

Communication: Double-hybrid functionals from adiabatic-connection: The QIDH model

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A new approach stemming from the adiabatic-connection (AC) formalism is proposed to derive parameter-free double-hybrid (DH) exchange-correlation functionals. It is based on a quadratic form that models the integrand of the coupling parameter, whose components are chosen to satisfy several well-known limiting conditions. Its integration leads to DHs containing a single parameter controlling the amount of exact exchange, which is determined by requiring it to depend on the weight of the MP2 correlation contribution. Two new parameter-free DHs functionals are derived in this way, by incorporating the non-empirical PBE and TPSS functionals in the underlying expression. Their extensive testing using the GMTKN30 benchmark indicates that they are in competition with state-of-the-art DHs, yet providing much better self-interaction errors and opening a new avenue towards the design of accurate double-hybrid exchange-correlation functionals departing from the AC integrand. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4890314>]

The recent interest for double-hybrid (DH) approximations within the field of density-functional theory (DFT) strongly increased since the pioneering work of Ernzerhof in 1996.¹ Popularized by Grimme with the so-called B2-PLYP approach,² this class of approximation introduces a fraction of second-order Møller-Plesset (MP2) correlation into a standard global-hybrid (GH) exchange and correlation expression:

$$E_{xc}^{\text{DH}}[\rho] = a_x E_x^{\text{HF}} + (1 - a_x) E_x^{\text{DFA}}[\rho] + (1 - a_c) E_c^{\text{DFA}}[\rho] + a_c E_c^{\text{MP2}}, \quad (1)$$

where E_x^{HF} denotes the Hartree-Fock like exchange, and E_x^{DFA} and E_c^{DFA} stand, respectively, for the semilocal exchange and correlation density-functional approximation (DFA). Like for a global-hybrid, the first three terms are computed following a self-consistent pathway. The last term is generally added *a posteriori* and evaluated from the optimized GH Kohn-Sham (KS) orbitals, even if orbital-optimized approaches already exist.³ Following Eq. (1), plethora of DHs raised in the literature: some are based on the generalized-gradient approximation (GGA)⁴⁻⁹ or meta-GGA,¹⁰⁻¹³ another scale spin components of the MP2 part,¹⁴⁻¹⁶ some others are built with a perturbative term computed from B3LYP^{17,18} or PBE0^{19,20} KS orbitals.²¹⁻²³ All these DHs share the same basement: two empirical parameters a_x and a_c , sometimes more, fitted on different datasets according to the property of interest.

More recently, some tentative of rationalization explained the origin of DHs, especially the relationship between

the two empirical parameters. Starting from the adiabatic-connection (AC) formalism,²⁴⁻²⁷ Toulouse *et al.* derived a family of *one-parameter* DHs,²⁸⁻³⁰ underlining a quadratic ($a_c = a_x^2$), and a cubic ($a_c = a_x^3$) relation between a_x and a_c . Fromager extends these studies to a more general *two-parameter* DH formalism with a fraction of exact exchange and perturbation parts staying for $a_c \leq a_x^2$.³¹ While this theoretical purpose points out a rigorous formalism, it does not precise specific values for the parameters, which is the key point in the birth of a new double-hybrid. Still working on this formalism, some of us demonstrated that an average on the AC, a cubic relation between a_x and a_c , and the PBE density-functional led to an excellent parameter-free candidate: the PBE0-DH double-hybrid.^{32,33} Later, mimicking PBE0-DH, Chai *et al.* promoted a new parameter-free DH: the PBE0-2 functional.³⁴

If the previous mentioned tentatives of rationalization focused on the AC Hamiltonian, link between the non-interacting KS Hamiltonian ($\lambda = 0$) and the exact Hamiltonian ($\lambda = 1$), they overstep the coupling-constant integral formula and the developments linked to its integrand:

$$E_{xc}[\rho] = \int_{\lambda=0}^1 \mathcal{W}_\alpha[\rho] d\alpha, \quad (2)$$

where $\mathcal{W}_\alpha[\rho]$ stands for the exchange and correlation integrand. Some really recent investigations follow this route. We especially think about the work of Fromager and coworkers which underlines B2-PLYP like DHs made from AC integrands³⁵ or the PBE-ACDH³⁶ functional from Xu *et al.* built from a complex integrand function.

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Our goal in this Communication is to propose a simple model for $\mathcal{W}_\alpha[\rho]$ and use it to develop a new double-hybrid form that provides self-interaction errors (SIEs) for many electron systems as low as possible.³⁷

As for the exchange and correlation energy, the exact integrand is unknown and lets place some approximations. Yang and coworkers already proposed a bench of mathematical expressions, starting from a linear to an exponential model integrand.³⁸ One of the simplest cases, yet keeping the correct curvature of the interpolation path, consists in developing the integrand as a quadratic function (QI) of α :

$$\mathcal{W}_\alpha[\rho] = a[\rho] + b[\rho]\alpha + c[\rho]\alpha^2, \quad (3)$$

where a , b , and c are functionals of density and orbitals. The identification of these three functionals has to follow the limit conditions.

