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A range-separated double-hybrid functional from nonempirical constraints

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Abstract

On the basis of our previous developments in the field of nonempirical double hybrids, we present here a new exchange-correlation functional based on a range-separated model for the exchange part and integrating a nonlocal perturbative correction to the electron correlation contribution. Named RSX-QIDH, the functional is free from any kind of empirical parameterization. Its range-separation parameter is set to recover the total energy of the hydrogen atom, thus eliminating the self-interaction error for this one-electron system. Subsequent tests on some relevant benchmark datasets confirm that the self-interaction error is particularly low for RSX-QIDH. This new functional provides also correct dissociation profiles for charged rare-gas dimers, and very accurate ionization potentials directly from Kohn-Sham orbital energies.

Above all, these good results are not obtained at the expense of other properties. Indeed, further tests on standard benchmarks show that RSX-QIDH is competitive with the more empirical ω B97X-2 double hybrid, and outperforms the parent LC-PBE long-range corrected hybrid, thus underlining the important role of the nonlocal perturbative correlation.

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1. Introduction

Among the plethora of methods based on Kohn-Sham density-functional theory (KS-DFT)¹, hybrid density functionals are undoubtedly the most widely used class of approximations to tackle the accurate modeling of chemical systems^{2,3}. Based on the adiabatic connection model⁴, they (partially) cure most of the KS-DFT issues that years of benchmarks and tests have clearly identified (for recent and detailed examples see references 5-7). Among others, the so-called self-interaction error (SIE)⁸ arises, in one electron systems, from the non-cancellation of the spurious Coulomb self-repulsion energy by the approximate exchange-correlation contribution. More recently, the delocalization error (DE) was defined as a generalization of the many-electron SIE, thus suggesting that functionals with null DE are also SIE-free⁹.

The introduction of a significant contribution of exact-like exchange (EXX) into the functional reduces the SIE. The resulting global hybrid (GH) functional contains a constant weight (i.e. electron-coordinate independent) of the EXX contribution which provides a non-negligible nonlocal character to the functional (and, of course, to the corresponding potential). This approach shows improved numerical accuracy in estimating a large number of physico-chemical properties such as reaction energy barriers^{10,11} or optical spectra^{12,13}. Global hybrids like B3LYP¹⁴⁻¹⁶, PBE0^{17,18} or those belonging to the Minnesota family¹⁹, are among the most representative models.

Generally speaking, the exchange-correlation energy (E_{xc}) of a GH can be expressed as:

$$E_{xc}^{GH} = a_x E_x^{EXX} + (1 - a_x) E_x^{GGA} + E_c^{GGA} \quad (1)$$

where GGA stands for Generalized Gradient Approximation, one of the most used semilocal DFT approaches.

The fraction of EXX exchange, a_x , can be set on nonempirical basis^{20,21} or by pragmatic fitting to reference chemical databases. EXX values typically range from 10 (as in TPSSH²²) to 100% (as in M06-HF²³). In practice, an EXX contribution between 20 and 40% is often required to balance the different sources of errors, but larger contributions are required in some cases. Among them, properties like ionization potentials (IPs)²⁴, bond-length alternations (BLAs) of long-conjugated chains²⁵ or long through-space charge-transfer excitations²⁶ are probably the most concerned. However, it is worth to note that a large excess can deteriorate other important properties, such as molecular structures²⁷.

From a more formal point of view, the exchange potential of a GH behaves in the asymptotic region as $-\frac{a_x}{r_{12}}$ thus not exactly recovering the correct behavior $-\frac{1}{r_{12}}$, r_{12} being the inter-electronic distance²⁸.

The concept of range-separated exchange (RSX), originally proposed by Savin²⁹, is a physically-sound solution to correct the asymptotic behavior of the exchange potential. Over the past few years, it has led to the development of several long-range corrected (LC) approaches, such as LC-PBE³⁰, LC- ω PBE³¹ or ω B97³², just to mention some of the most popular. For these functionals, the EXX contribution ranges between 0% and 100% at short and long inter-electronic distances, respectively. In the original LC scheme, the junction between short- and long-range regions is assured by the *erf* function and tuned by a parameter, ω ³⁰. The Coulomb-attenuating method (CAM)^{33,34} is a generalization of the LC scheme, coupling a GH (such as B3LYP) at short r_{12} distance, with an high percentage of EXX at long r_{12} distance. These functionals provide low SIE, thus significantly improving a number of molecular properties, including dissociation limits for one-electron bound molecules, charge-transfer states or reaction energy barriers^{35,36}. Among others, CAM-B3LYP³³, ω B97X³² and M11³⁷ can be mentioned as representatives of the most recent RSX hybrids. The ω parameter is often determined on the basis of empirical criteria^{30-33,35,37,38}, even if some efforts have been done to determine it from physical arguments³⁹.

As for most of the hybridized density functionals, LC and CAM main limitation is related to the wrong description of weakly interacting systems, even if it is proved that they tend to better capture dispersion interactions than standard GHs^{40,41}. This drawback is often overcome by coupling the range-separated scheme to a classical dispersion correction⁴⁰⁻⁴³, even if the limits of the method clearly appear in some difficult cases^{44,45}.

