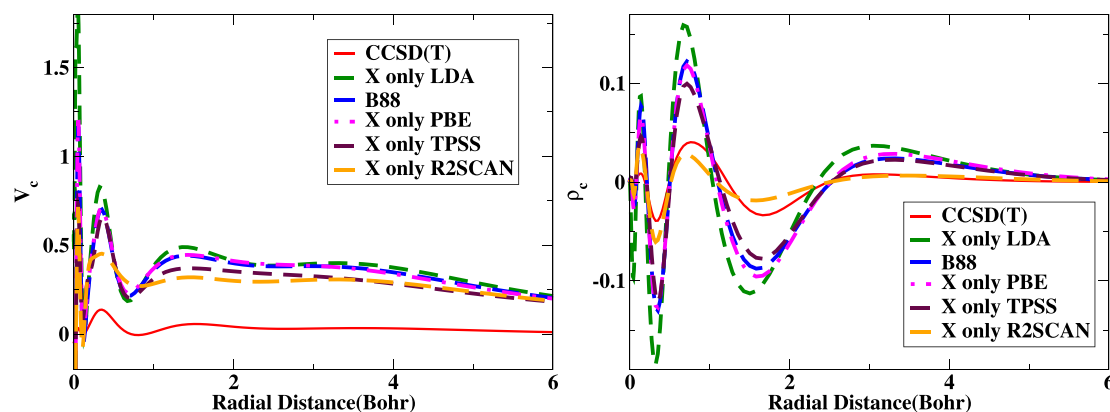


Figure 3. Correlation potentials (eq 9) and correlated densities (eq 8) of the Ar atom computed from standard semilocal X-only DFA functionals.

Table 2. Average Errors for Different Physical Quantities for Full and Exchange-only Parts of Hybrid Functionals^a

	XC						X-only					
	Δv_{xc}	Δv_c	$\Delta \rho$	ΔE_t	ΔIP	$\Delta \rho^{ref} v_{xc}$	Δv_{xc}	Δv_c	$\Delta \rho$	ΔE_t	ΔIP	$\Delta \rho^{ref} v_{xc}$
PBE0	0.667	9.973	0.002	0.001	0.259	0.092	0.671	10.060	0.004	0.008	0.32	0.106
B3LYP	0.713	10.710	0.004	0.002	0.276	0.103	0.72	10.773	0.004	0.008	0.346	0.111
QTP17	0.334	5.118	0.005	0.004	0.085	0.059	0.343	5.275	0.006	0.014	0.157	0.073
LC- ω PBE	0.118	1.863	0.004	0.001	0.057	0.102	0.130	2.063	0.005	0.006	0.118	0.117
HFLYP	0.088	1.266	0.003	0.001	0.099	0.029	0.092	1.0	0.003	0.007	0.061	0.017
UMK26	0.223	3.544	0.002	0.001	0.035	0.034	0.220	3.301	0.002	0.007	0.084	0.038
UMK26x							0.103	1.528	0.003	0.007	0.038	0.025

^aThe error metrics are elaborated in ref 30.

class of XC approximations, which has been discussed to some extent in the literature.^{35,36} Thus, the semilocal and HF exchange difference ($E_c^{XDiff}[\rho]$) can be used not only as a measure of the inaccuracy of the semilocal exchange energy approximation but also as an indicator of the accuracy of the exchange potential which, as we can observe here, evidently includes correlation effects too.

To verify that this trend persists for standard exchange-only DFA functionals, Figure 3 shows v_c and the DRDs for the Ar atom, obtained from self-consistent exchange-only calculations with the most commonly used exchange functionals, namely LDA, PBE, B88, TPSS, and R2SCAN, using eqs 8 and 9. In this case, correlation effects are substantially overestimated, which justifies scaling this contribution in eq 7 within the HYB class of functionals. Even so, the qualitative behavior remains very close to that of the reference data. These results further confirm that widely used standard DFT exchange functionals, in addition to their nominal exchange role, also encode significant amounts of correlation effects.

Furthermore, to enable a quantitative comparison of HYB DFAs, we analyze the effect of the semilocal $E_c^{DFA}[\rho]$ term in eq 7 on self-consistent quantities. To this end, we employ the recently developed error metrics introduced in ref 30, to directly assess the quality of the XC and correlation KS potentials, electron densities, total energies, and ionization potentials (IPs) derived from the HOMO energy (see ref 30, for details). The resulting error values for the XC and exchange-only HYB DFAs are reported in Table 2.

One can note that the average density ($\Delta \rho$) and XC potential (Δv_{xc}) errors barely change between the XC and X-only cases. The same is visible for the average correlation potential (Δv_c) errors. This indicates a significant similarity in

the correlation potentials between XC and X-only cases, especially in the asymptotic region.³⁰ In the core and valence region ($\Delta \rho^{ref} v_{xc}$ indicator), X-only v_c potentials give slightly larger errors, which is consistent with previous visual analysis. A similar behavior is also observed in the case of IP error (ΔIP). Here, the inclusion of the $E_c^{DFA}[\rho]$ term improves in most cases (except HFLYP) the IPs of about ~6–7% in MARE (~0.03–0.04 E_h in MAE) computed with respect to IP-EOM-CCSD data in comparison to the X-only case (see Table S1 in SI file). This indicates that the semilocal v_c^{DFA} contribution improves the full HYB correlation potentials in the core and valence regions, which impacts the HOMO energy quality. This is because the most semilocal correlation potentials yield a negative contribution in this region,^{34,35} which reduces the substantial positive overestimation of the correlation effects represented by the XDiff part.

The most significant deviations are visible on ΔE_t errors once the $E_c^{DFA}[\rho]$ term in the energy expression is neglected. However, this behavior is not surprising since we miss a dominant part of the correlation energy expression (see Table 1). Nonetheless, the above analysis clearly shows that the difference between the semilocal and exact-exchange potentials ($v_x^{DFA} - v_x^{HF}$) behaves qualitatively similarly to the reference correlation potential. This property is crucial for the proper restoration of these effects in all HYB DFAs, which can partially explain the large success of this type of DFA.

At this point, we would like to emphasize that the Δv_c correlation-potential error indicator and methodology introduced in ref 30, enable the assessment of how correlation effects are encoded in present-day semilocal DFA exchange-only KS potentials. To this end, we examined all semilocal exchange-only functionals available in the LIBXC library (version 7.0.0)⁵⁷ and evaluated the extent to which they

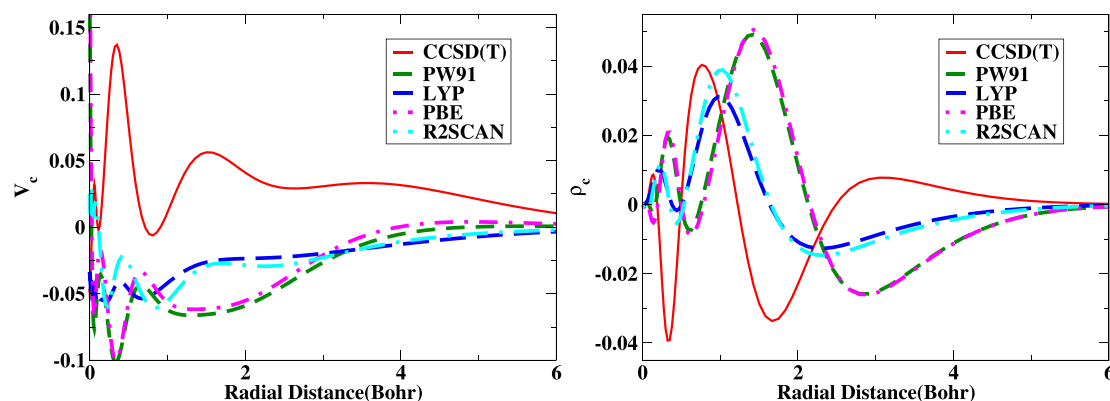


Figure 4. Correlation potentials (eq 9) and correlated densities (eq 8) computed from the self-consistent HF+ $E_c^{\text{DFA}}[\rho]$ calculations for the Ar atom.

incorporate correlation effects by computing their correlation potentials, as defined in eq 9. In most cases, we find Δv_c errors in the range of 12.3 to 14.4, values that are very similar to those of the worst-performing hybrid functionals reported in ref 30. (see the Δv_c results in Table 1 of ref 30.). For example, widely used exchange functionals such as LDA, B88,⁵⁸ PBE,⁵⁹ TPSS,⁶⁰ and R2SCAN⁶¹ yield Δv_c errors of 12.97, 12.95, 12.91, 12.79, and 12.77, respectively. This is further illustrated in Figure 3 (left), which shows the correlation potentials for the Ar atom obtained from self-consistent X-only DFA calculations using eq 9. Their qualitative behavior is very similar to that of the reference CCSD(T) correlation potential, although their magnitudes are substantially overestimated. We may therefore conclude that all semilocal X-only functionals incorporate a significant portion of the true correlation effect. This observation is also consistent with earlier density-based analyses.^{35,36,48,62}

Let us now turn our attention to eq 6 but with $n = 1$. In that case, HYB DFA functional is the simple sum of 100% nonlocal HF exchange functional and semilocal DFA correlation functional, $E_{xc}^{\text{HYB}}[\rho] = E_x^{\text{EXX}} + E_c^{\text{DFA}}[\rho]$. One example of this type of hybrid DFA is the HFLYP^{63,64} where LYP correlation with 100% HF is solved self-consistently in the Generalized Kohn–Sham scheme. As shown in ref 30., this construction yields the lowest errors in the XC and correlation potentials among all HYB DFAs assessed in ref 30. However, a closer look at the LYP correlation potentials reported in Figure 4 reveals that it fails to describe the reference correlation potential features.^{34,35} The same applies to correlated densities reported in the right panel. One can note that HFLYP DRDs are out of phase with the reference data.^{35,36} Moreover, as illustrated in Figure 4, other widely used correlation functionals, such as PW91, PBE, and R2SCAN, exhibit similarly unphysical behavior. In particular, their correlation potentials are predominantly negative, which leads to noticeable errors in the correlated electron densities. These results highlight the fundamental incompatibility between semilocal correlation DFA expressions and an HF-like energy framework. Nevertheless, despite their inadequate description of correlation effects, these functionals remain important because they partially compensate for the overestimated correlation contributions arising from the $E_c^{\text{XDiff}}[\rho]$ term in the HYB $n \neq 1$ construction. This interplay gives rise to the well-known error-cancellation mechanism³⁴ that underlies standard DFAs and hybrid functionals.

The above analysis clearly shows that HYB DFA XC functionals produce qualitatively correct correlation potentials, although their magnitudes are generally overestimated. We have also demonstrated that the XDiff term in eq 7 provides the key contribution determining both the shape of the correlation potential and the correlated density. This suggests that the semilocal exchange functional captures a large portion of the correlation effects, whereas semilocal correlation functionals represent them incorrectly.

Consequently, eq 6 for the case $n \neq 1$ can be effectively employed as a constructive framework for achieving a qualitatively correct description of correlation effects in HYB DFAs. Furthermore, analysis of the XC potentials enables a direct interpretation of the $(n-1)/n$ prefactor in terms of its role in representing correlation effects at the levels of energy, potential, and density. Therefore, eq 7 may be straightforwardly adopted as a practical recipe for constructing an EXX-compatible correlation energy functional within the HYB DFA framework.

This consideration brings us to the final part of the present study. Based on the conclusions drawn from the above analysis, we propose an interpretable and a physically motivated methodology for constructing new HYB DFA functionals as

$$E_{xc}^{\text{UMK}}[\rho] = E_x^{\text{EXX}} + \gamma(E_x^{\text{DFA}}[\rho] - E_x^{\text{EXX}}) + E_c^{\text{DFA}}[\rho] \quad (10)$$

where UMK stands for Uniwersytet Mikołaja Kopernika in Toruń (Nicolaus Copernicus University in Toruń). In the construction defined by eq 10, the parameter $\gamma = (n-1)/n$ scales the difference between the semilocal and the exact-exchange HF parts. This term effectively captures the dominant part of the correlation effects incorporated in HYB DFAs through exchange mixing, providing a transparent physical interpretation of the hybrid construction. As a proof of concept, we implement this methodology using the B88 and LYP functionals for the semilocal exchange and correlation components, respectively. Nonetheless, the proposed framework is general, and other semilocal exchange and correlation functionals can be employed and tested within eq 10. In that case, the optimal value of γ may change and should be reoptimized.

The crucial step in our construction is the optimal choice of the γ parameter. Once again, we rely on the measures introduced in ref 30. Unfortunately, for global hybrid DFAs, the Δv_{xc} and Δv_c error indicators cannot be used directly, because they receive relatively large contributions from the

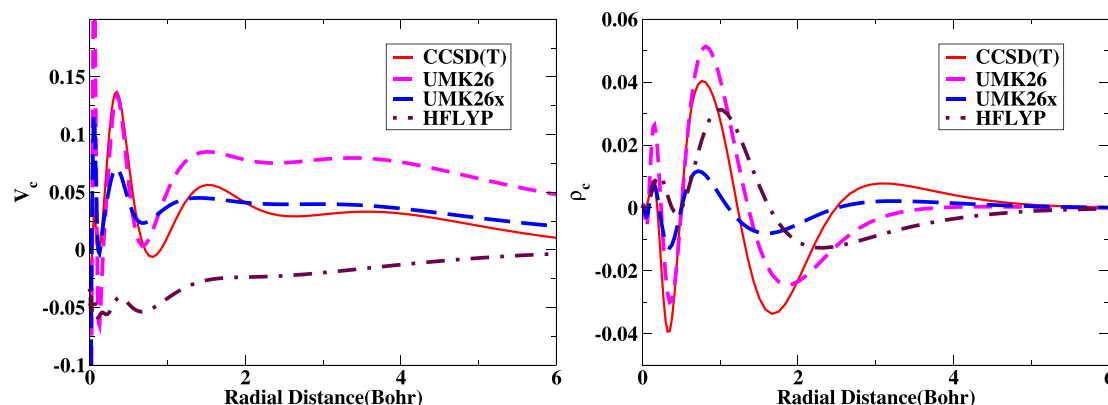


Figure 5. Correlation potentials and correlated densities calculated for the Ar atom using HFLYP, UMK26, and UMK26x, with respect to the reference CCSD(T) plots.

incorrect asymptotic decay of the XC potential in the density tail. As an alternative, we consider HOMO ionization-potential energies, which have been shown to directly reflect the quality of the XC and correlation potentials^{30,47,65,66} (see, e.g., Figure 6 in ref 30.). This optimization strategy can also be justified from the perspective of correlated orbital theory (COT).⁶⁷ Therefore, the γ parameter in eq 10 was determined by a one-dimensional line-search procedure in the interval $0 \leq \gamma \leq 1$. For each trial value of γ , fully self-consistent calculations were performed for 16 systems (listed in Table 3) of the CCSD(T) benchmark set introduced in ref 30., computing their average ΔIP error. The minimum of this error ($\Delta IP = 0.035$) curve was obtained for $\gamma = 0.25$, which defines the UMK26 functional. This is presented in Figure S17 in the SI file.