At the weak-interaction limit ($\alpha \rightarrow 0$), the integrand tends to the exact exchange term at zeroth-order, and to the second-order Görling-Levy^{39,40} (GL2) at first-order of α :

$$\mathcal{W}_0[\rho] = E_x^{\text{HF}}, \quad \left. \frac{\partial \mathcal{W}_\alpha[\rho]}{\partial \alpha} \right|_{\alpha=0} = 2E_c^{\text{GL2}}, \quad (4)$$

where E_c^{GL2} is written as

$$E_c^{\text{GL2}} = E_c^{\text{MP2}} + E_c^{\Delta\text{HF}}. \quad (5)$$

In the previous expression (5), E_c^{MP2} denotes the known second-order Møller-Plesset correlation energy computed from the KS orbitals, and $E_c^{\Delta\text{HF}}$ stands for the single-excitation contribution. As this last term is negligible for most of the systems ($E_c^{\text{GL2}} \approx E_c^{\text{MP2}}$), the identification of expressions (3) and (4), plus the decomposition (5) give:

$$a[\rho] = E_x^{\text{HF}}, \quad (6)$$

$$b[\rho] = 2E_c^{\text{MP2}}. \quad (7)$$

The last quadratic term c has still to be determined. For that, we will focus on the integrand behavior close to the upper limit ($\alpha \rightarrow 1$). Using scaling relations derived from the work of Levy and Perdew,⁴¹ the integrand is expressed as

$$\begin{aligned} \mathcal{W}_\alpha[\rho] &= \frac{\partial}{\partial \alpha} (\alpha^2 E_{xc}[\rho_{1/\alpha}]) \\ &= E_x^{\text{DFA}}[\rho] + 2E_c^{\text{DFA}}[\rho_{1/\alpha}]\alpha + \frac{\partial E_c^{\text{DFA}}[\rho_{1/\alpha}]}{\partial \alpha} \alpha^2, \end{aligned} \quad (8)$$

where $\rho_{1/\alpha}$ is the coordinate-scaled density such as $\rho_{1/\alpha}(\mathbf{r}) = \alpha^{-3}\rho(\mathbf{r}/\alpha)$. Close to the upper limit, the coordinate-scaled density is very close to the density itself $\rho_{1/\alpha}(\mathbf{r}) \approx \rho(\mathbf{r})$. As a result, the density-scaled correlation energy tends to the density-functional correlation energy:

$$E_c^{\text{DFA}}[\rho_{1/\alpha}] \approx E_c^{\text{DFA}}[\rho], \quad (9)$$

and its derivative with respect to α vanishes. At the upper limit, the integrand can be approximated by

$$\mathcal{W}_1[\rho] \approx E_x^{\text{DFA}}[\rho] + 2E_c^{\text{DFA}}[\rho], \quad (10)$$

or more generally by

$$\mathcal{W}_{1,\lambda_x}[\rho] = \lambda_x E_x^{\text{HF}} + (1 - \lambda_x) E_x^{\text{DFA}}[\rho] + 2E_c^{\text{DFA}}[\rho], \quad (11)$$

with the parameter $\lambda_x \in [0, 1]$ controlling the amount of exact exchange present. When λ_x tends to zero, $\mathcal{W}_{1,\lambda_x}$ tends to Eq. (10), and when λ_x tends to one, the exchange part is estimated with full exact exchange. From Eqs. (3) and (11), the identification of c gives

$$\begin{aligned} c[\rho] &= (\lambda_x - 1)E_x^{\text{HF}} + (1 - \lambda_x)E_x^{\text{DFA}}[\rho] \\ &\quad - 2E_c^{\text{MP2}} + 2E_c^{\text{DFA}}[\rho]. \end{aligned} \quad (12)$$

The model integrand of Eq. (3) is now a function of known energy terms. Applying the integration formula (2) to the quadratic exchange and correlation integrand (3) leads to

$$\begin{aligned} E_{xc,\lambda_x}[\rho] &= \left[a[\rho]\alpha + \frac{1}{2}b[\rho]\alpha^2 + \frac{1}{3}c[\rho]\alpha^3 \right]_{\lambda=0}^1 \\ &= a[\rho] + \frac{1}{2}b[\rho] + \frac{2}{3}c[\rho], \end{aligned} \quad (13)$$

and replacing a , b , and c functionals by their corresponding assignments (see Eqs. (6), (7), and (12)) gives the quadratic integrand double-hybrid (QIDH) model:

$$\begin{aligned} E_{xc,\lambda_x}^{\text{QIDH}}[\rho] &= \frac{\lambda_x + 2}{3}E_x^{\text{HF}} + \frac{1 - \lambda_x}{3}E_x^{\text{DFA}}[\rho] \\ &\quad + \frac{1}{3}E_c^{\text{MP2}} + \frac{2}{3}E_c^{\text{DFA}}[\rho]. \end{aligned} \quad (14)$$