A viable alternative consists in introducing nonlocal effects into the correlation contribution, using the so-called double-hybrid (DH) approximations⁴⁶⁻⁴⁹. DH functionals were introduced by Ernzerhof in 1996⁵⁰, firstly tested by Truhlar in 2004⁵¹, and then later popularized by Grimme⁵² by merging wavefunction and density-based approaches to get the best of both worlds. They sum to the self-consistent GH exchange-correlation energy (Eq. 1) a fraction of nonlocal correlation computed a posteriori according to the second-order perturbation theory (PT2), so that the exchange correlation energy can be expressed as:

$$E_{xc}^{DH} = a_x E_x^{EXX} + (1 - a_x) E_x^{GGA} + (1 - a_c) E_c^{GGA} + a_c E_c^{PT2} \quad (2)$$

where a_c governs the fraction of nonlocal PT2 correlation. In line with GHs, the a_x and a_c coefficients can be set by empirical construction (see for instance B2-PLYP⁵² as

representative case) or by theoretical arguments founded on the adiabatic connection model⁴ and exemplified by PBE0-DH^{53,54} and PBE-QIDH⁵⁵ functionals. From a conceptual point of view, these latter functionals are particularly appealing, since they well show how the increase of physical constraints, with respect to the parent GGA (PBE⁵⁶) and GH (PBE0^{17,18}) functionals, leads to an improvement of the performances over a wide range of properties^{57,58}. Furthermore, the increased contribution of nonlocal EXX ($\sim 70\%$ in PBE-QIDH), imposed by the fulfillment of defined theoretical constraints, leads also to a global reduction of the SIE⁵⁵. In this context, the next natural step is the introduction of the range-separated scheme within a double-hybrid functional in order to cumulate the advantages of both approaches. Originally developed by Ángyán and co-workers⁵⁹, this approach evolved a few years later with the development of the ω B97X-2 functional⁶⁰. This latter is an excellent method to target the modeling of systems especially prone to SIE and to model weak interactions (see for instance references 61 and 62). As part of the ω B97 family³², ω B97X-2 contains a significant number of empirical parameters (i.e. 16), a construction which often leads to improved performances for properties within the domain of training, but which is also source of numerical instabilities^{63,64}. Other valuable efforts were focused on the range separation of the correlation energy mainly having in mind the treatment of weak van der Waals interactions^{65,66}.

Within this context, we propose in the present work to integrate a RSX scheme within our nonempirical ‘quadratic-integrand double hybrid’ (QIDH) model⁵⁵, using fully nonempirical arguments. This new model, named RSX-QIDH, is the first exchange range-separated double-hybrid functional based on a simple and nonempirical exchange-correlation expression developed in a parameter-free fashion to solely satisfy physical constraints.

We show that by imposing two further theoretical conditions to the functional, i.e. the recovery of the correct asymptotic behavior of the exchange potential and of the hydrogen total energy, the resulting RSX-QIDH model allows to safely tackle challenging systems particularly prone to SIE that more standard exchange range-separated hybrids still fail to model.

2. The RSX-QIDH model

The starting point of the RSX-QIDH functional is the QIDH scheme⁵⁵ which is fully derived from the adiabatic connection⁴. In this framework, the exchange-correlation energy, E_{xc} , is defined as

$$E_{xc}[\rho] = \int_0^1 E_{xc,\lambda}[\rho] d\lambda, \quad (3)$$

where the coupling integrand $E_{xc,\lambda}$ is

$$E_{xc,\lambda} = \langle \Psi_\lambda | V_{ee} | \Psi_\lambda \rangle - \frac{1}{2} \iint dr' dr \frac{\rho(r)\rho(r')}{|r-r'|} \quad (4)$$

V_{ee} is the electron-electron interaction potential and Ψ_λ is the wavefunction minimizing the first term of Eqn.(4), under the constraint of producing a given density ρ . Three conditions can be defined for Eqn.(3). The first one is that for $\lambda=0$:

$$E_{xc,\lambda=0} = E_x^{EXX} \quad (5)$$

while the real interacting system corresponds to $\lambda=1$ and it is described (here) by a given GGA approach:

$$E_{xc,\lambda=1} = E_{xc}^{GGA} \quad (6)$$

Another constraint is then introduced by considering the weak interaction limit ($\lambda \rightarrow 0$), where the first-order derivative of the integrand of Eqn.(3) is the second-order Görling-Levy (GL2) correlation energy⁶⁷, which could be approximated by a second-order perturbation term (PT2)

$$\left. \frac{\partial E_{xc,\lambda}}{\partial \lambda} \right|_{\lambda=0} = 2E_c^{GL2} \approx 2E_c^{PT2} \quad (7)$$

Eqn.(3) can be then solved using a simple dependency of $E_{xc,\lambda}$ upon λ .⁶⁸

$$E_{xc,\lambda} = a[\rho] + b[\rho]\lambda + c[\rho]\lambda^2, \quad (8)$$

where a and b are determined by respecting the conditions expressed by equations 5 and 6, while c is determined by the behavior of the integrand (1) close to the upper integral limit ($\lambda=1$)⁵⁵. The resulting model, named Quadratic Integrand Double-Hybrid (QIDH)⁵⁵ is defined as:

$$E_{xc}^{QIDH,\alpha_x} = \frac{\alpha_x+2}{3} E_x^{EXX} + \frac{1-\alpha_x}{3} E_x^{GGA} + \frac{1}{3} E_c^{PT2} + \frac{2}{3} E_c^{GGA} \quad (9)$$