As demonstrated in ref 30. (see Figure 5), a larger fraction of HF exchange leads to a substantial reduction of the Δv_{xc} error, which is consistent with our expectations. Consequently, this reduces the overestimation of correlation potentials in the core, valence, and asymptotic tail.

We note also that while the precise value of γ is functional-dependent, we expect that the optimal scaling factor for many semilocal exchange functionals will remain close to the value obtained for the B88/LYP realization due to the similar overestimation of correlation effects carried by the functional itself (see Figure 3). As a test, we have performed the same minimalization analysis for a PBE-based UMK hybrid construction and obtained the minimum ΔIP at $\gamma = 0.26$, which is almost identical to the value found for UMK26; see also Figure S18 in the SI.

As shown in the first part of this paper, the majority of the correlation effects is carried by the XDiff term eq 6 of the HYB DFA functional. Thus, to evaluate the behavior at the level of pure exchange, we used eq 11 to define an additional variant of UMK26, denoted as UMK26x, in which the LYP correlation term is fully neglected, and the difference of the semilocal and HF exchange terms entirely represents the correlation effects i.e.,

$$E_{xc}^{\text{UMK26x}}[\rho] = E_x^{\text{EXX}} + \gamma(E_x^{\text{B88}}[\rho] - E_x^{\text{EXX}}) \quad (11)$$

Using the same γ -optimization procedure, we found the optimal γ for the UMK26x variant to be 0.1, indicating the dominant role of HF exchange.

To assess the performance of the UMK26 and UMK26x HYB DFA functionals, we first analyze the corresponding correlation potentials and correlated densities computed for a

representative set of atomic and molecular systems (see also the SI). As shown in Figure 5, the correlation potentials obtained with the UMK26 and UMK26x functionals are qualitatively consistent with the CCSD(T) reference potential. Importantly, we observe a substantial reduction in the overestimation of the correlation potentials characteristic of standard HYB DFAs (see Figures 2 and 3 for the exchange-only case). This clearly demonstrates that the proposed methodology performs as intended. A similar trend is observed for the correlated densities obtained from fully self-consistent UMK26 and UMK26x calculations. The resulting densities are in phase with the CCSD(T) reference data and reproduce both their spatial profiles and magnitudes. This agreement is particularly pronounced for the UMK26 functional. Comparable improvements are found for other systems, including Be, Ne, CO, and H₂O (see Figures S13–S16). Nevertheless, noticeable deviations remain in the asymptotic region of the correlation potentials. These discrepancies arise from the different asymptotic decay behaviors of the semilocal and exact-exchange components of the potential.³⁰ Addressing this limitation will be the subject of future work.

Next, we apply the UMK26 and UMK26x functionals to directly calculate IPs from orbital energies in fully self-consistent hybrid DFT calculations. To this end, we consider two widely used and well-established benchmark sets: the GW100 test set⁶⁸ and the IP benchmark set developed by Bartlett's group.⁶⁶ We note that the GW100 set contains 12 of the 16 systems used in the γ line-search optimization. However, GW100 itself was not used during the optimization, and the reported GW100 statistics are evaluated over the complete benchmark set, which contains a much broader and chemically more diverse collection of systems. Therefore, do not expect this partial overlap to introduce a significant bias in the GW100 assessment.

For the GW100 benchmark set, we compute the mean absolute deviation (MAD) of the HOMO energies (HOMO IPs) obtained with the GKS and G_0W_0 approaches for our new functionals, as well as for several other popular global and RS hybrids. The errors are evaluated relative to the CCSD(T)/def2-TZVPP reference data⁶⁸ and are reported in Table 3. Notably, the global hybrid UMK26 yields a very low MAD of 0.38 eV, substantially outperforming other global hybrids and most RS counterparts, while remaining comparable to the best range-separated QTP variants.⁶⁶ A similar trend is observed for UMK26x, which also performs well, with a relatively small

Table 3. Mean Absolute Deviation (MAD) (in eV) on GW100 Reference Data Set Computed Using HOMO Energies Obtained with GKS and G_0W_0 Approaches^a

	GKS	G_0W_0
UMK26x	0.48	0.27
UMK26	0.38	0.18
PBE0	2.63	0.33
B3LYP	2.90	0.38
QTP17	0.71	0.15
HFLYP	1.30	0.25
LC- ω PBE	0.66	0.29
LC- ω PBEH	0.86	0.29
CAM-B3LYP	1.33	0.30
QTP00	0.33	0.31
QTP01	0.34	0.16
QTP02	0.31	0.19

^aThe errors are computed with respect to CCSD(T)/def2-TZVPP reference data.

MAD of 0.48 eV. These results indicate that reducing the overestimation of the potential has a strong positive effect on the quality of the HOMO orbital energies, even though the XC potential still does not recover the correct asymptotic $-1/r$ behavior in the tail region. Consistent with this, G_0W_0 calculations based on both global and RS hybrids also demonstrate excellent performance for UMK26 and UMK26x. In particular, UMK26 achieves a MAD of 0.18 eV at the G_0W_0 level, again matching the accuracy of the QTP family of functionals, which represent the leading RS hybrid functionals for reliable IP prediction.

As an additional assessment, we consider the benchmark set from ref 66, which, in addition to HOMO ionization potentials, also enables the evaluation of valence IPs. The results obtained with the same global and range-separated hybrid functionals used for the GW100 set are summarized in Table 4. For the HOMO IPs, UMK26 and UMK26x follow the same trend observed previously, outperforming conventional global hybrids and some range-separated hybrids, and achieving an accuracy comparable to that of the QTP family of functionals. For the valence IP benchmark, UMK26's

Table 4. Mean Absolute Deviation (MAD) (in eV) Calculated the Benchmark Set from Ref 66 for Several Global and Range-separated Hybrid Functionals with Respect to IP-EOM-CCSD/cc-pVTZ Data^a

	MAD HOMO	MAD val.
UMK26x	0.53	1.00
UMK26	0.42	0.75
PBE0	2.97	3.10
B3LYP	3.23	3.44
QTP17	0.79	0.47
HFLYP	1.51	2.58
LC- ω PBE	0.31	0.39
LC- ω PBEH	1.09	1.17
CAM-B3LYP	1.53	1.58
QTP00	0.32	0.65
QTP01	0.29	0.30
QTP02	0.24	0.35
HF	0.74	1.68

^aAt the bottom, we report the HF data for comparison.

performance deteriorates somewhat; however, the results remain qualitatively comparable to those of QTP00. UMK26x, in turn, shows slightly worse performance than UMK26, although it still outperforms LC- ω PBEH and CAM-B3LYP. Given that UMK26 functionals are global hybrids that effectively compete with RS variants in describing IPs, these findings are highly encouraging.

One of the fundamental issues in KS-DFT is the integer (derivative) discontinuity, which arises when electrons are removed from or added to a chemical species. The exact XC functional is expected to yield a total energy that varies linearly with the electron number between systems with integer electron occupations, i.e., it should produce a straight line connecting the energies of the systems with N_0 , $N_0 - 1$, and $N_0 + 1$ electrons.

Figure 6a illustrates this behavior for the fluorine atom (number of electrons, $N = 9$) and its cationic ($N = 8$) and anionic ($N = 10$) forms, showing how the total energies of the fractional-electron systems deviate from the ideal piecewise linear interpolation defined by the corresponding integer-electron energies for a few representative DFAs. Both PBE0 and B3LYP present convex curvature in the electron removal and electron addition regions. In these cases, the deviation is more pronounced under ionization.

A similar trend is observed for the QTP17 functional; however, its deviation from linearity is significantly smaller. QTP17 also performs notably well in describing electron attachment. It is noteworthy that the hybrid parameters of QTP17 were optimized to reproduce all five experimental ionization potentials of the water molecule,⁵¹ following the correlated orbital theory's IP condition of Bartlett,⁶⁷ which states that the negative of each occupied orbital eigenvalue should correspond to its respective IPs. In contrast, as mentioned previously, UMK26 parameters were optimized using only the first ionization potentials (HOMO IPs) of a series of several chemical species.

In this context, UMK26x exhibits concave curvature in both the electron addition and electron removal regions, as indicated by the violet curve in Figure 6. Here, the error is slightly larger in the ionization description. Finally, UMK26 (black line) shows excellent performance in the electron removal region, producing an almost perfectly linear interpolation. Although its description of electron attachment is not strictly linear, the deviation is substantially lower than for all other hybrid functionals (except QTP17). This behavior indicates nearly negligible localization/delocalization errors during ionization and minimal errors upon electron attachment.

In the case of the carbon atom (Figure 6b), a similar trend is observed overall. However, UMK26 performs better in the electron attachment region, while UMK26x is as good as or slightly better in the electron removal region.

We remark that the integer discontinuity error is known to lead to a poor performance of KS-DFT for charge-transfer (CT) excitations.^{69,70} For example, at a large separation of the donor–acceptor (DA) species, the excitation energy of a CT state can be approximated as $\omega_{CT} = IP_D - EA_A - \frac{1}{R_{DA}}$.⁷¹ Therefore, UMK26 is an excellent candidate for future photophysical studies of systems containing excited states exhibiting CT character.

To verify the previous statement, Table 5 shows how UMK26 and the other functionals perform for long-range

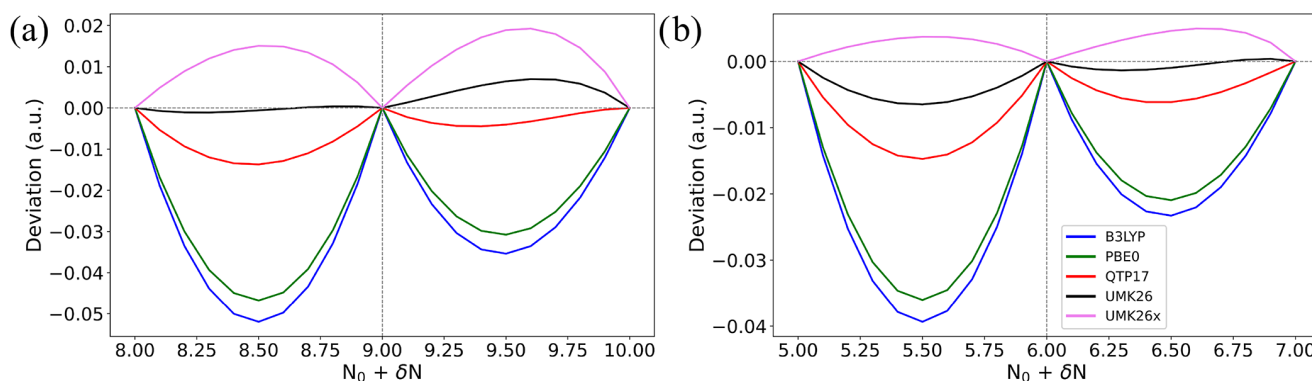


Figure 6. Deviation of hybrid XC functionals from the piecewise linear interpolation regarding the fractional electron occupancies of (a) fluorine atom and (b) carbon atom.

Table 5. Vertical Excitation Energies (eV) for Long-Range Charge-Transfer Excited States of the $\text{NH}_3\cdots\text{HNO}_2$ Dimer Obtained in TDDFT Calculations with the jul-cc-pVTZ Basis Set and Deviations with Respect to Reference Results from Verma et al.⁷²

$1/r_{\text{DA}}$	ref	PBE0	B3LYP	UMK26	QTP17	LC- ω PBE	LRC- ω PBEH	CAM-B3LYP	QTP00	QTP01	QTP02
3.6772	7.10	3.95	3.56	7.46	6.48	6.74	5.15	5.24	7.17	6.49	6.87
6.1133	8.22	3.90	3.44	8.04	6.89	7.69	5.98	5.70	7.97	7.41	7.93
8.5632	8.75	3.97	3.49	8.42	7.18	8.41	6.21	6.04	8.44	7.94	8.32
11.016	9.13	4.03	3.53	8.65	7.37	8.53	6.82	6.21	8.73	8.26	8.64
13.471	9.35	4.07	3.56	8.70	7.49	8.74	7.04	6.34	8.92	8.47	8.85
15.927	9.51	4.10	3.58	8.92	7.58	8.90	7.19	6.44	9.06	8.62	9.01
18.387	9.62	4.13	3.60	9.00	7.65	9.01	7.30	6.51	9.16	8.73	9.12
23.303	9.77	4.17	3.63	9.11	7.75	9.16	7.46	6.61	9.30	8.89	9.27
25.763	9.83	4.18	3.64	9.16	7.78	9.22	7.51	6.65	9.35	8.94	9.33
MAD		4.98	5.47	0.49	1.68	0.56	2.26	2.84	0.37	0.84	0.46
MAX		5.65	6.19	0.67	2.05	0.61	2.32	3.18	0.48	0.89	0.51
MSD		-4.98	-5.47	-0.41	-1.68	-0.56	-2.26	-2.84	-0.35	-0.84	-0.46

charge transfer, i.e., when $1/r_{\text{DA}}$ is very small. In this situation, the charge transfer can be approximated by the simple expression $\omega_{\text{CT}} = I_{\text{D}} - E_{\text{A}}$. For this analysis, we used the test set from Verma et al.,⁷² in which the $\text{NH}_3\cdots\text{HNO}_2$ dimer is evaluated at nine intermolecular distances ranging from 3.68 to 25.76 Å. With a MAD of 0.49 eV, UMK26 is by far the best-performing global hybrid functional. The second-best result is obtained with QTP17, which has a MAD of 1.68 eV (1.19 eV higher!). Moreover, UMK26 outperforms most RSH functionals, except for QTP00 and QTP02, which yield MADs of 0.37 and 0.46 eV, respectively.

Next, Figure 7 presents a CT analysis for excitations across different dimers at a fixed distance. In this case, the description

	MAD	MAX	MSD
PBE0	2.80	4.19	-2.80
B3LYP	3.07	4.64	-3.07
UMK26	0.74	2.72	-0.30
QTP17	0.88	2.63	-0.88
CAM-B3LYP	1.88	3.25	-1.88
LC- ω PBE	1.16	3.15	-0.99
LRC- ω PBEH	1.95	3.39	-1.95
QTP00	0.81	2.68	-0.61
QTP01	1.10	3.10	-1.04
QTP02	0.96	2.32	-0.81

Figure 7. Heat map showing the mean absolute deviation (MAD) and mean signed deviation (MSD), in eV, of the calculated charge-transfer excited states with respect to EOM-CCSDT-3 reference data from Kozma et al.⁷³ The cc-pVDZ basis set was used.

of CT states is no longer given simply by the difference between IPs and EAs. Under these conditions, UMK26 stands out as the best-performing functional overall, with a MAD of 0.74 eV. The only other functionals achieving MADs below 1 eV belong to the QTP family (MADs ranging from 0.81 to 0.96 eV), except for QTP01 (MAD = 1.10 eV).