A direct comparison with Eq. (1) reveals that

$$\forall \lambda_x \in [0, 1], \quad a_x(\lambda_x) = \frac{\lambda_x + 2}{3}, \quad a_c = \frac{1}{3}, \quad (15)$$

which means that for all considered values of λ_x , a_x varies between 0.66 and 1.00. Another important consideration is the verification of the inequality³¹ $a_c \leq a_x^2$ for all λ_x .

To evaluate the DFA exchange and correlation terms of Eq. (14), the PBE⁴² and the TPSS⁴³ semilocal functionals are chosen. The advantage of such functionals is their non-empirical background, and especially for TPSS, a correlation component free of self-interaction. In this way, the two models defined as PBE-QIDH and TPSS-QIDH just contain one parameter: the fraction of exact exchange.

The fraction of exact exchange has still to be determined. As a_c is fixed, a parallelism can be established with the *linearly scaled one-parameter double-hybrid*,^{29,30} pragmatically known for the relation $a_c = a_x^3$ and its nice performances for the chosen semilocal functionals, will help to determine λ_x . In this way, a first idea is $a_x = 3^{-1/3}$, so $\lambda_x = 3^{2/3} - 2$. To validate this hypothesis, the influence of the amount of exact exchange a_x on the performances of the QIDH model is measured on two different types of properties (Fig. 1): atomization reactions through the AE6 dataset⁴⁴ and self-interaction error related problem through the SIE11⁴⁵ test set. The first set is a simple benchmark test over six representative atomization energies, and the second set brings together 11 SIE-prone chemical systems. On atomization energies, our hypothesis works very fine for PBE-QIDH ($a_{x,\text{min}} = 0.70$), and overestimates the minimum for TPSS-QIDH ($a_{x,\text{min}} = 0.60$). For self-interaction errors, the one-dimensional surfaces are very flat around the minima, and both QIDH approaches show a respective minimum close to $a_{x,\text{min}} = 0.75$ and $a_{x,\text{min}} = 0.70$. These values are still in agreement with our hypothesis and

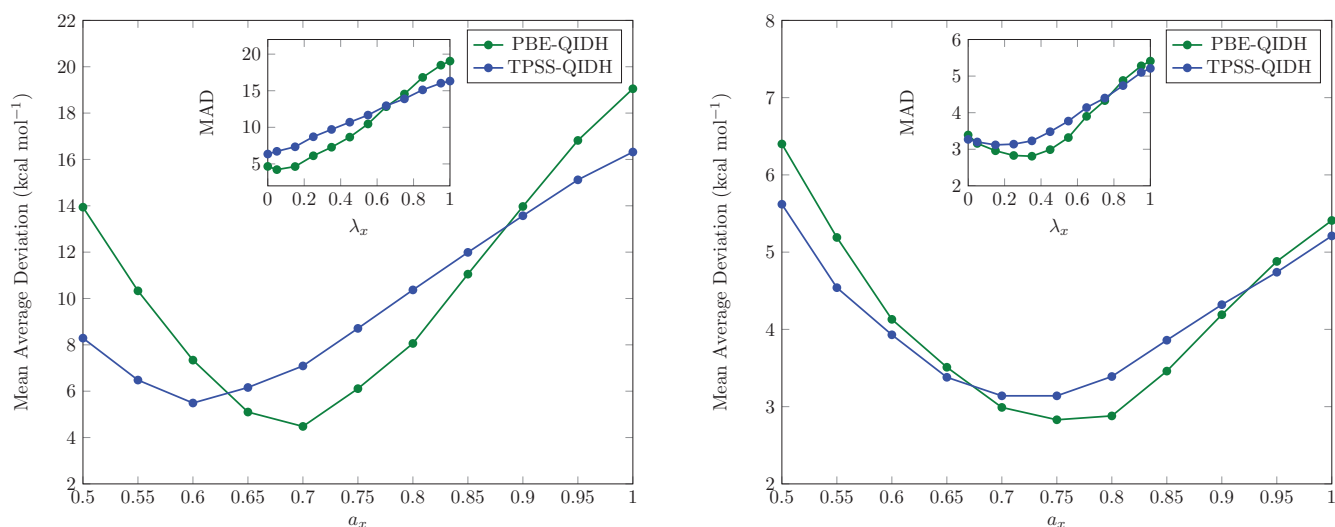


FIG. 1. Mean absolute deviations for the AE6 (left) and SIE11 (right) test sets as function of the parameters a_x for QIDH based on PBE and TPSS exchange and correlation density functionals. All the reactions are evaluated with the quadruple- ζ def2-QZVP basis set.

confirm the validity of a parameter-free approach. As a result we fix $a_x = 3^{-1/3}$, so $\lambda_x = 3^{2/3} - 2$.