The α_x coefficient is determined following the linear-scaled one-parameter DH expression⁵⁴:

$$a_c = a_x^3 \Rightarrow \frac{1}{3} = \left(\frac{\alpha_x+2}{3} \right)^3 \quad (10)$$

so that $a_x = 3^{-1/3}$ and $a_c = \frac{1}{3}$. The PBE-QIDH model is thus obtained by casting the PBE functional in Eqn.(9):

$$E_{xc}^{PBE-QIDH} = \alpha_x E_x^{EXX} + (1 - \alpha_x) E_x^{PBE} + (1 - a_c) E_c^{PBE} + a_c E_c^{PT2} \quad (11)$$

The self-consistent exchange-correlation ‘quadratic-integrand hybrid’ (QIH(SCF)) energy is derived from Eqn.(11) by neglecting the E_c^{PT2} contribution:

$$E_{xc}^{PBE-QIH(SCF)} = \alpha_x E_x^{EXX} + (1 - \alpha_x) E_x^{PBE} + (1 - a_c) E_c^{PBE} \quad (12)$$

The CAM approach consists in splitting the Coulomb interaction into a short- and a long-range (SR and LR, respectively) term³³:

$$\frac{1}{r_{12}} = \frac{1 - [\alpha + \beta f(\omega r_{12})]}{r_{12}} + \frac{\alpha + \beta f(\omega r_{12})}{r_{12}} \quad (13)$$

Where f is the error function (erf) in order to get analytic expressions of the bi-electronic integrals with a Gaussian basis set³⁰ and ω rules the long- and short-range separation. The α parameter determines the inclusion of an EXX contribution scaled by α over the whole r_{12} range, while β ruled the GGA exchange contribution scaled by a factor $1 - (\alpha + \beta)$. Please note that $0 \leq \alpha + \beta \leq 1$, $0 \leq \alpha \leq 1$ and $0 \leq \beta \leq 1$ ³³. Imposing $\beta = 1 - \alpha$ in Eqn.(13) assures the recovery of 100% of EXX at long interelectronic distance, thus constraining the right $-\frac{1}{r_{12}}$ asymptote for the exchange potential.

Setting $\alpha = a_x$ imposes the QIDH model for short interelectronic distances. The resulting RSX-QIDH thus reads:

$$E_{xc}^{RSX-QIDH} = a_x E_x^{EXX} + (1 - a_x) E_x^{LR-EXX}(\omega) + (1 - a_x) E_x^{PBE} - (1 - a_x) E_x^{SR-PBE}(\omega) + (1 - a_c) E_c^{PBE} + a_c E_c^{PT2} \quad (14)$$

where $a_x = 3^{-1/3}$ and $a_c = \frac{1}{3}$, as above. As before, the self-consistent exchange-correlation RSX-QIH(SCF) energy is obtained by neglecting the perturbative contribution in Eqn.(14):

$$E_{xc}^{RSX-QIH(SCF)} = a_x E_x^{EXX} + (1 - a_x) E_x^{LR-EXX}(\omega) + (1 - a_x) E_x^{PBE} - (1 - a_x) E_x^{SR-PBE}(\omega) + (1 - a_c) E_c^{PBE} \quad (15)$$

The range-separated parameter, ω , is yet to be determined in order to fully define the functional. The most common way is to set this parameter in order to minimize the error with respect to a training dataset^{30-33,37,38}. An alternative but system-dependent way, consists in determining ω from the fulfillment of the Koopmans' theorem, as done for the optimal tuned functionals³⁹, or as function of the electron density⁶⁹. Here, following previous works^{70,71}, we determine ω by imposing an additional physical constraint, which is the exact treatment of the ground state energy of the hydrogen atom. Figures S1 and S2 report the variation of the RSX-QIDH total energy of the hydrogen atom with respect to the ω value, obtained with the Hartree-Fock (HF) or RSX-QIH(SCF) densities, respectively. In both cases, the minimum is obtained for $\omega = 0.27 \text{ bohr}^{-1}$, a value not far from that used in ω B97X-2 (0.3 bohr^{-1})⁶⁰. For the sake of clarity, all the nonempirical parameters of the RSX-QIDH are reported in Table 1.

3. Computational details

All computations were performed with a locally modified version of the Gaussian program⁷² in which the range-separated exchange quadratic-integrand hybrid and double hybrid (RSX-QIH(SCF) and RSX-QIDH, respectively) were fully implemented using the PBE exchange-correlation density functional⁵⁶ to evaluate the semilocal energy terms in Eq.(6). For comparison purposes, the range-separated double hybrid ω B97X-2⁶⁰, in its LP version, was also implemented in the same version of the software. In order to have a complete evaluation with other recent and commonly-used functionals, some computations were carried out with the ω B97X, and ω B97XD models, so to complete the ω B97 class³², while the M06-HF, M06-2X and M11 functionals^{23,37} were selected as representatives of the large Minnesota family. The aug-cc-pVQZ basis set⁷³ was used to compute the dissociation profiles of the cationic dimers (H_2^+ , He_2^+ , Ne_2^+ and Ar_2^+), while the def2-QZVP basis set⁷⁴ was considered for all the benchmarks concerning the Minnesota datasets⁷. Following previous recommendations⁶, electron affinities (EA/13 dataset) were computed using the aug-def2-QZVP basis, obtained by adding diffuse s and p functions from the Dunning aug-cc-pVQZ⁷⁵ to def2-QZVP. To complete the investigation, the SIE4x4 and the IPK/7 datasets were also considered. The former is a recent evolution of the SIE11 dataset⁷⁶ and it probes systems particularly prone to SIE. The latter is composed by the experimental IPs of 7 molecules containing a double bond, $\text{Y}=\text{X}$ ($\text{X}=\text{Si}$, C $\text{Y}=\text{N}$, P), bonded to hydrogen or methyl groups, so that the electronic properties depend on the X and Y atoms and on the substituents⁷⁷. The delocalization error was estimated using the so-called “well-separated” He clusters^{9,78}. They are planar rearrangements of He_n clusters ($n=1$ to 16) in which the atoms are distributed on a circle, two neighboring atoms being at 10 Å of distance. The delocalization error is then defined as the difference between the computed IP and the IP of a single He atom at the same level of theory⁷⁸.