For completeness, a final test on CT states is presented in Figure 8. This set comprises 19 organic molecules exhibiting intramolecular charge transfer. In this case, CAM-B3LYP performs best among the selected functionals, with a MAD of 0.23 eV. Mester and Kállay⁷⁴ also reported this favorable performance, although their study employed the TDA approach. Among the global hybrids, the best performer is QTP17 (MAD = 0.33 eV), while UMK26 shows similar performance, with a MAD of 0.38 eV. Interestingly, the “exchange-only” variant, UMK26x, yields a considerably good result, with a MAD of 0.67 eV. Despite containing no correlation (functional) contribution, its performance is comparable to, or even slightly better than, that of widely used XC functionals such as B3LYP (MAD = 0.74 eV) and PBE0 (MAD = 0.64 eV), for example.

As a final observation, all functionals underestimate intermolecular CT excitations relative to the reference values (see the MSD values in Table 5 and Figure 7). For intramolecular CT excitation, however, although the overall trend remains (underestimation), the “IP corrected functionals”, i.e., QTP family and UMK26 variants, exhibit the opposite behavior and instead overestimate these results (see Table S5 in SI).

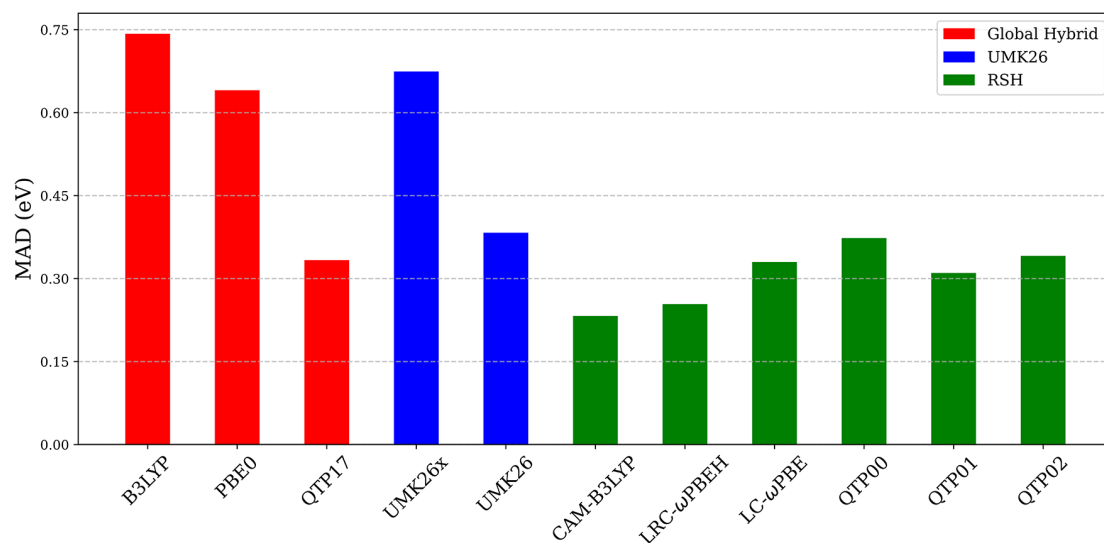


Figure 8. Mean absolute deviations (MADs) of intramolecular charge-transfer excitations w.r.t theoretical best estimates (TBE) from Loos et al.⁷⁵ The basis set was cc-pVTZ.

As a final part of this paper, we assess the performance of UMK26 on energy and energy-related data sets.^{76,77} To this end, we employ the recently proposed SLIM20 data set⁷⁸ developed to mimic the statistics of the large GMTKN55 data set⁷⁶ and enables a faster assessment of exchange-correlation functionals.

The results collected in Figure 9 show that UMK26 exhibits a highly nonuniform but physically meaningful performance pattern on the SLIM20 benchmark. In terms of the overall WTMAD-2, UMK26 gives 12.46 kcal/mol, which is better than HFLYP (14.13) and close to B3LYP (12.84), but still worse than PBE0 (10.31) and more balanced RSHs, such as QTP17 (9.77), QTP02 (9.23), and LC- ω PBE (10.06). Thus, UMK26 is clearly not the best general-purpose functional within the present set as judged solely by the global SLIM20 aggregate. The functional is clearly weaker across several thermochemical and bond-dissociation subsets, including ALKBDE10 (19.90), YBDE18 (6.40), G21EA (9.13), G21IP (6.09), W4-11 (35.32), and especially MB16-43 (51.84). It is also not among the best methods for subsets such as WATER27 or PA26. However, one can note that this simple global-hybrid construction performs exceptionally well in situations dominated by self-interaction and delocalization errors. This is most evident from the SIE4 $\times$ 4 subset in Figure 9, where UMK26 yields by far the lowest MAD, 0.65 kcal/mol, outperforming PBE0 (9.83), B3LYP (11.47), HFLYP (4.00), QTP17 (2.67), QTP02 (4.47), and LC- ω PBE (5.83). Such behavior is particularly noteworthy because UMK26 does not use the additional flexibility of range separation and nevertheless surpasses the other tested hybrid forms for these strongly self-interaction-sensitive systems. In addition to SIE4 $\times$ 4, UMK26 is also the best performer for PX13 (2.51) and ISO34 (0.37), and remains very competitive for FH51 (1.01), IL16 (1.19), RSE43 (0.62), and TAUT15 (0.22). These trends consistently indicate that the UMK26 DFA effectively suppresses spurious delocalization and improves the description of difficult energetic balances involving localized charge distributions, consistent with the conclusions drawn from Figure 6.

The physical origin of this behavior is directly illustrated by the dissociation curves in Figure 10. For H_2^+ and He_2^+ , approximate functionals affected by self-interaction error tend to show an unphysical residual attraction at large interatomic separation, reflecting an incorrect stabilization of fractionally delocalized charge. In both systems, UMK26 reduces this spurious long-range binding more effectively than the other DFAs considered. The effect is especially clear for He_2^+ , where UMK26 approaches the correct dissociation limit substantially better than PBE0, QTP17, QTP02, and LC- ω PBE. A similar tendency is also observed for ArKr^+ , where UMK26 avoids the severe overbinding seen with PBE0 and follows the reference curve more closely in the asymptotic region. These results provide direct molecular-level confirmation of the SIE4 $\times$ 4 benchmark trend, i.e., the excellent performance of UMK26 for self-interaction-sensitive subsets is not accidental, but reflects a genuine improvement in the dissociation behavior of charged systems.

At the same time, the significance of UMK26 extends beyond self-interaction tests alone. As shown in Figure 11, UMK26 lies in a favorable region of the ΔE_t - $\Delta\rho$ diagram,³⁰ indicating a good compromise between density accuracy and total-energy accuracy. This is an important observation because, although UMK26 does not perform uniformly well across all SLIM20 subsets, its position in Figure 11 suggests that its total-energy description is quite good and, in fact, better balanced than for several other considered here DFAs. This finding is further supported by the AE18 subset, extracted from the MGCDB84 data set, which contains the absolute total atomic energies of the atoms from hydrogen through argon. For this subset, UMK26 again yields the lowest MAD, 8.21 kcal/mol, improving upon HFLYP (9.01) and clearly outperforming B3LYP (17.84), PBE0 (41.98), QTP02 (57.45), and especially QTP17 (183.84). Since AE18 directly probes the quality of absolute total energies, its favorable result for UMK26 is fully consistent with the ΔE_t analysis in Figure 11. Taken together, these two observations suggest that UMK26 benefits from a favorable energetic balance and, consequently, from a useful degree of error cancellation at the energy level. Thus, even though it is not the best functional for

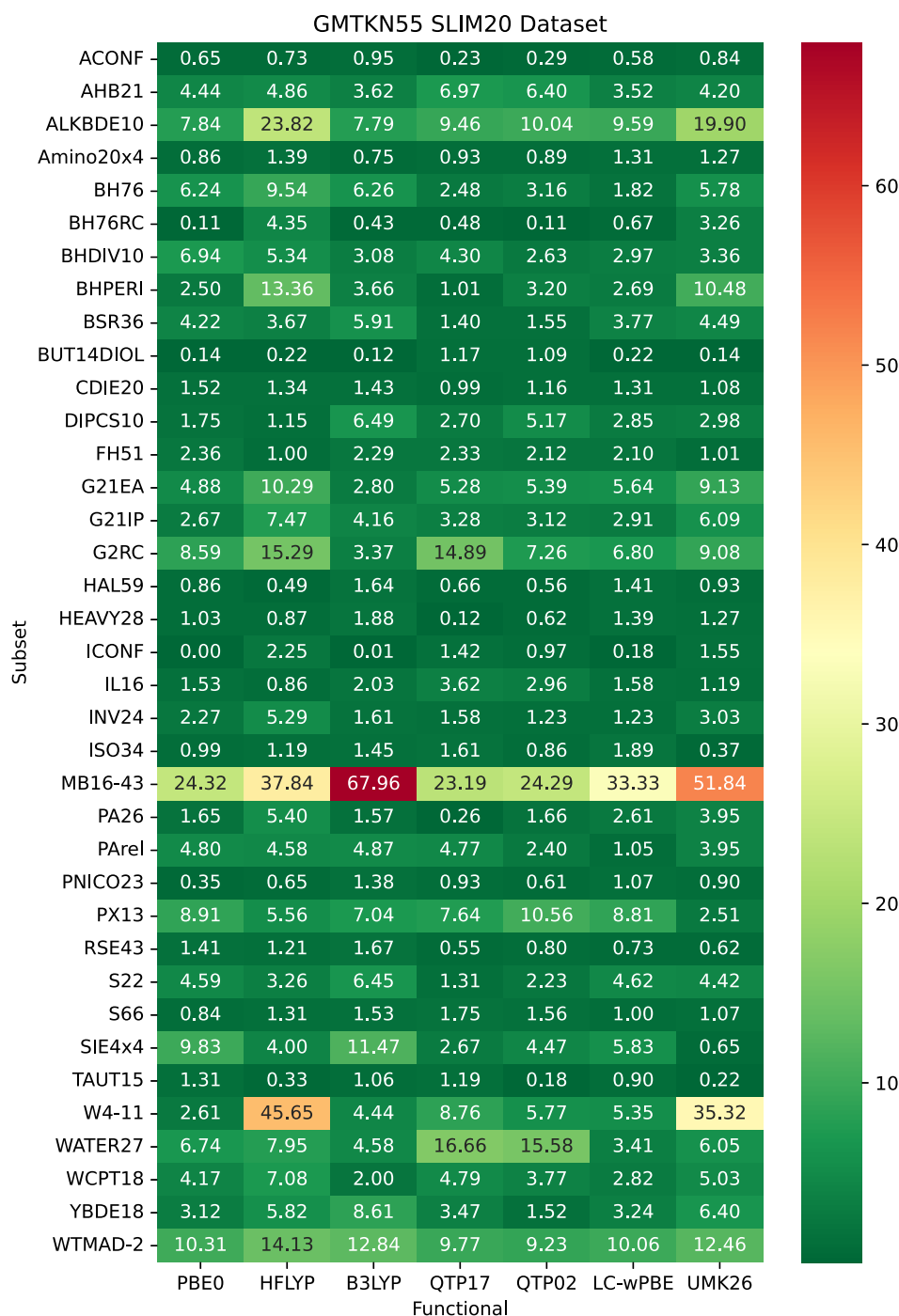


Figure 9. Mean absolute deviation for GMTKN55 SLIM20 data set. def2-TZVP basis set is employed here, and the values are reported in kcal/mol. WTMAD-2 is computed with the original GMTKN55 formula with MAD from SLIM20 subsets.

many chemically diverse subsets in SLIM20, the underlying total energies are described rather well, which can partly compensate for more localized deficiencies in specific reaction or bonding categories.

Therefore, UMK26 cannot be regarded as a uniformly superior replacement for the better-balanced RSH DFAs in broad benchmark applications. Nevertheless, the present results show that UMK26 combines a simple global-hybrid form with excellent performance in SIE-dominated cases and a robust description of total energies, making it a promising, physically well-motivated construction.

4. CONCLUSIONS

In this work, we analyzed how correlation effects are represented in hybrid density functional approximations from the perspectives of the KS XC potential, correlated densities, and energy-related observables. The present results show that, within the hybrid framework, the dominant qualitative features of correlation are not generated primarily by the semilocal correlation functional alone, but rather by the difference between the semilocal exchange and exact-exchange contributions. This term accounts for a substantial portion of the correlation effect and is essential for restoring the physically

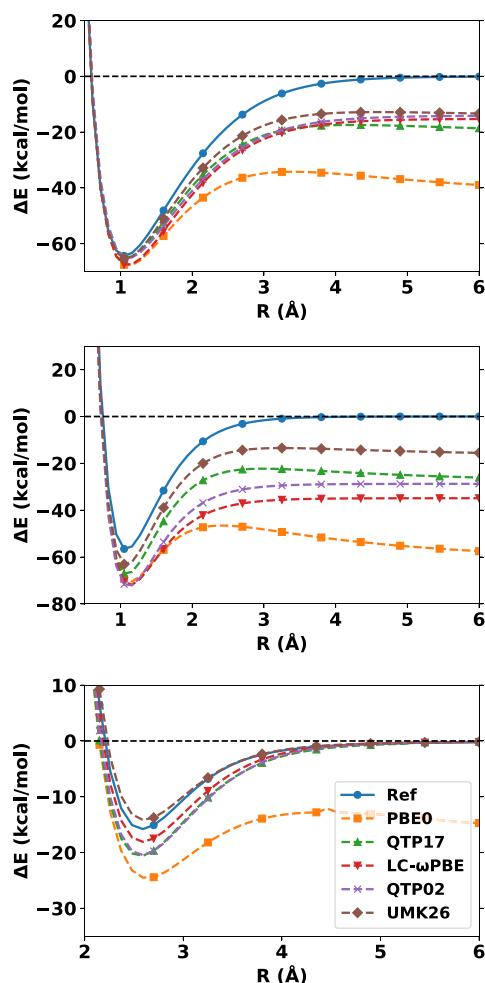


Figure 10. Dissociation Curve for H_2^+ (Top), He_2^+ (Middle) and $ArKr^+$ (Bottom). The Def2-QZVP basis set is employed together with HF and CCSD(T) reference (ref) for H_2^+ , and He_2^+ (Middle), $ArKr^+$, respectively.

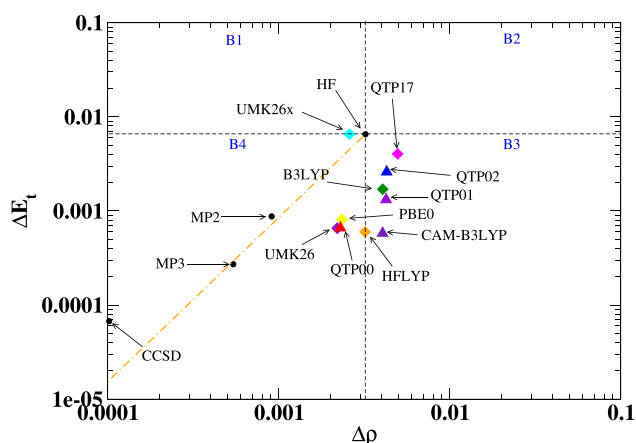


Figure 11. A comparison of $\Delta\rho$ vs ΔE_t for UMK26 and UMK26x with other well-known global and range-separated hybrid functionals studied in ref 30.

decomposition, since it directly controls how correlation is represented in the local v_{xc} potential.

Our analysis further shows that semilocal correlation functionals applied on top of full exact-exchange are not compatible with a physically correct description of correlation effects in the potential. Their role in standard hybrid constructions is largely compensatory, i.e., they reduce the systematic overestimation of correlation encoded by the exchange-difference contribution, especially in the core and valence regions. This provides a transparent interpretation of conventional hybrid mixing and explains why hybrid DFAs can produce qualitatively meaningful correlation potentials even when neither constituent part is satisfactory on its own. On this basis, we propose an interpretable construction principle for hybrid functionals in which the key ingredient is the controlled scaling of the semilocal/exact-exchange difference term.

As a proof of concept, this methodology was used to construct the simple global hybrid UMK26, together with its exchange-only counterpart UMK26x. Despite their uncomplicated global-hybrid form, both functionals substantially reduce the overestimation of correlation effects observed in standard hybrids and yield correlation potentials and correlated densities that closely follow the high-level reference behavior. Most importantly, UMK26 delivers very accurate IPs from orbital energies and shows excellent performance for CT excitations, placing it on a comparable footing with several recently proposed RSHs. This is a particularly encouraging result because it demonstrates that a physically motivated global hybrid, designed through analysis of the XC potential rather than empirical energy fitting alone, can recover much of the performance often associated with more flexible range-separated forms.

At the same time, the present study clarifies both the physical interpretability and the limitations of the proposed construction. The introduction of parameter γ provides a physically interpretable strategy for controlling the semilocal/exact-exchange difference and, consequently, the representation of correlation in the XC potential and correlated density. However, its optimized value is generally system-, property-dependent. This dependence reflects the approximate DFA ingredients used in the construction and residual error-cancellation effects, which are not yet controlled systematically. Thus, although the construction principle in eq 10 is physically motivated, a single value of γ cannot be expected to provide universally reliable results across different systems and properties. Further limitations arise from the asymptotic behavior associated with the DFA ingredients and the exact-exchange fraction. In particular, the 75% exact-exchange coefficient in UMK26 produces an asymptotic $-0.75/r$ tail rather than the exact $-1/r$ behavior. These limitations motivate future work on range-separated extensions, additional DFA ingredients, basis-set effects, systematic control of error cancellation, and potential- and density-guided optimization of γ .

We believe that this perspective opens a useful route for the rational development of future hybrid approximations, including improved global hybrids, range-separated hybrids, and double-hybrid forms built on the same physical principles. In the latter case, the present analysis should apply directly to the hybrid part of conventional double hybrids, while the effect of the additional perturbative correlation contribution on the

density and local potential^{79,80} remains an important subject for future work.

The present framework also provides a natural target for future ML-assisted hybrid-functional design. Unlike recent adaptive hybrid approaches,²⁵ which predict system-dependent exact-exchange fractions mainly from energetic and electronic-property targets, the present analysis points to training objectives based directly on XC potentials, correlation potentials, correlated densities, and IP-related indicators.

5. COMPUTATIONAL DETAILS

PySCF (version 2.9)^{81,82} and KS-Pies⁸³ package is employed for the generation of the Wu-Yang XC potential and electron densities at the DFT level. The reference potential and densities at the CCSD(T) level were computed using the PSI4 package⁸⁴ and the n2v⁸⁵ package. An uncontracted aug-cc-pVTZ⁸⁶ basis set is used to expand both orbitals and potentials to generate the XC potential and density on a 3D DFT grid. The trust-exact optimization procedure with the Fermi-Amaldi guide is employed in the Wu-Yang inverse procedure. The guide potential is scaled with respect to the long-range Hartree–Fock coefficient in the case of hybrid density functionals, and a regularization value of 1×10^{-5} is used to avoid artificial oscillations in the core of the XC potential. The PySCF package is used to benchmark against the GMTKN55 SLIM20⁷⁸ data set with the def2-TZVP basis set,⁸⁷ and to generate dissociation curves as depicted in Figure 10 with the def2-QZVP basis.⁸⁸ The PSI4 package with cc-pVTZ basis is employed to benchmark the HOMO and valence IPs against the IP-EOM-CCSD reference⁶⁶ as depicted in Table 4. For the GW100 benchmark,⁶⁸ the def2-TZVPP basis set was employed, which requires effective core potentials (ECPs) for heavy elements. In this case the GKS and G_0W_0 data have been obtained with MOLGW code.⁸⁹ The fractional occupations were also performed with PSI4 using the aug-cc-pVTZ basis set.^{86,90,91} Charge-transfer calculations were performed using a combination of PSI4 (Tables 5 and Figure 7) and the Orca package (Figure 8). For these charge-transfer calculations, the jul-cc-pVTZ,⁹² cc-pVDZ,^{86,90} and cc-pVTZ basis sets were employed, respectively.

■ ASSOCIATED CONTENT

Data Availability Statement

The data underlying this study are available in the published article and the Supporting Information. Data have been generated using the software described in the Computational Details section.

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jctc.6c00843>.

Additional information, such as plots for Ne, Be, CO, and H₂O (PDF)

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Notes

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Supplementary Information for "Primary Role of Semi-Local and Exact-Exchange Difference in the Description of Correlation Effects in Hybrid Functionals"

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I) Hybrid and Exchange only Hybrid Functionals

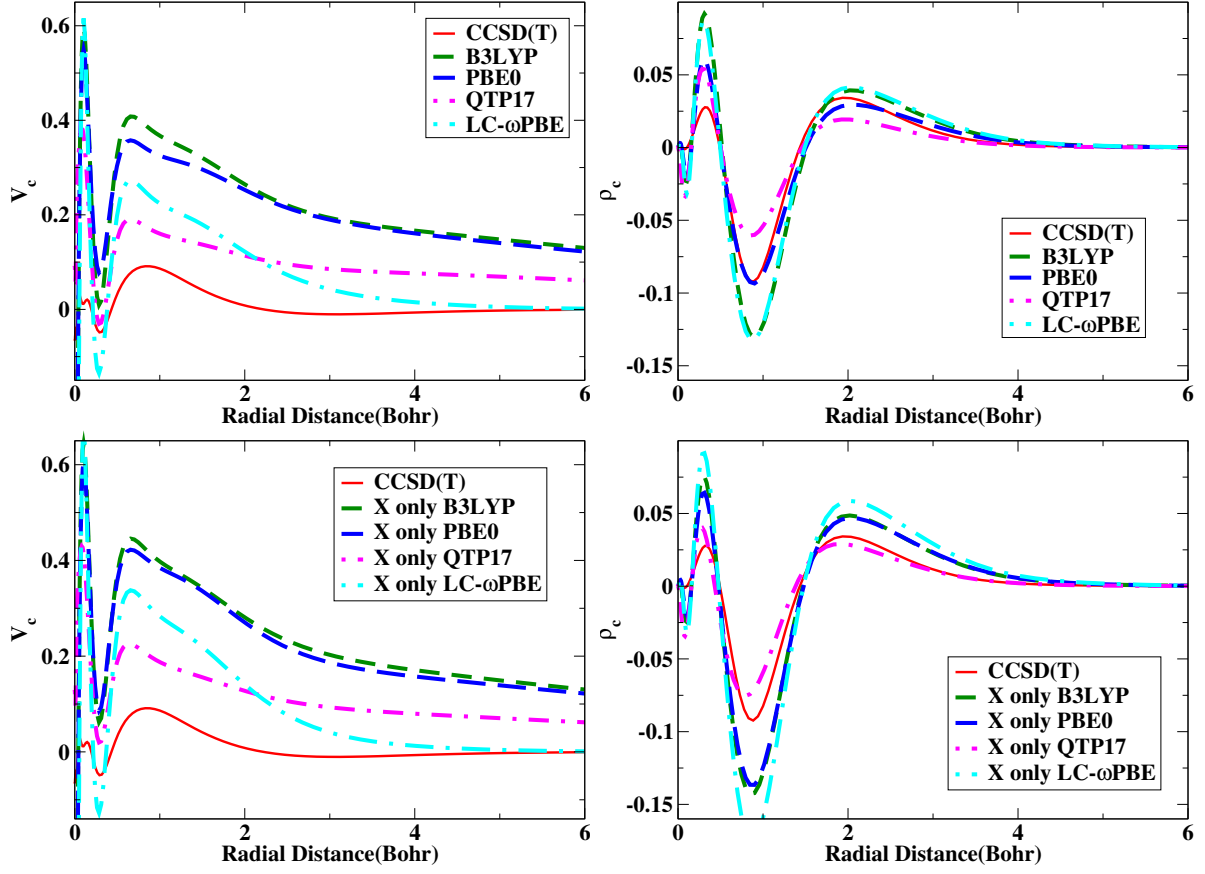


Figure S1: The correlation potentials (Eq. (9)) and correlated densities (Eq. (8)) of the Ne atom, calculated for several popular HYB DFAs with (top panel) and without (bottom panel) semi-local DFA correlation functional ($E_c^{\text{DFA}}[\rho]$) in Eq. (6).

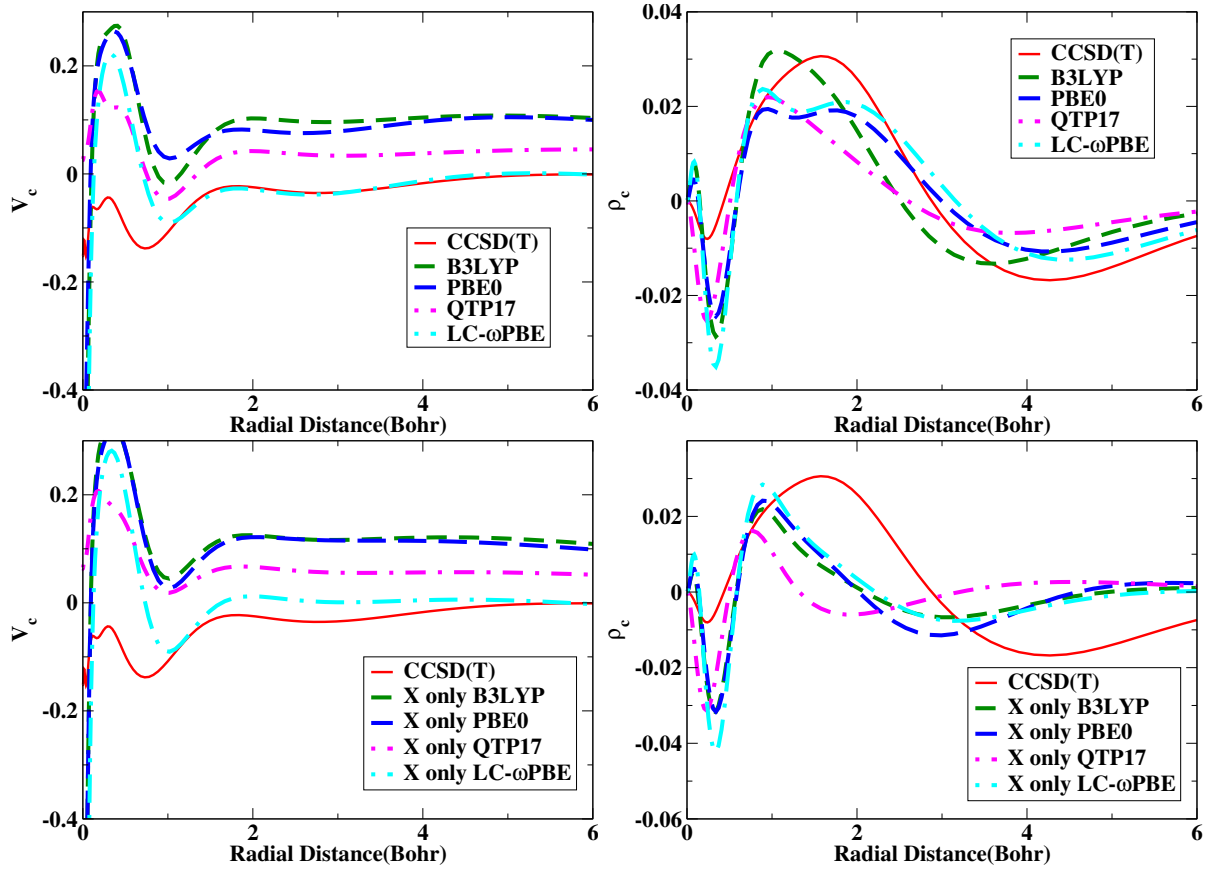


Figure S2: The correlation potentials (Eq. (9)) and correlated densities (Eq. (8)) of the Be atom, calculated for several popular HYB DFAs with (top panel) and without (bottom panel) semi-local DFA correlation functional ($E_c^{\text{DFA}}[\rho]$) in Eq. (6).