4. Results and discussions

Choosing the parameter ω so to recover the total energy of the hydrogen atom, implies the cancellation of SIE for this one-electron system. It is interesting to verify, as first step, if this feature concerns also other systems affected by one- and many-electrons SIE. At the same time, a (full) correction of this error implies that the Kohn-Sham orbital energies should be closer to the corresponding IPs, within the Koopmans' theorem⁷⁹. These points are discussed in some details in the next subsection. Then, the performances of the new RSX-QIDH functional are tested on a number of other molecular properties, in order to verify that the

improvements on the SIE-related systems have been not obtained at the expense of other and equally important properties. Finally, the role of the PT2 contribution is dissected by comparing RSX-QIDH and RSX-QIH(SCF) results.

4.1 Self-interaction error, ionization potentials and delocalization error.

As a first step in the assessment of the RSX-QIDH performances, we consider 4 ionized dimers for which the one-electron SIE has been clearly evidenced, namely H_2^+ , He_2^+ , Ne_2^+ and Ar_2^+ . Indeed, as pointed a few years ago for H_2^{+80} , standard functionals give an incorrect dissociation limit with a spurious charge delocalization on the two atoms at large interatomic distances^{60,81}. As can be seen from the plots of Figure 1, the RSX-QIDH energy profile has not only the correct qualitative behavior with no dissociation barrier, but it is also practically coincident to that obtained with $\omega\text{B97X-2}$ and it is very close to the exact HF curve. The other RSX hybrid functionals also have a correct behavior, but the dissociation limit is significantly underestimated, thus clearly indicating that their SIE errors are only partially compensated by the EXX contributions. Table 2 collects the differences in energy between X_2^+ and $\text{X}+\text{X}^+$ ($\text{X}=\text{H}$, He , Ne and Ar) obtained with different functionals at an interatomic distance of 100 Å. For H_2^+ , RSX-QIDH has a value of -6.9 kcal/mol (10% of the energy minimum) lower than the correct HF reference, while $\omega\text{B97X-2}$ gives -7.6 kcal/mol (about 12% of the corresponding energy minimum). A standard RSX functional like LC-PBE gives an error of -10.4 kcal/mol, significantly higher than that of PBE0 (-48.7 kcal/mol) or PBE (-66.0 kcal/mol). The B2-PLYP functional, which can be considered as the reference empirical DH, gives -31.3 kcal/mol⁶⁰.

Slightly more involved is the situation for the heavier dimers (i.e. He_2^+ , Ne_2^+ and Ar_2^+) since also the nonlocal correlation plays a non-negligible role. Indeed for He_2^+ and Ne_2^+ , all the considered functionals shows larger deviations with respect to the CCSD(T) reference. However, RSX-QIDH is still the best performer, followed by LC-PBE and ωB97X , respectively. In particular, the RSX-QIDH asymptote is -8.8 kcal/mol lower than the reference value (15% of the corresponding energy minimum, see Table 2), significantly better than $\omega\text{B97X-2}$ (-14.1 kcal/mol, 23%). Literature data indicate -44.0 kcal/mol for B2-PLYP⁶⁰. More interesting, RSX-QIDH provides better results for He_2^+ than a recent local hybrid functional, constructed to be SIE-free⁸². Lower errors are observed for Ar_2^+ (see Figure 1 and Table 2). The RSX-QIDH profile is again the closest to the reference, showing a deviation at

100 Å of only -3.2 kcal/mol, more than one half that found for ω B97X-2 (-7.8 kcal/mol) and ten times lower than the value computed for B2-PLYP (-27.6 kcal/mol)^{60,83}.

It is worth to notice that literature data suggest that the parent QIDH scheme⁵⁵ already provides good results for He_2^+ and Ar_2^+ , when coupled with the PBE functional⁵⁶ or the recent SCAN meta-GGA⁸⁴, albeit the correct asymptotic limit is apparently not reached (see Figure 4 in reference 85).

In the last years, some datasets were built to specifically tackle severe SIE-related issues. Among others, the recent SIE4x4 dataset collects the interactions energies of four cationic dimers (H_2^+ , He_2^+ , $(\text{NH}_3)_2^+$, and $(\text{H}_2\text{O})_2^+$) at different inter-atomic or molecular distances, for a total of 23 energy evaluations⁶. The results obtained with the selected functionals are reported in Figure 2. On this dataset, the RSX-QIDH approach provides a Mean Absolute Deviation (MAD) of 1.9 kcal/mol. All the other functionals show larger errors, encompassed between 4.7 and 13.4 kcal/mol (ω B97XD and ω B97X-2, respectively). An even better picture of the RSX-QIDH performances is obtained by analyzing the data reported in a very recent test on 217 functionals⁶. Here the lowest error on the SIE4x4 dataset is found for the combination of DSD-PBEP86 with the D3(BJ) classical dispersion correction⁸⁶, which gives a MAD of 5.0 kcal/mol, a value more than two times higher than that found for RSX-QIDH. Other DHs provide even larger errors. For instance, the deviation for B2-PLYP is 9.9 kcal/mol and 6.5 kcal/mol for B2GP-PLYP⁶⁰.

Another advantage of adopting the range-separated exchange is its accuracy in estimating IPs directly from Kohn-Sham orbital energies, since RSX functionals approximately satisfy the Koopmans' theorem⁷⁹. Figure 4 reports the results on the IPK/7 dataset, which we have already used some years ago for some tests on SIE⁷⁷. Here, the best accuracy is obtained with ω B97X, LC- ω PBE and RSX-QIDH, all providing a MAD around 7.0 kcal/mol. Significantly larger errors are shown by ω B97X-2 and LC- ω PBE (about 11 kcal/mol in both cases). Performances similar to RSX-QIDH are obtained with other RSX hybrid approaches, specifically tuned on IPs or SIE-prone systems, such as cam-QTP-00 (MAD=7.1 kcal/mol), LC-PR-BOP (MAD=3.9 kcal/mol) and scOT-RSH (MAD=4.6 kcal/mol)^{87,88}. The good performances for IPs have been also verified on the IP/13 dataset, where the values are computed in an adiabatic fashion, as the energy difference between the neutral and cationic molecules. The good performance of the RSX-QIDH functional is confirmed, with a MAD close to those observed for ω B97X and ω B97XD. In addition, the deviations are significantly lower than those obtained for most of the functionals considered in a recent benchmark⁷. For

instance the M05, M06 and M08 families of functionals show deviations ranging between 2.8 (M05) and 3.8 (M06-HF) kcal/mol⁷. Other functionals give even larger deviations: CAM-B3LYP, 4.7 kcal/mol, PBE0 3.2 kcal/mol B3LYP 4.8 kcal/mol⁷.

Strictly related to the SIE is the so-called delocalization error, which represents the unphysical over-delocalization of electrons and it is associated to the non-linear behavior of the total energy as function of the fractional electron occupation⁹. However, as pointed out by Yang and co-workers, a functional with null DE is SIE-free, but the reverse is not necessarily true⁹. A simple way to estimate DE is to evaluate the difference between the computed IPs of “well-separated” He clusters and the IP of a single He atom⁹. This difference increases with the cluster size and it is very large for local and semilocal functionals. Indeed, their typical errors are between 3 and 8 eV⁷⁸, due to the large delocalization of the positive hole created upon ionization over the whole cluster. As shown in Figure 3, the IP curves decrease as a function of the He_n cluster size until reaching a plateau. The deviation with respect to the reference is particularly small for M06-HF and RSX-QIDH. All other functionals have a significantly different behavior, the worst being the semilocal PBE approach. As a general trend, the DE decreases in going from semilocal to hybrids functionals and, in particular, the inclusion of range-separated exchange has a drastic effect on the deviations. Indeed, CAM-B3LYP provides a very low error (-4.33 eV) with respect to the parents BLYP (-8.09 eV) and B3LYP (-6.31 eV). The high ratio of EXX (~ 70 %) in the QIDH model already assures a small deviation for PBE-QIDH (-2.03 eV), an error which is further reduced in RSX-QIDH (-0.93 eV). The DE is not null as in the sophisticated Multi-Configuration Pair-DFT (MC-PDFT) approach and it is slightly higher than in M06-HF, which contains 100% of EXX (-0.67 eV)⁷⁸. In short, the RSX-QIDH functional provides improved performances on a number of properties related to the SIE and DE. These performances are competitive with respect to similar approaches, parametrized or tuned on specific properties.

4.2 Other molecular properties

In order to check that the very encouraging results reported in the previous section are not obtained at the expense of other properties relevant for chemical applications, and to have a comparison with recent and commonly used functionals, we have carried out some further tests using representative datasets⁷. Table 3 collects the MADs obtained for all the considered functionals and datasets. Looking at the whole performance of each functional (MADs label “Total” in Table 3) it clearly appears that ω B97X-2 and RSX-QIDH perform significantly better than the other range-separated hybrids based on PBE. Both of them are also competitive

with the recent M11, which has having 44 parameters fitted to most of the datasets reported in Table 3³⁷. These three functionals are slightly worse than the robust M06-2X.

However, some significant differences appear looking at the results of the different datasets. Starting from the most classical benchmark, that is atomization energies (AE/6 dataset), the RSX-QIDH model outperforms the LC-PBE long-range corrected hybrid by 8.3 kcal/mol but performs less well than the LC- ω PBE variant by 1.7 kcal/mol. With respect to parametrized RSX hybrids (ω B97X and ω B97XD) and the ω B97X-2 double hybrid, the RSX-QIDH model remains less accurate by 3 to 4 kcal/mol. The same holds if M06-2X and M11 are considered (see Table 3). Such an unfavorable trend on atomization energy properties was already observed in a previous investigation regarding nonempirical global hybrids and double hybrids, and was underlined as the consequence of the underpinning PBE semilocal functional⁵⁷. This is, indeed, true for the PBE-QIDH approach^{55,85} and the situation is even worst when the recent SCAN functional is considered in the QIDH model⁸⁵. Furthermore, it should be noticed that ω B97X-2 remains also less accurate than its parent hybrids.