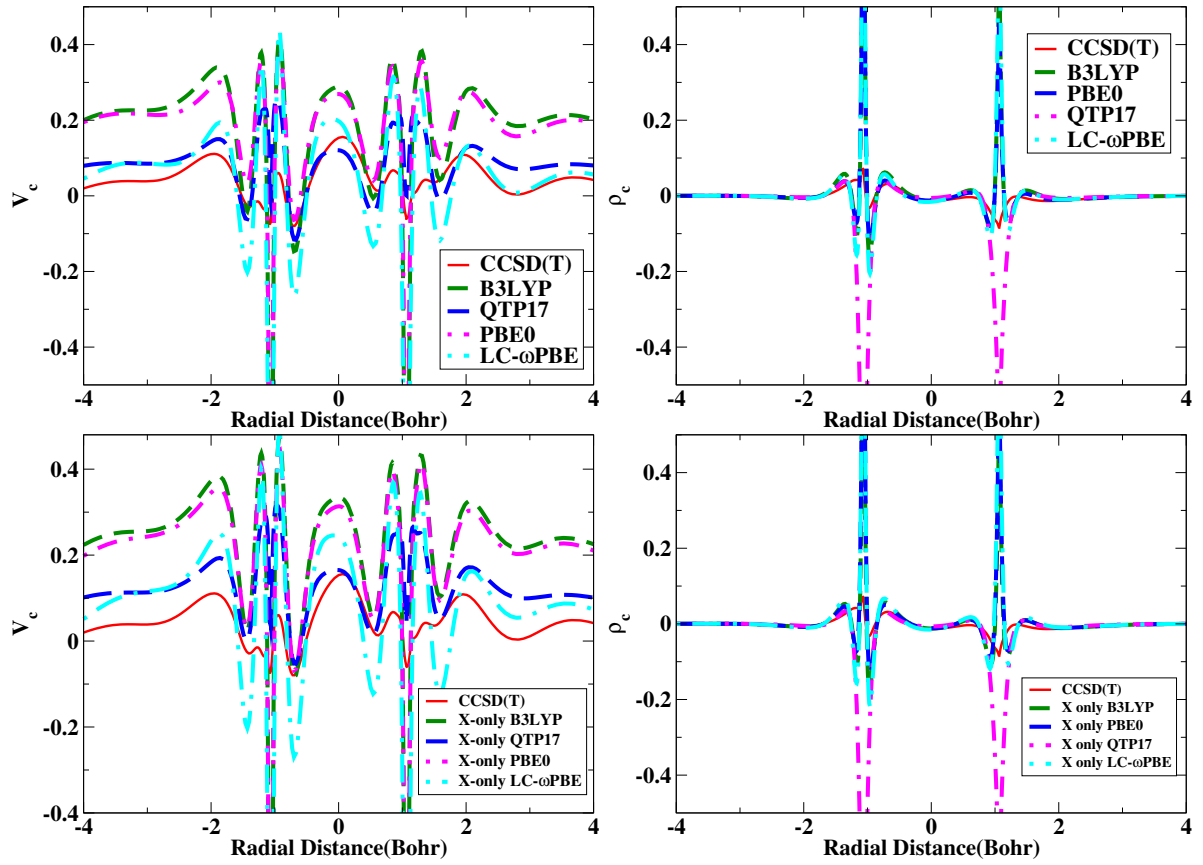


Figure S3: The correlation potentials (Eq. (9)) and correlated densities (Eq. (8)) of the CO molecule, calculated for several popular HYB DFAs with (top panel) and without (bottom panel) semi-local DFA correlation functional ($E_c^{\text{DFA}}[\rho]$) in Eq. (6).

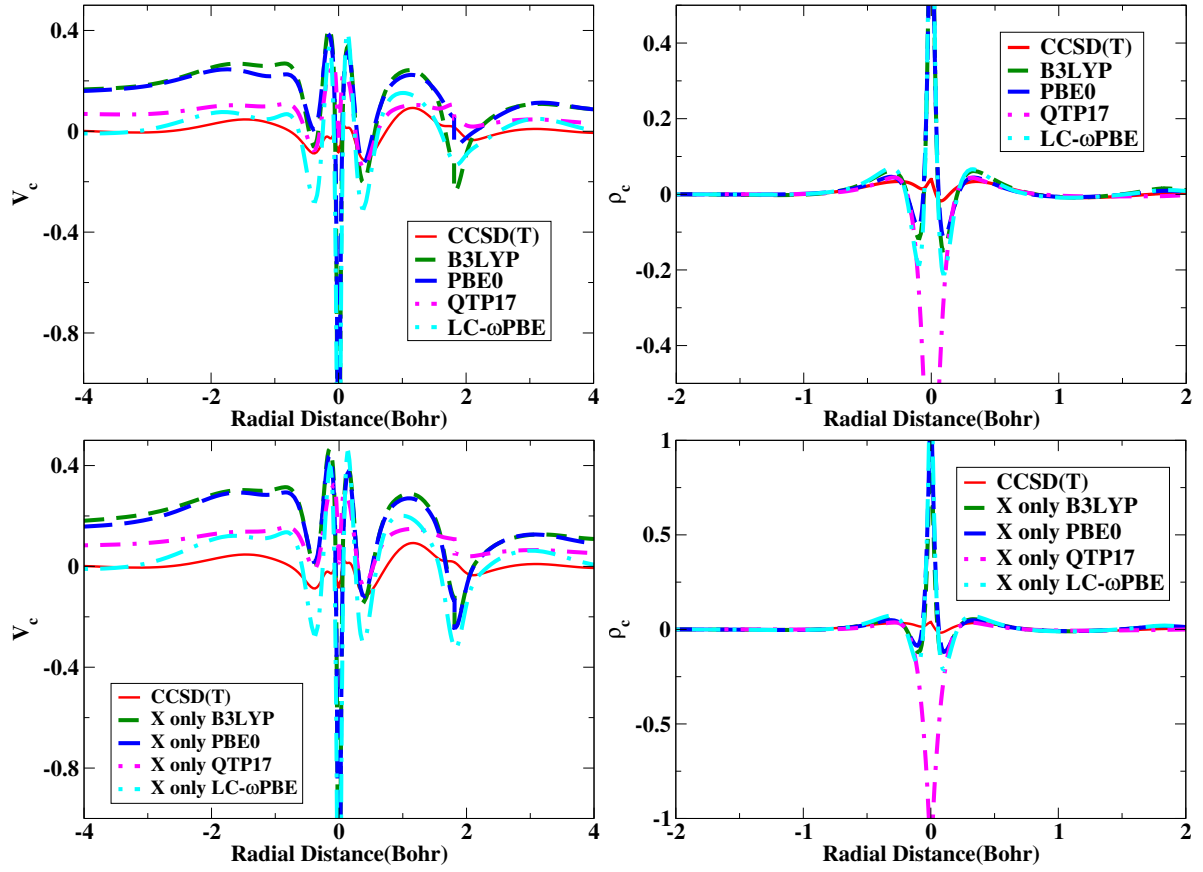


Figure S4: The correlation potentials (Eq. (9)) and correlated densities (Eq. (8)) of the H_2O molecule, calculated for several popular HYB DFAs with (top panel) and without (bottom panel) semi-local DFA correlation functional ($E_c^{\text{DFA}}[\rho]$) in Eq. (6).

II) Exchange only Local/Semilocal Functionals

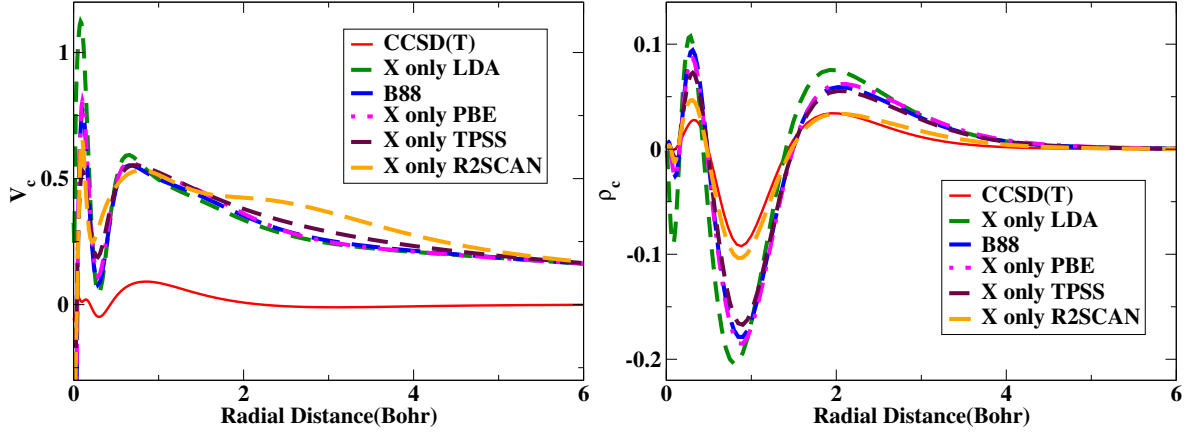


Figure S5: The correlation potentials (Eq. (9)) and correlated densities (Eq. (8)) of the Ne atom computed from standard semi-local X-only DFA functionals.

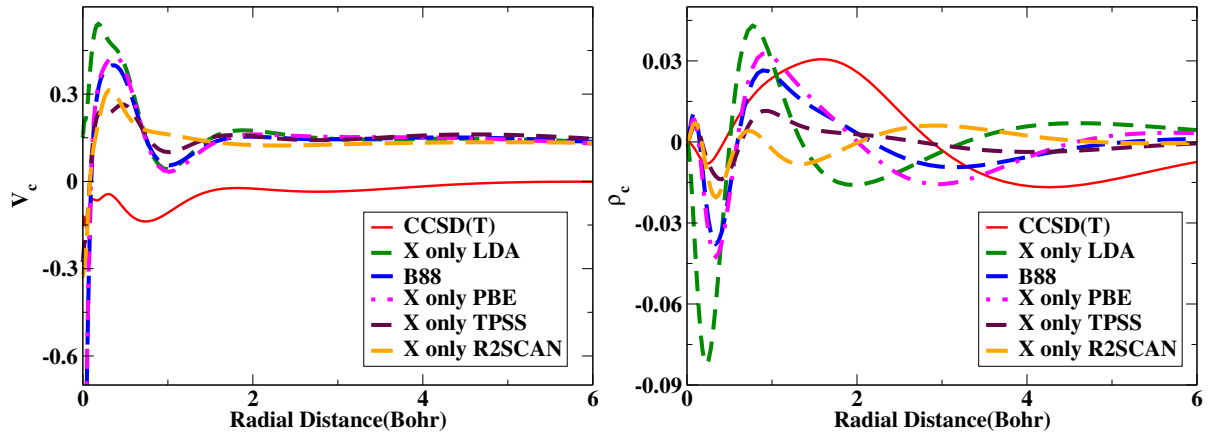


Figure S6: The correlation potentials (Eq. (9)) and correlated densities (Eq. (8)) of the Be atom computed from standard semi-local X-only DFA functionals.

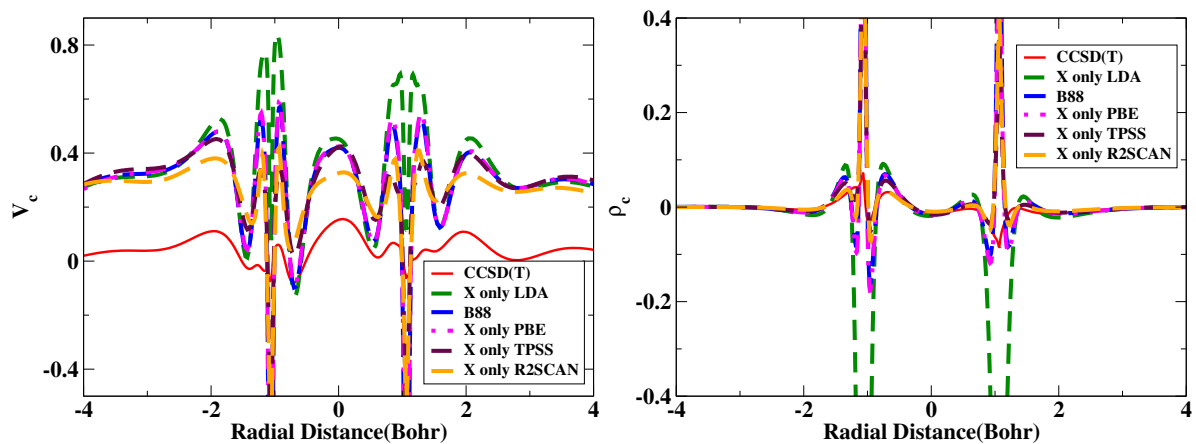


Figure S7: The correlation potentials (Eq. (9)) and correlated densities (Eq. (8)) of the CO molecule computed from standard semi-local X-only DFA functionals.

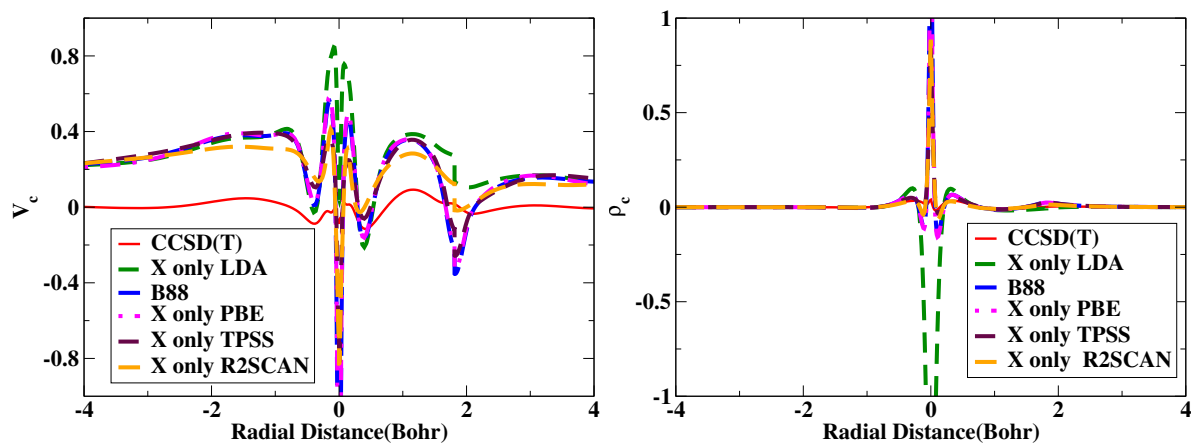


Figure S8: The correlation potentials (Eq. (9)) and correlated densities (Eq. (8)) of the H₂O molecule computed from standard semi-local X-only DFA functionals.