A significant improvement is, in contrast, observed for bond dissociation energies (ABDE/4 dataset), where RSX-QIDH provides lower deviations than the other range-separated density functionals, with a MAD of 1.4 kcal/mol. The ω B97X-2 functional shows an error of 2.6 kcal/mol, close to that of ω B97X and ω B97XD (2.4 and 2.6, in the order). It is noteworthy to point out that for the ABDE/4 dataset, RSX-QIDH is better than 76 functionals (out of 77) reported in a recent extensive investigation, also including the Minnesota functionals from '05 to '11 millesimal, and some of the most-common RSX hybrids, such as CAM-B3LYP⁷. The exception is represented by the M06-2X which gives a very low error (0.8 kcal/mol, see Table 3).

Such a comparison can be extended to recently developed functionals such as the B97M-V⁸⁹ and ω B9M-V⁹⁰. The former is a meta-GGA approach, while the latter is its range-separated evolution. Both functionals are coupled with a dispersion correction and their numerous parameters were determined using a careful combinatorial optimization on many properties, including most of those present in our benchmark. Even if a direct comparison cannot be done since these functionals were benchmarked on different data sets, it is worth to notice that B97M-V performs less well than M06-2X and ω B97XD on bond dissociation energies, ω B9M-V shows a similar error⁹⁰. It could be then inferred that RSX-QIDH provides similar results to ω B9M-V on this property.

Regarding proton affinities (PA/8 dataset), the RSX-QIDH model confirms its first position with respect to the other functionals considered in the present paper. Furthermore, its performance (1.2 kcal/mol) is comparable to those obtained by recent functionals, such as M11 (1.0 kcal/mol), M08-HX (1.1 kcal/mol)⁷ or SCAN-QIDH (1.2 kcal/mol)⁸⁵ and better than B97M-V (3.0 kcal/mol) which includes proton affinities in its training set⁸⁹.

Analogously, dipole interactions (DI/6 dataset) are also accurately reproduced at the RSX-QIDH level, with a MAD comparable to that obtained with ω B97D or M06-2X (0.27 vs. 0.25 kcal/mol). Once again, literature data show that similar accuracies (0.22-0.27 kcal/mol) are obtained only by the Minnesota functionals (M05, M05-2X, M06, M08-HX), all the other standard functionals providing larger deviations⁷.

Regarding the HAT/6, UA/6 and HT/6 datasets, the addition of nonlocal correlation decreases systematically the mean absolute deviation of the RSX-QIDH model with respect to LC-PBE with variations ranging from 0.2 to 2.2 kcal/mol. The same behavior is observed for ω B97X-2 with respect to ω B97X, but both these functionals provide errors lower than RSX-QIDH. This is particularly evident for HAT/6 where this latter functional gives a MAD of 3.2 kcal/mol, while ω B97X-2 result is 1.1 kcal/mol. Even better accuracy is obtained at M06-2X or M11 level (0.6 and 0.7 kcal/mol, respectively) while M06-HF is less accurate than RSX-QIDH (4.3 kcal/mol). A comparison with other recent functionals suggests that RSX-QIDH provides an accuracy on hydrogen transfer reaction similar to that found at PBE-QIDH or SCAN-QIDH level⁸⁵, but significantly better than B97M-V or ω B97X-D, this latter being less accurate than M06-2X⁹⁰.

A larger effect of nonlocal correlation is, instead observed for another class of reactions, the nucleophilic substitution (NS/6 dataset), where RSX-QIDH gives 1.9 kcal/mol, a value lower than those obtained with most of all the other functionals, except ω B97XD (1.2 kcal/mol), M06-2X (1.3 kcal/mol) and M11 (1.4 kcal/mol).

The positive effect of the nonlocal PT2 correlation is also observed for the EA/13 and HB/6 datasets, where a decrease of the error is found in going from LC-PBE to RSX-QIDH. However, the result for the EA dataset is disappointing, the MAD being as high as 2.8 kcal/mol. If this value is lower than that obtained at the ω B97X-2 level (3.2 kcal/mol), it remains significantly higher than the best results of our benchmark (M11, 0.7 kcal/mol). However, similar values have been obtained for other commonly-used functionals, such as M06-HF (2.6 kcal/mol), PBE0 (2.8 kcal/mol)⁷ and ω B97M-V (2.2 kcal/mol)⁹⁰. Only for electron affinities (EA/13 dataset), the RSX-QIDH model performs not as well as the parent

long-range corrected hybrids, but this behavior is also observed in the case of empirical approaches of the ω B97 family, including B97M-V and ω B97M-V⁹⁰.

The results on the charge transfer dataset (CT/7) show that LC-PBE and RSX-QIDH have the same accuracy (0.5 kcal/mol), higher than that offered by ω B97X-2 (1.0 kcal/mol), but lower than that found for ω B97X (0.4 kcal/mol) or ω B97XD (0.3 kcal/mol). The performances of RSX-QIDH are close to that provided by CAM-B3LYP (0.5 kcal/mol)⁷, M06-HF (0.6 kcal/mol), while standard GHs like PBE0 and B3LYP give higher deviations (1.1 and 0.7 kcal/mol, respectively)⁷. Others Minnesota functionals, such as M11 and M06-2X, are slightly more accurate, with deviations of 0.6 and 0.8 kcal/mol, respectively (see Table 3). On this property the recent ω B97M-V functional is particularly performing, showing an error as low as 0.1 kcal/mol⁹⁰.