III) Semilocal correlation with 100% HF

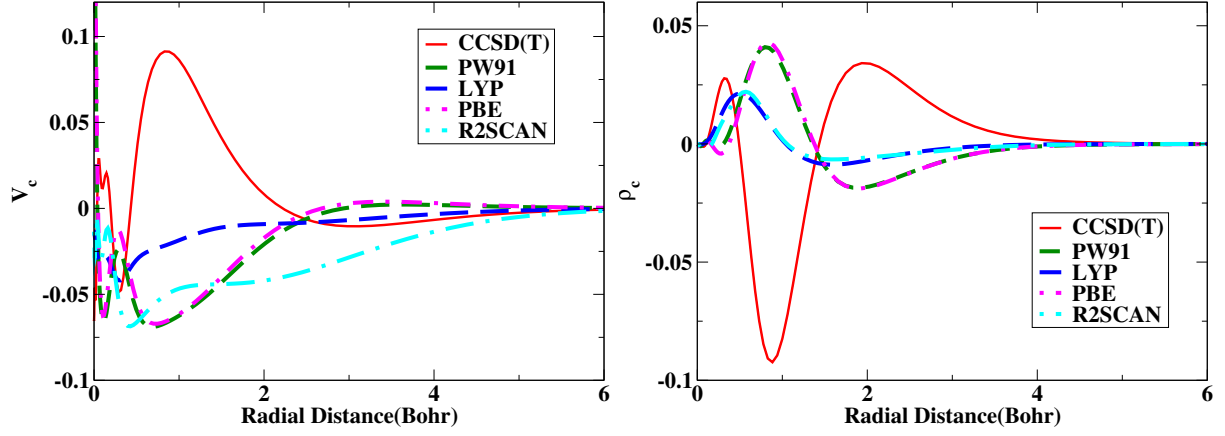


Figure S9: The correlation potentials (Eq. (9)) and correlated densities (Eq. (8)) computed from the self-consistent 100% HF + $E_c^{\text{DFA}}[\rho]$ calculations for Ne atom

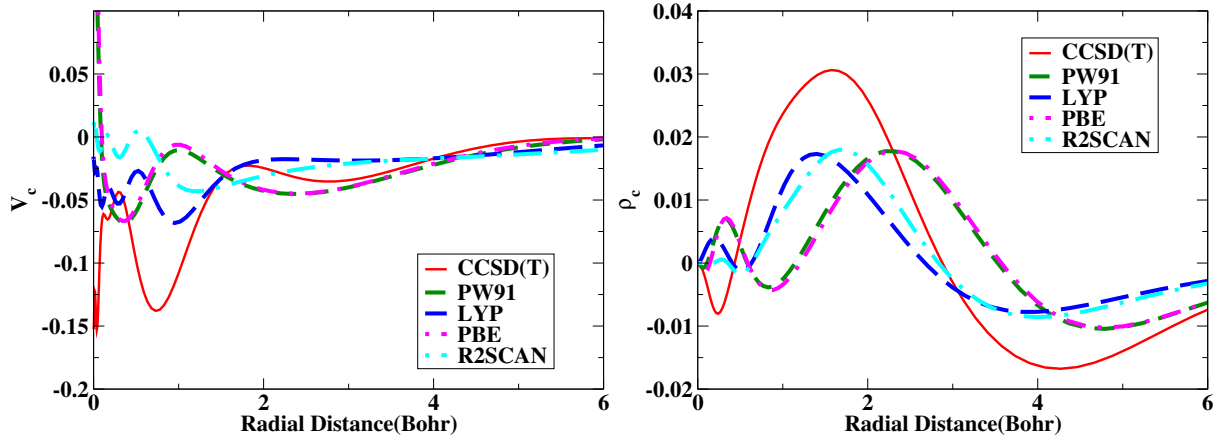


Figure S10: The correlation potentials (Eq. (9)) and correlated densities (Eq. (8)) computed from the self-consistent 100% HF + $E_c^{\text{DFA}}[\rho]$ calculations for Be atom

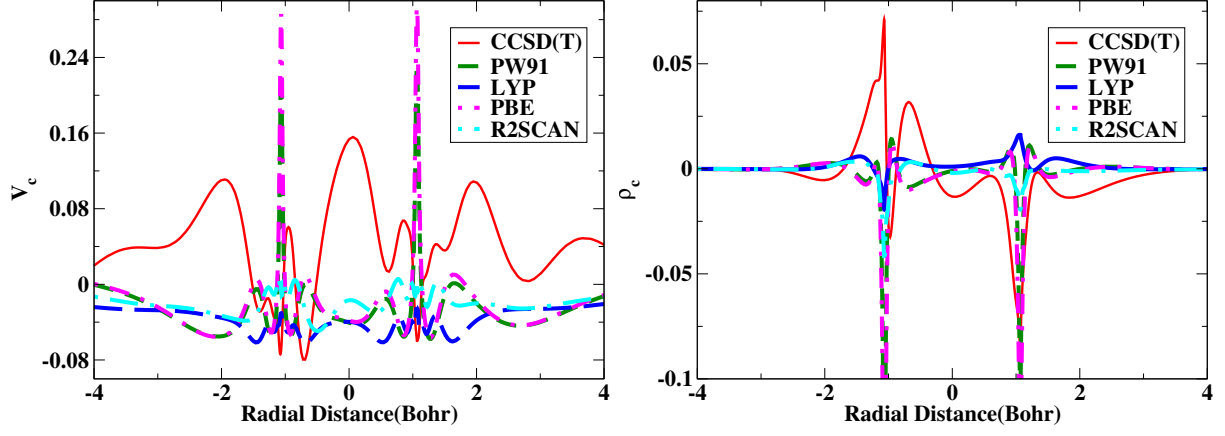


Figure S11: The correlation potentials (Eq. (9)) and correlated densities (Eq. (8)) computed from the self-consistent 100% HF+ $E_c^{\text{DFA}}[\rho]$ calculations for CO molecule

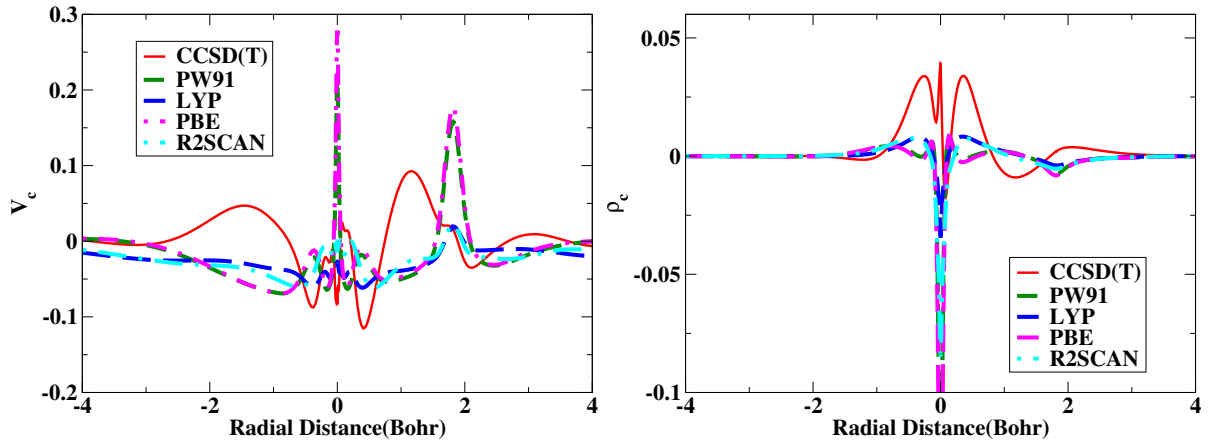


Figure S12: The correlation potentials (Eq. (9)) and correlated densities (Eq. (8)) computed from the self-consistent 100% HF+ $E_c^{\text{DFA}}[\rho]$ calculations for the H₂O molecule

IV) UMK26 and UMK26x

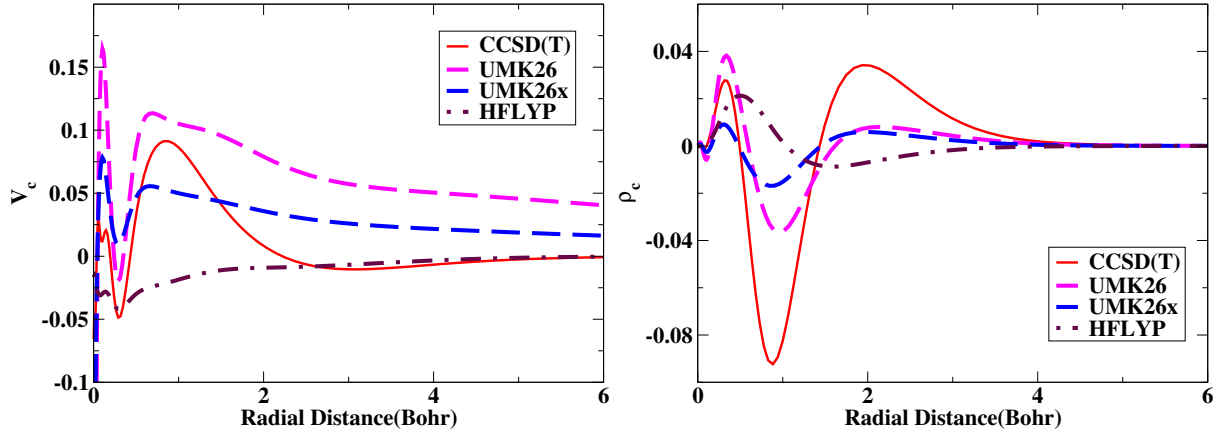


Figure S13: The correlation potentials and densities of UMK26 and UMK26x for Ne atom

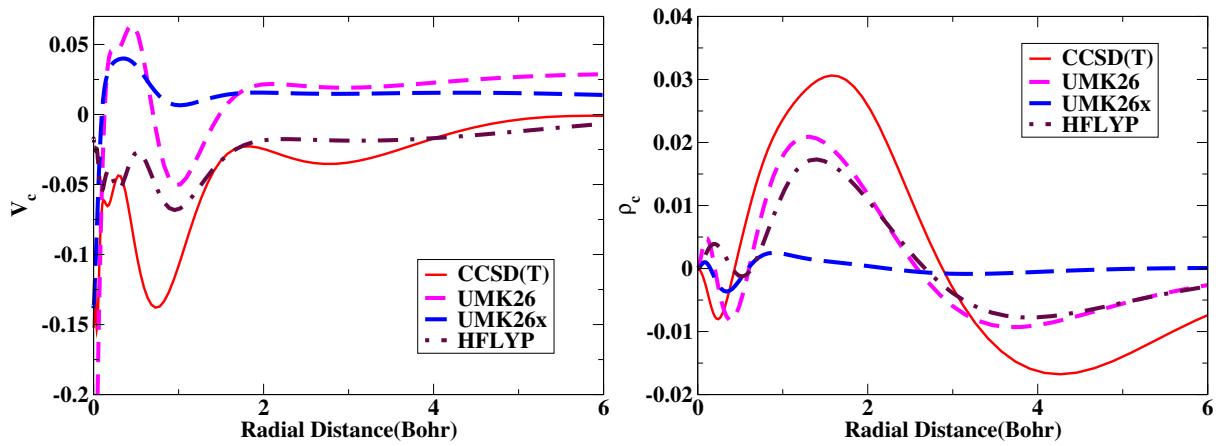


Figure S14: The correlation potentials and correlated densities of UMK25 and UMK25x for the Be atom

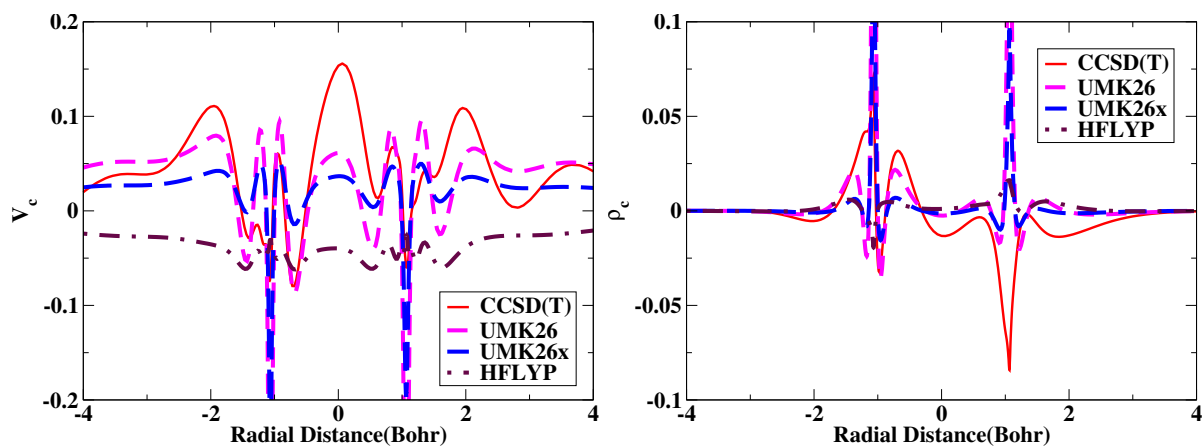


Figure S15: Correlation potential and correlated density for UMK25 and UMK25x for the CO molecule

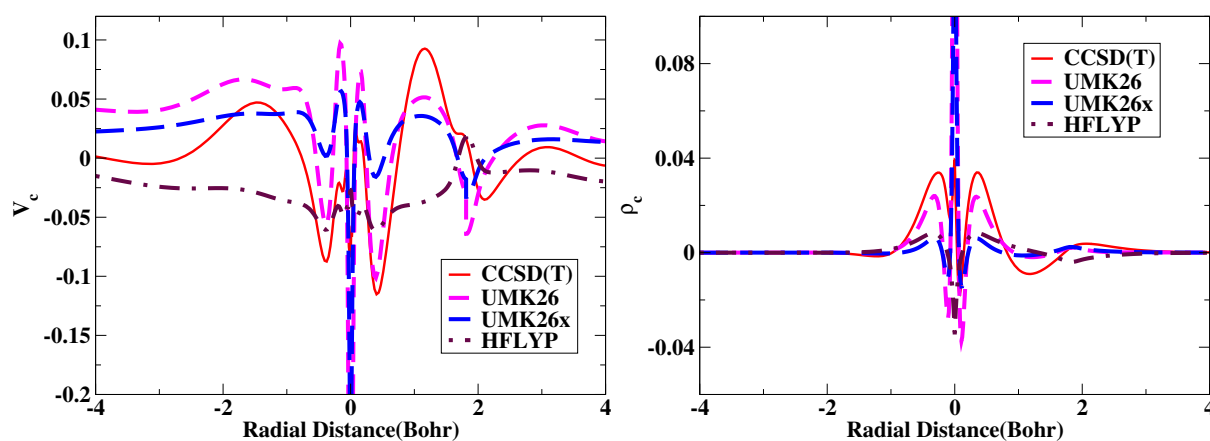


Figure S16: The correlation potentials and correlated densities of UMK25 and UMK25x for the H₂O molecule

Table S1: Vertical ionization potential (a.u.) computed for several systems with full and exchange-only parts of different hybrid functionals. All calculations have been performed in the uncontracted aug-cc-pVTZ basis set.