Finally, a particular attention is given to weak interactions, here represented by two datasets, namely WI/7 and PPS/5. The RSX-QIDH errors are 0.2 and 0.3 kcal/mol, respectively. The ω B97X model provides a lower error for the former dataset (WI/7, 0.1 kcal/mol), but, unexpectedly, the deviation increases after the inclusion of nonlocal correlation (ω B97X-2, 0.2 kcal/mol). This behavior could be related to the larger contribution of EXX in the functional, which overcomes the PT2 treatment of dispersion forces. The π - π interactions are, instead not affected by this contribution, the MAD being always about 0.4 kcal/mol for all the three functionals of the ω B97X family. More in general, it should be pointed out that the RSX-QIDH functional is among the few approaches to provide low deviations on both WI/7 and PPS/5. Indeed, most of the functionals are unbalanced towards one of the two datasets. For instance, PBE is particularly good on the first set (MAD of 0.1 kcal/mol) but not particularly accurate on the second (2.2 kcal/mol)⁷. A similar behavior is observed for PBE0 (0.1 and 1.7 kcal/mol, respectively) and CAM-B3LYP (0.1 and 1.9 kcal/mol), just to mention few examples.

Functionals belonging to the Minnesota family provide a similar error on the two datasets, albeit with slightly higher variations (see Table 3 and reference 7), while B97M-V and ω B97M-V, both containing a dispersion correction, are particularly accurate on the large S22 and S66 datasets⁹⁰. For all these functionals, however, dispersion interactions were also included in the training sets.

In order to have more insights on model systems for weak interactions and to complete the investigation started with the cationic rare-gas dimers, the dissociation energy profiles of the He₂, Ne₂ and Ar₂ dimers have been also considered. The results are plotted in Figure 4, where

CCSD(T) data are taken as reference. The dissociation curves for He_2 are encompassed by the repulsive profile of LC-PBE, which does not show any energy minimum, and the very attractive potential of $\omega\text{B97X-2}$ which is more than 5 times deeper than the reference (-0.11 vs. -0.02 kcal/mol). This behavior suggests a double counting of the electron correlation, due to the large PT2 contribution in the functional. RSX-QIDH shows an attractive minimum, even if the energy is quite low (-0.01 kcal/mol) with respect to ωB97X (-0.02 kcal/mol), this latter being very close to the CCSD(T) reference. This trend is also observed for the other two dimers (Ne_2 and Ar_2): LC-PBE is always repulsive, the $\omega\text{B97X-2}$ functional significantly overbinds and RSX-QIDH gives a shallow description of the minima. The ωB97X is always the closest to the reference. Taken together, these results well underline how the RSX-QIDH gives fairly good performances on a number of molecular properties of interest for chemical applications.

4.3 On the role of the PT2 contribution

From the above reported data, it could be argued that, for some datasets, the larger EXX contribution predominantly rules the performances of the RSX-QIDH functional, confining the nonlocal PT2 correlation to a subsidiary part. In order to investigate this effect, we have carried out some computations using the RSX-QIH(SCF) functional defined by Eq. (6), which does not contain the PT2 contribution. The obtained results are reported in Figure 5 and clearly illustrates how the nonlocal PT2 contribution strongly affects all the considered properties, with a large increase of the errors in going from RSX-QIH(SCF) to RSX-QIDH. This is particular evident for some datasets, where nonlocal correlation is expected to play a major role: AE/6 (+246%), ABDE/4 (+939 %), HAT/6 (+270 %), PPS/5 (+432 %). The only exception in this general trend is represented by the hydrogen bond energies (HB/6), which are better reproduced at the RSX-QIH(SCF) level than at RSX-QIDH (-200 %). The negative effect of the nonlocal PT2 correlation can be also observed in going from ωB97XD to $\omega\text{B97X-2}$, where the MAD on the HB/6 dataset increases from 0.25 to 0.75 (+300 %). A similar behavior is present in the PBE0 and PBE-QIDH functionals^{57,85}.

In short, the inclusion of nonlocal PT2 correlation has a beneficial effect on almost all the properties.

5. Conclusions and perspectives

In the present paper, we propose a new nonempirical functional, RSX-QIDH, based on two well-established models, namely the exchange-range separation and the nonlocal electron correlation. Based on strong physical arguments, the proposed functional contains an additional parameter, ruling the short- and long-range electron separation in the exchange, which is chosen so to recover the total energy of the hydrogen atom. The cancellation of one-electron self-interaction error and the restoration of the correct $-\frac{1}{r_{12}}$ behavior in the potential have a beneficial effect on some difficult cases, such as the dissociation profiles of cationic rare-gas dimers and the ionization potentials directly evaluated from Kohn-Sham orbital energies. Further tests on standard molecular benchmarks show that RSX-QIDH performs at least as well as more empirical range-separated hybrids, eventually including nonlocal PT2 correlation term.

Pleasant characteristics of this functional are its numerical stability and high-order derivability envisaging its use for a number of properties.

Of note, and as for the vast majority of the functionals developed up to now, the domain of applicability of this functional is linked to the benchmark sets considered. This opens some questions, for instance, concerning its extensibility to periodic systems, which are scarcely represented in the current benchmark sets. In general and up to now the question of an exchange-correlation functional describing on an equal foot molecules and solids is still open. Different functionals seem to work for several properties⁹¹. For instance, GGA functionals are more suitable to describe metallic solids, while they fail for some properties (e.g. gap) of semiconductors. The opposite is true for GHs. Screened hybrid density functionals, such as HSE⁹², significantly improve gaps, but not necessarily structural parameters⁹³. The few tests carried out with RSXs are somehow contradictory^{94,95}. Double hybrids are probably unsuitable for metallic solids⁹⁶, due to divergence problems that could derive from the PT2 terms but they are rather promising for molecular crystals (see for instance reference 97). A recent paper proposed a RSX-DH approach applied to solids and the results are encouraging, albeit only a few systems were tested⁹⁸. Since efficient implementations of perturbative approach within Periodic Boundary Conditions were done both with Gaussian and planewave basis sets^{99,100}, opening the perspectives of more systematic tests of both DHs and RSX-DHs functionals, we expect that a definitive answer on their use for solid state could be assessed in the near future.