System	IP-EOM-CCSD	PBE0	PBE0 _x	B3LYP	B3LYP _x	QTP17	QTP17 _x	LC- ω PBE	LC- ω PBE _x
<i>He</i>	0.90156	0.66954	0.64252	0.66159	0.62246	0.80186	0.76157	0.77887	0.75210
<i>H₂</i>	0.60196	0.44014	0.41360	0.43361	0.40028	0.52559	0.49129	0.55544	0.52855
<i>Be</i>	0.34225	0.23863	0.21359	0.23222	0.20609	0.28319	0.25594	0.32767	0.30150
<i>He₂</i>	0.90151	0.66954	0.64252	0.66158	0.62245	0.80185	0.76156	0.77886	0.75209
<i>Ne</i>	0.78515	0.58841	0.55193	0.57562	0.53134	0.73886	0.69299	0.69047	0.65443
<i>H₂O</i>	0.46410	0.33397	0.30179	0.32467	0.28706	0.43773	0.39845	0.44402	0.41138
<i>HF</i>	0.59046	0.43548	0.40162	0.42469	0.38428	0.55997	0.51795	0.54341	0.50954
<i>NH₃</i>	0.38703	0.27239	0.24129	0.26397	0.22869	0.35829	0.32127	0.38149	0.34951
<i>Mg</i>	0.27789	0.1994	0.17549	0.19452	0.16946	0.2374	0.21112	0.27545	0.25036
<i>CO</i>	0.52234	0.39503	0.36363	0.38696	0.34991	0.48948	0.45109	0.50819	0.47644
<i>N₂</i>	0.57640	0.44869	0.41605	0.43992	0.40074	0.55805	0.51762	0.56159	0.52880
<i>Ar</i>	0.57617	0.44050	0.40395	0.42918	0.39053	0.53221	0.49238	0.55046	0.51350
<i>C₂H₆</i>	0.46270	0.34876	0.31866	0.34210	0.30649	0.42647	0.39000	0.45443	0.42407
<i>HCl</i>	0.46748	0.34954	0.31519	0.33948	0.30341	0.42836	0.39108	0.45726	0.42219
<i>Ne₂</i>	0.77988	0.58469	0.54787	0.57175	0.52714	0.73517	0.68907	0.68594	0.64950
<i>Cl₂</i>	0.42353	0.32079	0.28524	0.31112	0.27381	0.39769	0.35921	0.42501	0.38891
MAE		0.14531	0.17659	0.15421	0.19102	0.04676	0.08486	0.0403	0.07172
MARE [%]		25.941	31.982	27.608	34.553	8.496	15.694	05.748	11.839

Table S2: Correlation energies (in E_h) for several systems computed for B3LYP HYB functional using equation 7 (third column) and the correlation energy expression (fourth column) using self-consistent B3LYP. The last column presents the scaled energy difference. The MAE (in E_h) and MARE are calculated with respect to CCSD(T) reference data (second column). All calculations have been performed in the uncontracted aug-cc-pVQZ basis set.

Systems	CCSD(T)	Eq. (7)	$E_c^{\text{B3LYP}}[\rho]$	$E_c^{\text{XDiff}}[\rho]$
<i>He</i>	-0.0411819	-0.0546614	-0.0638648	0.0092034
<i>H₂</i>	-0.0404878	-0.0478979	-0.0556636	0.0077657
<i>Be</i>	-0.088351	-0.1023425	-0.1339201	0.0315776
<i>He₂</i>	-0.082365	-0.1093229	-0.1277298	0.0184069
<i>Ne</i>	-0.3621118	-0.4421277	-0.4901434	0.0480157
<i>H₂O</i>	-0.3509719	-0.4154888	-0.4387008	0.023212
<i>HF</i>	-0.3644942	-0.4388767	-0.4646248	0.0257481
<i>NH₃</i>	-0.3222876	-0.3772973	-0.4131716	0.0358743
<i>Mg</i>	-0.2189615	-0.4972266	-0.5882979	0.0910713
<i>CO</i>	-0.5025411	-0.5951173	-0.6256263	0.030509
<i>N₂</i>	-0.5173779	-0.6026224	-0.6238206	0.0211982
<i>Ar</i>	-0.4433619	-0.7598174	-0.9500528	0.1902354
<i>C₂H₆</i>	-0.534443	-0.6236359	-0.7188351	0.0951992
<i>HCl</i>	-0.4369698	-0.7509983	-0.9215902	0.1705919
<i>Ne₂</i>	-0.7244349	-0.8842862	-0.9806755	0.0963893
<i>Cl₂</i>	-0.8398284	-1.4675816	-1.7861369	0.3185553
MAE		0.144	0.22	
MARE[%]		37.27	58.55	

Table S3: Correlation energies (in E_h) for several systems computed for HYB functional LC- ω PBE using equation 7 (third column) and correlation energy expression (fourth column) of self-consistent LC- ω PBE. The last column presents the scaled energy difference. The MAE (in E_h) and MARE are calculated with respect to CCSD(T) reference data (second column). All calculations have been performed in the uncontracted aug-cc-pVQZ basis set.

Systems	CCSD(T)	Eq. (7)	$E_c^{\text{LC-}\omega\text{PBE}}[\rho]$	$E_c^{\text{XDiff}}[\rho]$
<i>He</i>	-0.0411819	-0.044564	-0.0411048	-0.0034592
<i>H₂</i>	-0.0404878	-0.0455631	-0.0431769	-0.0023862
<i>Be</i>	-0.088351	-0.0702062	-0.0857197	0.0155135
<i>He₂</i>	-0.082365	-0.0891291	-0.0822094	-0.0069197
<i>Ne</i>	-0.3621118	-0.380318	-0.34728	-0.033038
<i>H₂O</i>	-0.3509719	-0.3725685	-0.325567	-0.0470015
<i>HF</i>	-0.3644942	-0.3877069	-0.3355512	-0.0521557
<i>NH₃</i>	-0.3222876	-0.3423704	-0.3153051	-0.0270653
<i>Mg</i>	-0.2189615	-0.3877376	-0.4093355	0.0215979
<i>CO</i>	-0.5025411	-0.5160867	-0.4489112	-0.0671755
<i>N₂</i>	-0.5173779	-0.5276496	-0.4519499	-0.0756997
<i>Ar</i>	-0.4433619	-0.6137617	-0.7053523	0.0915906
<i>C₂H₆</i>	-0.534443	-0.5685066	-0.5603639	-0.0081426
<i>HCl</i>	-0.4369698	-0.6118993	-0.6873467	0.0754473
<i>Ne₂</i>	-0.7244349	-0.760682	-0.6946542	-0.0660278
<i>Cl₂</i>	-0.8398284	-1.1844388	-1.3282728	0.143834
MAE		0.067	0.090	
MARE[%]		17.87	20.33	

Table S4: Vertical excitation energies (eV) for charge-transfer excited states of different dimers, obtained in TDDFT calculations with the cc-pVDZ basis set and deviations with respect to the reference (J. Chem. Theory Comput. 2020, 16, 7, 4213).

System	Symm.	Ref.	PBE0	B3LYP	UMK26	QTP17	CAM-B3LYP	LC- ω PBE	LRC- ω PBEH	QTP00	QTP01	QTP02
NH ₃ ...F ₂	A ₁	6.62	5.25	5.16	7.00	6.36	5.47	5.75	5.38	6.52	5.85	6.08
C ₃ H ₆ O...F ₂	A''	5.90	1.76	1.32	6.32	5.02	2.82	3.89	2.51	5.47	4.04	4.59
C ₄ H ₄ N ₂ ...F ₂	B ₂	6.33	2.16	1.71	6.77	5.42	3.34	4.59	3.08	5.29	4.54	5.18
C ₃ H ₆ O...CH ₃ NO ₂	A	6.42	3.93	3.62	7.24	6.30	4.91	5.92	4.71	6.78	5.89	6.26
C ₄ H ₅ N...C ₄ H ₄ N ₂ ^a	B ₁	5.27	2.77	2.50	5.39	4.68	4.16	5.62	4.38	5.55	5.39	5.61
	A ₁	6.00	3.62	3.32	6.37	5.62	5.04	6.58	5.30	6.51	6.32	6.55
C ₄ H ₅ N...C ₄ H ₄ N ₂ ^b	A''	5.48	3.71	3.50	5.48	5.04	4.58	5.51	4.57	5.49	5.33	5.49
	A'	6.07	4.40	4.19	6.26	5.78	5.29	6.20	5.29	6.23	6.00	6.17
C ₂ F ₄ ...C ₂ H ₄ (5Å)	B ₁	10.56	6.84	6.49	7.84	7.93	8.36	9.50	8.38	7.88	9.76	8.43
C ₂ F ₄ ...C ₂ H ₄ (3.5Å)	B ₁	8.09	6.14	5.88	7.49	7.43	6.95	7.48	6.87	7.49	7.39	7.45
NH ₃ ...OF ₂	A'	7.09	2.90	2.45	7.18	6.01	4.13	5.45	3.77	6.58	5.35	5.87
NH ₃ ...C ₄ H ₄ N ₂	A'	7.53	4.10	4.06	5.60	5.59	4.28	4.38	4.20	5.54	4.43	5.47
	A'	7.83	5.26	5.05	6.33	6.56	5.40	5.38	5.40	5.95	5.44	5.51
MAD			2.80	3.07	0.74	0.88	1.88	1.16	1.95	0.81	1.10	0.96
MAX			4.19	4.64	2.72	2.63	3.25	3.15	3.39	2.68	3.10	2.32
MSD			-2.80	-3.07	-0.30	-0.88	-1.88	-0.99	-1.95	-0.61	-1.04	-0.81

^a H-bonded.

^b Stacked.

Table S5: Intramolecular charge-transfer excitations (eV) w.r.t theoretical best estimates (TBE) from Loos et al (J. Chem. Theory Comput. 2021, 17, 6, 3666–3686). The basis set was cc-pVTZ.

System	Symm.	TBE	PBE0	B3LYP	QTP17	UMK26	UMK26x	CAM-B3LYP	LC- ω PBE	LRC- ω PBEH	QTP00	QTP01	QTP02
Aminobenzonitrile	2A ₁	5.26	5.10	5.02	5.38	5.40	5.70	5.21	5.34	5.23	5.38	5.32	5.35
Aniline	2A ₁	5.87	5.70	5.61	5.89	5.87	6.10	5.77	5.87	5.80	5.87	5.84	5.86
Azulene	2A ₁	3.89	3.71	3.63	3.82	3.76	3.99	3.75	3.84	3.76	3.78	3.80	3.81
	2B ₂	4.55	5.86	4.66	5.00	5.04	5.47	4.79	4.88	5.99	4.98	4.87	4.91
Benzonitrile	1A ₂	7.10	6.31	6.21	6.64	6.63	6.88	6.62	6.87	6.60	6.73	6.79	6.81
Benzothiadiazole	1B ₂	4.37	3.94	3.83	4.26	4.57	4.64	4.15	4.43	4.18	4.32	4.34	4.37
Dimethylaminobenzonitrile	2A ₁	4.94	4.80	4.72	5.16	4.77	5.55	4.97	5.11	4.97	5.19	4.85	5.14
Dimethylaniline	1B ₁	4.47	4.57	4.48	5.07	5.21	5.53	4.74	4.88	4.72	5.10	4.89	4.96
	2A ₁	5.54	5.40	5.32	5.71	5.74	6.00	5.53	5.65	5.54	5.72	5.64	5.68
Dipeptide	7A'	8.15	7.24	7.07	8.48	8.51	7.98	7.83	8.67	7.95	8.28	8.24	8.38
β -dipeptide	7A'	8.51	6.77	6.51	7.80	8.04	8.53	7.28	7.60	7.96	7.84	7.51	7.62
	10A''	8.90	6.90	6.84	8.64	9.11	9.41	7.92	8.87	8.12	8.89	8.45	8.59
HCl	1 Π	8.10	7.93	7.68	8.25	8.34	8.45	7.82	8.23	7.99	8.20	7.94	8.01
Nitroaniline	2A ₁	4.57	4.18	4.04	4.78	4.95	5.35	4.47	4.79	4.51	4.88	4.74	4.81
Nitrobenzene	2A ₁	5.57	5.00	4.83	5.45	5.52	5.83	5.22	5.55	5.27	5.51	5.45	5.51
Nitrodimethylaniline	2A ₁	4.28	3.92	3.78	4.56	4.75	5.17	4.25	4.58	4.30	4.69	4.53	4.61
Nitropyridine-N-Oxide	2A ₁	4.24	4.04	3.92	4.43	4.47	4.91	4.26	4.45	4.32	4.46	4.42	4.44
N-Phenylpyrrole	2B ₂	5.53	4.82	4.66	5.35	5.45	5.72	5.08	5.24	5.10	5.38	5.23	5.28
	3A ₁	6.04	5.17	5.01	6.46	6.69	7.01	6.00	6.70	6.06	6.68	6.64	6.67
Phthalazine	1A ₂	3.93	3.64	3.50	4.71	5.09	5.42	4.05	4.26	3.94	4.84	4.37	4.51
	1B ₁	4.34	4.05	4.64	4.83	5.10	5.48	4.39	4.59	4.32	4.95	4.66	4.76
Quinoxaline	1B ₂	4.74	3.58	4.15	4.21	4.84	5.17	4.57	3.95	4.57	4.30	4.82	4.11
	3A ₁	5.75	5.89	4.47	6.26	6.36	6.79	6.00	6.15	4.61	6.28	6.13	6.19
	2B ₁	6.33	5.92	5.76	6.46	6.54	7.00	6.28	7.02	6.40	6.53	7.09	6.52
Twisted-Dimethylaniline	1A ₂	4.17	3.38	3.23	4.73	5.31	5.86	3.98	4.40	3.90	5.02	4.48	4.66
	1B ₁	4.84	4.10	3.91	5.52	5.59	5.84	4.78	5.34	4.64	5.50	5.36	5.41
Twisted-N-Phenylpyrrole	2B ₂	5.73	4.57	4.37	5.73	5.81	6.05	5.38	5.56	5.41	5.73	5.58	5.62
	2A ₁	5.82	4.68	4.46	6.05	6.10	6.30	5.62	6.30	5.68	6.16	6.21	6.23
	1A ₂	6.04	5.20	5.00	6.51	6.62	7.27	5.94	6.60	5.98	6.87	6.56	6.71
	1B ₁	6.28	5.34	5.11	6.85	6.45	7.92	6.19	7.04	6.24	7.27	6.95	7.12
MAD			0.64	0.74	0.33	0.38	0.67	0.23	0.33	0.25	0.37	0.31	0.34
MAX			2.00	2.07	0.78	1.16	1.69	1.23	0.91	1.44	0.99	1.00	0.89
MSD			-0.54	-0.71	0.17	0.29	0.65	-0.17	0.16	-0.13	0.25	0.13	0.16

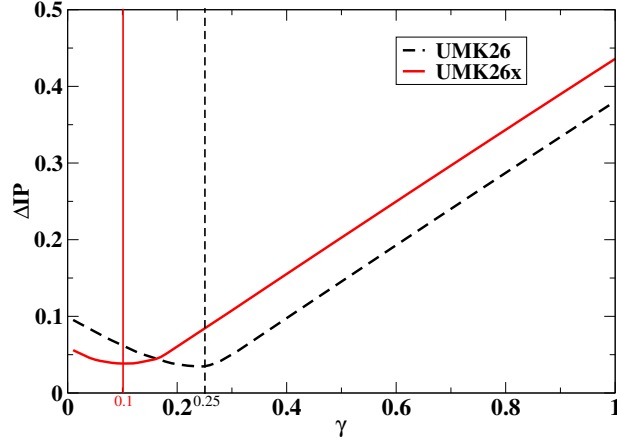


Figure S17: ΔIP error with respect to the γ parameter for the optimization of UMK26 and UMK26x BLYP-based functional. The vertical lines indicate the optimal values obtained for UMK26 and UMK26x DFAs.

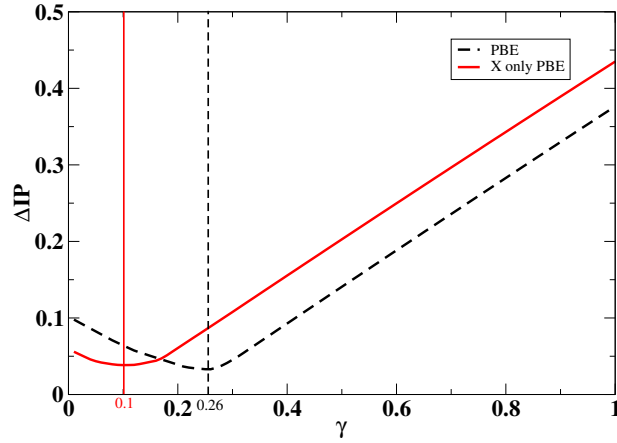


Figure S18: ΔIP error with respect to the γ parameter for the optimization of γ in Eq. 10 with PBE exchange and correlation expressions. The dashed black curve represents the full hybrid functional constructed as $E_{xc}^{\text{HYB}}[\rho] = E_x^{\text{EXX}} + \gamma(E_x^{\text{PBE}}[\rho] - E_x^{\text{EXX}}) + E_c^{\text{PBE}}[\rho]$ and the red curve corresponds to exchange only construction as $E_{xc}^{\text{HYB}}[\rho] = E_x^{\text{EXX}} + \gamma(E_x^{\text{PBE}}[\rho] - E_x^{\text{EXX}})$. The vertical lines indicate the optimal values obtained for both cases.

Chapter 4

Summary of Most Important Findings of the Study and Future Directions

4.1 Summary of Most Important Findings of the Thesis

- Historically, the development and evaluation of Density Functional Theory relied predominantly on energy and energy-based benchmarks. This is not surprising, as energy is a crucial quantity, and many properties, such as forces and static polarizability, are derived from it. This inclination towards energy has necessitated a focus on and improvement of other vital quantities, such as XC potentials and ionization potentials.
- The early stages of the doctoral research involved analyzing and developing techniques to address challenges in inverse Kohn-Sham schemes, which are elaborated in section [1.2.6](#) of chapter 1.
- We developed and applied a systematic methodology for evaluating XC functionals across diverse quantum-chemical properties, incorporating the latest developments in inverse Kohn-Sham schemes.
- We performed a comprehensive evaluation of 155 hybrid DFT functionals, which reveals current trends among existing functionals for these physical quantities. The observation of a clear hierarchy of errors and its comparison with well-known, different wavefunction theory-based methods constitute the first scientific observation.

- The study demonstrates a direct relationship between the quality of the XC potential, ionization potentials, and the long-range Hartree-Fock coefficient. This indicates the crucial implications of improving the quality of KS orbital energies via improving the quality of XC potentials.
- The evaluation in terms of the Density-Driven(DD) and the Functional-Driven(FD) error indicated the dominant contribution from the functional-driven error, requiring systematic focus to improve the functional-driven error.
- We showed that the dominant qualitative features of correlation in hybrid DFAs do not arise primarily from the semilocal correlation functional itself, but instead from the difference between the semilocal exchange and exact-exchange contributions.
- We proposed an interpretable construction principle for hybrid functionals in which the difference between semilocal and exact-exchange is scaled in a controlled way.
- We developed a new global hybrid functional, UMK26, to address these observations. UMK26 is based on the adiabatic connection formalism, and the optimization is based on the ΔIP error indicated in chapter 2.
- UMK26 possesses increased accuracy for correlation potential and correlated densities, an implication we expect given the observations in chapter 2. Evaluations of HOMO and valence ionization potentials in atomic and molecular systems revealed consistent improvements.
- UMK26 also demonstrated increased accuracy in describing charge transfer excitations compared to other conventional functionals. It also performed well in describing integer discontinuities, a critical testbed for XC functionals.
- UMK26 showed superior performance in reducing the electron self-interaction error, which is a long-standing challenge for Density functional approximations. Both evaluations on the SIE4x4 GMTKN55 SLIM20 benchmarks, and the dissociation curve for charged species, provided a clear edge for UMK26 over other well-known XC functionals.
- In summary, the doctoral thesis performs an extensive evaluation of the existing accuracy and efficiency of XC functionals for DFT. We propose a new methodology for such evaluations, which are necessary for developing robust density functionals across a wide range of applications. In this endeavor, we have developed a new global hybrid XC functional and have demonstrated its scope and limitations. The findings of the thesis are valuable tools in pushing the limits of Kohn-Sham Density Functional Theory.

4.2 Future Directions

- UMK26 is a global hybrid functional constructed by mixing B88 and LYP semilocal functionals with Hartree-Fock exchange. UMK26 possesses an asymptotic of the potential which scales as $-\frac{0.75}{r}$ rather than the correct $-\frac{1}{r}$. This can be addressed within the range-separated formalism, which offers flexibility via long- and short-range Hartree-Fock coefficients.
- It is also expected that the range-separated formalism and more semi-local ingredients would provide further flexibility to enhance the thermochemistry benchmarks. Hence, augmenting UMK26 through the range-separated scheme has a clear scope.
- Another key area is the evaluation of correlation functionals. Our study already shows that a dominant part of the correlation features arises from the exchange difference between semi-local and Hartree-Fock terms, and our analysis of correlation functionals demonstrates their inability to describe quantities such as the correlation potential and correlated densities.
- One key area is developing correlation functionals and optimizing parameters to fit physical quantities such as the correlation potential and correlated densities. Well-known and widely employed correlation functionals, such as LYP [95, 98], can be optimized because they possess tunable semi-empirical parameters that can also be re-parametrized [99].

4.3 List of publications

4.3.1 Publications which constitute the findings of the PhD thesis

1. A Critical Evaluation of the Hybrid KS DFT Functionals Based on the KS Exchange-Correlation Potentials[88]

Vignesh Balaji Kumar, Szymon Śmiga, Ireneusz Grabowski. *J. Phys. Chem. Lett.* 10 October 2024; 15 (40): 10219–10229.

<https://doi.org/10.1021/acs.jpcclett.4c01979>

Contributions of the Doctoral Student:

- The doctoral candidate developed the Python program to automate all the routines for the calculations.
- The doctoral candidate installed and managed parallelized scientific packages

necessary to perform the calculations in the High Performance Computing cluster.

- The doctoral candidate performed tests and analysis of installed open-source scientific packages and in-house-developed computational routines.
- The doctoral candidate performed the computational calculations and simulations and produced the scientific results.
- The doctoral candidate actively participated in the result analysis, interpretation, and deriving scientific conclusions.
- Doctoral candidate prepared the initial draft of the manuscript and actively participated in subsequent revisions and final publication.

2. Primary Role of Semi-Local and Exact-Exchange Difference in the Description of Correlation Effects in Hybrid Functionals[100]

Vignesh Balaji Kumar, Szymon Śmiga, Rodrigo Araújo Mendes, Bogumiła Jezierska, Rodney Bartlett, Ireneusz Grabowski. *J. Chem. Theory Comput.*, XXX, 2026

<https://doi.org/10.1021/acs.jctc.6c00843>

Contributions of the Doctoral Student:

- The doctoral candidate developed Python programs to compute correlation potentials and density using computational chemistry packages such as n2v [77], KS-Pies [101], PySCF [102], and Psi4 [103].
- The doctoral candidate developed Python programs to evaluate the XC approximations against the HOMO and valence IPs from reference [82].
- The doctoral candidate developed the Python package to benchmark XC functionals against well-known datasets such as the GMTKN55, MGCDDB84, and SLIM.
- The doctoral candidate developed a Python program to analyze the dissociation curve of charge species using different XC functionals.
- The doctoral candidate performed computational calculations using these programs to evaluate and develop the UMK26 global hybrid functional.
- The doctoral candidate optimized the UMK26 functionals, exploring different procedures and ingredients.
- The doctoral candidate actively participated in the result analysis, scientific discussion, and finalizing conclusions.

- The doctoral candidate actively participated in drafting the manuscript, in subsequent revisions, and final publications.

4.3.2 Other Publications during the doctoral research

In this section, we present the list of scientific publications published during the doctoral program that are outside the scope of the doctoral thesis.

1. The Best DFT Functional Is the Ensemble of Functionals[104]

Yuting Rui, Yuxinxin Chen, Elena Ivanova, **Vignesh Balaji Kumar**, Szymon Śmiga, Ireneusz Grabowski, Pavlo O. Dral. *Advanced Science*, 25th October 2024, 11, 2408239.

<https://doi.org/10.1002/advs.202408239>

Abstract: The development of better density functional theory (DFT) methods is one of the most active research areas, given the importance of DFT for ubiquitous molecular and materials simulations. However, this research primarily focuses on improving a specific exchange–correlation Kohn–Sham density functional. Here, a robust procedure is proposed for constructing transferable ensembles of density functionals that perform superior to any constituent individual density functional. It is shown that such ensembles built only with the density functionals predating the GMTKN55 benchmark of 2017 can reach a record-low weighted error of 1.62 kcal mol^{−1} on this benchmark compared to 3.08 kcal mol^{−1} of the best constituent density functional. The DENS24 density functional ensembles are also introduced as practical DFT methods with consistently accurate performance for various simulations at affordable cost. DENS24 ensembles are open-source and can be used for simulations online. Additionally, it is shown that the ensembles can be integrated into the SCF procedure by creating mixed DENS24 functionals, which have the same accuracy but are faster than ensembles of independent functionals.

2. Plasmon Induced Charge Transfer Dynamics in Metallic Nanoparticle-MoSe2 Nanoflake Heterostructures[105]

P. K. Verma, **Vignesh Balaji Kumar**, Varadharajan Srinivasan
Advanced Optical Materials, 13 February 2025, 2402679.

<https://doi.org/10.1002/adom.202402679>

Abstract: Plasmon-induced hot carrier dynamics are crucial in various practical applications such as water splitting and photovoltaics. A hybrid system formed by interfacing plasmonic Au or Ag metal nanoparticles with triangular MoSe2 nanoflakes is proposed, which also possess edge-localized plasmons. Using time-dependent density functional theory-based simulations, this bi-plasmonic system is shown to exhibit interfacial charge transfer induced by plasmonic excitations of either compo-

nent. Tracking the fate of photoinduced plasmons in the system reveals that a significant pathway to their decay involves the direct transfer of hot-carriers across the interface. This study finds that while the likelihoods of both the direct hot-electron and hot-hole transfers are comparable, in most cases considered, the latter dominates. The extent and net direction of direct charge transfer are found to depend on various tunable features of the interface, including the plasmon mode (nanoparticle or nanoflake) excited and the polarization of the light used. It is anticipated that this platform could prove extremely useful for widening the substrate scope in photocatalysis and photodetection applications.

3. Size and Composition Dependence of Plasmonic Excitations in Transition Metal Dichalcogenide Nanoflakes[106]

Paresh C. Rout, **Vignesh Balaji Kumar**, Nesta Benno Joseph, Shalini Tomar, Varadharajan Srinivasan.

10 August 2023, *The Journal of Physical Chemistry C*, 127 (33): 16464–16472.
<https://doi.org/10.1021/acs.jpcc.3c01931>

Abstract: Nanoparticles and nanostructures of two-dimensional semiconductors are being explored for their potential in photocatalysis, optoelectronics, and energy harvesting applications. Herein, we investigate the size and composition dependence of electronic, structural, and optical properties of triangular transition metal dichalcogenide (MX_2 , $\text{M} = \text{Mo}, \text{W}$ and $\text{X} = \text{S}, \text{Se}, \text{Te}$) nanoflakes. Structural optimizations reveal that, while all flakes undergo dimerization of X atoms along each edge, in large WS_2 flakes, the edge S forms trimers. All flakes are found to be metallic with dominant contributions to the conducting states from the edges. Our time-dependent density functional theory-based calculations find both surface (2D) and edge (1D) plasmonic excitations at low energies in all small flakes. However, only Se-containing flakes are found to support edge plasmons at all sizes. The corresponding plasmon peaks exhibit a red shift with flake size as expected from quantum confinement effects. Supported by induced charge density and potential analyses, transition contribution maps, as well as trends in generalized plasmonicity indices of the excitations, these findings assume significance given the role of plasmonic nanostructures in the aforementioned applications.

4. Physically meaningful solutions of optimized effective potential equations in a finite basis set within KS-DFT framework[65]

Aditi Singh, **Vignesh Balaji Kumar**, Ireneusz Grabowski, Szymon Śmiga, .
Advances in Quantum Chemistry, 4th April 2023, 87 , 297-31,
<https://doi.org/10.1016/bs.aiq.2023.01.003> ,

Abstract : The numerical evidence is provided showing that the physical solutions of the optimized effective potential equations (OEP) in a finite basis set, in the context of the Kohn–Sham (KS) Density Functional Theory, can only be obtained by employing the proper regularization procedure in the OEP method and a judicious choice of basis sets used in the KS OEP calculations. The regularization relies on the truncated singular value decomposition procedure to obtain the pseudoinverse of the density–density response matrix. We are showing that this is a critical aspect in determining the stable and numerically accurate solutions of the KS OEP equations for the exchange-only and correlated cases.

4.4 Conference Presentations During the Doctoral Program

- Presented research poster entitled ‘Emergent properties of lateral heterostructures of graphene and BC3 nanoribbons’ at the 25th International Workshop in Quantum Systems in Chemistry, Biology and Physics 2022 in Torun, Poland.
- Presented research poster entitled ‘Density functional theory study of armchair edged in-plane nanoribbon heterostructures of graphene and BC3’ at the 19th DFT2022 conference in Brussels, Belgium, Aug 28- Sep 2, 2022.
- Presented research poster entitled ‘Physically meaningful solutions of the Optimized effective potential Methods’ at the Quantum International Frontiers (QIF2023) conference in Łódź, Poland, June 20-24, 2023.
- Presented research poster entitled ‘On the convergence behavior of different optimized effective potential methods’ at the 17th International Congress of Quantum Chemistry in Bratislava, Slovakia, June 26-July 1, 2023.
- Presented research poster entitled ‘The need for accurate exchange-correlation potential in KS-DFT’ at the 2nd Symposium on Machine Learning in Quantum Chemistry in Uppsala, Sweden, Nov 28- Dec 1, 2023.
- Presented research poster entitled ‘An assessment of XC potentials among hybrid functionals’ at the 20th DFT2024 conference in Paris, France, Aug 25-30, 2024.
- Presented research poster entitled ‘Calibrating Hybrid DFT: A comprehensive evaluation of 155 Hybrid DFT functionals’ at the 19th Central European Symposium on Quantum Chemistry 2024 in Sveti Martin Na Muri, Croatia, Sep 11-14, 2024.

- Presented research poster entitled ‘UMK26-A new exchange tuned exchange-correlation functional for DFT with superior performance ’ at 57th conference of European Group on Atomic Systems in Torun, Poland from 21-25th June 2026.

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