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Supporting information

The Supporting Information is available free of charge on the ACS Publications website: variation of the total energy of the hydrogen atom as function of the ω parameter, raw data of Table 3 and Figures 1 to 5.

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Table 1. Nonempirical parameters used in the RSX-QIDH functional.

parameter	value	definition
a_x	$3^{-1/3}$	nonlocal EXX contribution (Eq. 6)
a_c	$1/3$	nonlocal PT2 contribution (Eq. 7)
α	$3^{-1/3}$	short/long range switching in $1/r_{12}$ term (Eq. 5)
ω	0.27	short/long range switching in erf function (Eq. 5)

Table 2. Deviations (kcal/mol) with respect to the correct dissociation asymptote for the H_2^+ , He_2^+ , Ne_2^+ and Ar_2^+ dimers computed at an interatomic distance of 100 Å.

dimer	PBE	PBE0	LC-PBE	ω B97X	ω B97X-2	RSX-QIDH
H_2^+	-66.0	-48.7	-10.4	-21.3	-7.6	-6.9
He_2^+	-94.6	-67.2	-24.8	-38.4	-14.3	-8.9
Ne_2^+	-96.3	-63.0	-28.3	-34.7	-17.1	-7.6
Ar_2^+	-62.0	-42.5	-5.5	-13.8	-7.8	-3.2

Table 3. Mean Absolute Deviations (MADs, kcal/mol) of selected hybrids, range-separated and double-hybrid functionals, computed on a representative benchmark dataset⁷.

set ^a	LC-PBE	LC- ω PBE	M06-HF ^b	M06-2X ^b	M11 ^b	ω B97X	ω B97XD	ω B97X-2	RSX-QIDH
AE/6	14.67	4.70	4.49	2.01	1.90	1.85	2.10	3.00	6.44
ABDE/4	3.06	5.06	5.01	0.81	1.67	2.42	2.58	2.61	1.38
EA/13	1.77	2.07	2.55	1.66	0.69	1.72	1.67	3.20	2.81
PA/8	1.60	2.22	2.81	1.69	1.03	2.00	2.87	2.34	1.18
HAT/6	3.45	2.22	4.32	0.62	0.73	2.13	1.92	1.13	3.17
NS/6	3.63	2.56	2.71	1.31	1.36	1.96	1.22	2.41	1.91
UA/6	2.42	2.09	1.79	1.03	1.47	2.30	1.98	0.96	1.80
HT/6	3.39	1.32	1.72	1.14	1.56	2.11	2.27	0.97	1.19
HB/6	1.03	0.74	0.59	0.33	0.29	0.76	0.25	0.75	0.86
CT/7	0.54	1.13	0.55	0.84	0.63	0.39	0.32	0.96	0.54
DI/6	0.31	0.85	0.50	0.25	0.44	0.45	0.25	0.71	0.27
WI/7	0.24	0.29	0.10	0.07	0.09	0.06	0.09	0.19	0.16
PPS/5	1.14	1.96	0.63	0.28	0.64	0.40	0.43	0.44	0.34
SIE4x4	6.94	9.35	4.20	8.63	9.55	11.36	13.37	4.71	1.91
IP/13	7.15	5.21	4.20	2.41	3.84	2.49	2.70	4.50	2.39
Total	3.43	2.78	2.41	1.54	1.73	2.16	2.27	1.93	1.76

- a) AE/6, atomization energies; ABDE/4, Alkyl bond dissociation energy; EA/13, electron affinities; PA/8, proton affinities; HAT/6, Heavy atom transfer, NS/6, nucleophilic substitutions ; UA/6, unimolecular associations; HT/6, hydrogen transfer; HB/6 hydrogen bond; CT/7, charge transfer; DI/6, dipole interactions; WI7, weak interactions; PPS5, π - π stacking, SIE4x4, self-interaction error; IP/13, adiabatic ionization potentials; b) Please note that the MAEs of the AE/6 dataset reported in reference 7 are systematically divided by 4.83, which is the mean number of bonds per molecule in the dataset. This explains the apparent discrepancy between the data reported in the table and those listed in reference 7.

Figure captions

Figure 1. Dissociation energy profiles for the X_2^+ dimers ($X=H, He, Ne$ and Ar). In all cases the zero energy reference is set to $E(X)+E(X^+)$.

Figure 2. Mean Absolute Deviations (MAD) for the benchmark on Ionization Potential from Kohn-Sham orbital energies (IPK/7), adiabatic Ionization Potential (IP/13) and Self-Interaction Error (SIE4x4). See text for details.

Figure 3. Ionization Potentials (IP) as functions of the size of the well separated He_n clusters ($n=1-16$).

Figure 4. Dissociation energy profiles for X_2 dimers ($X= He, Ne$ and Ar).

Figure 5. Mean Absolute Deviations (MADs) for several benchmarks computed with the RSX-QIDH functional and its variant RSX-QIH(SCF) not containing the nonlocal PT2 contribution.

Figure 1

Figure 2

Figure 3

Figure

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Figure 5

TOC Graphic