To evaluate the performances of the two defined QIDH on chemical properties, the well known GMTKN30 benchmark¹³ is investigated (Fig. 2), and the results are compared to those of a reference double-hybrid: PBE0-DH, for which $a_x = 1/2$ and $a_c = 1/8$. The new PBE-QIDH functional yields better results than PBE0-DH in almost every case, the only remarkable exception being the reaction energies of the DARC subset. On the other hand, the TPSS-QIDH functional performs slightly worse on average than PBE-QIDH. It is worth mentioning the large improvement on SIEs, around 50%, provided by both QIDH functionals over PBE0-DH, probably due to

the increase of exact exchange proportion in the new functionals. On the other hand, the larger fraction of MP2 correlation energy in QIDH functionals, as compared to that of PBE0-DH, would explain the better results on weak interaction and conformer errors obtained with the former. Another important tested property is the vertical-excitation process through 12 π -conjugated compounds.⁴⁶ Similar performances are denoted by direct comparison to PBE0-DH.

In this Communication, we built a new model of double-hybrid functional from the adiabatic-connection exchange and correlation integrand. We developed the integrand as a quadratic function of the AC parameter, and showed that after integration, the amount of correlation computed by

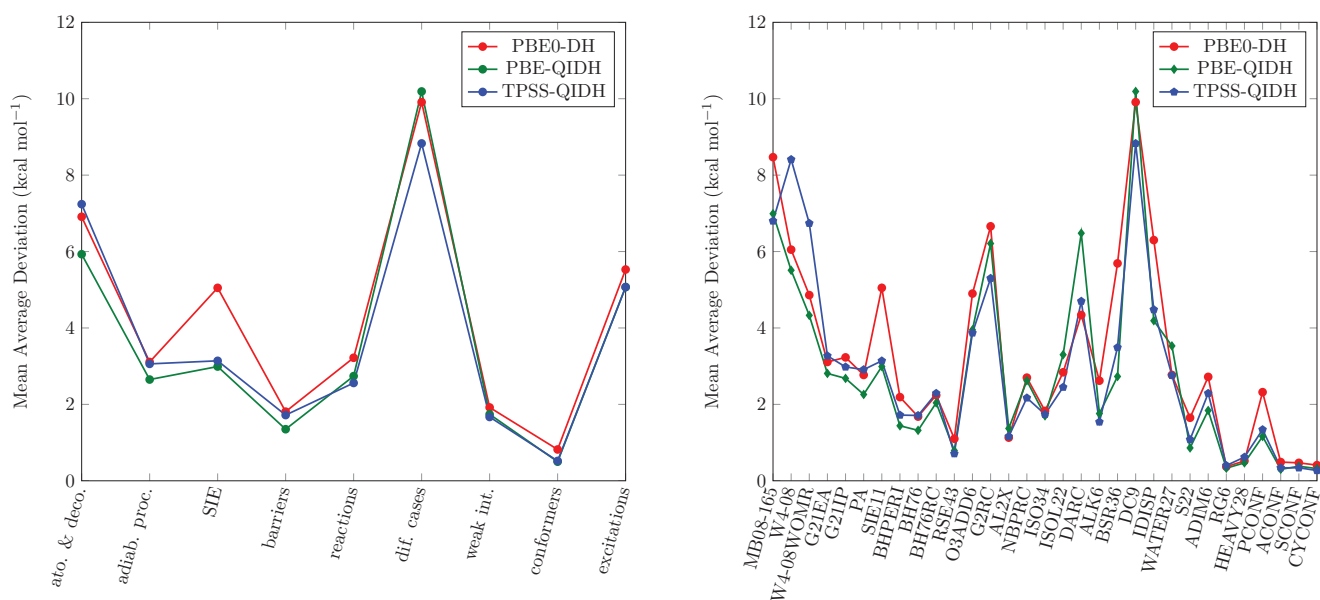


FIG. 2. Mean absolute deviations for all the subsets of the GMTKN30 database for QIDH based on PBE and TPSS exchange and correlation density functionals and $\lambda_x = 3^{2/3} - 2$. The left graph shows the performances of the three models of DHs according to the type of properties tested in the GMTKN30 database plus excitation energies. The right graph displays the DH performances on the different GMTKN30 subsets. All the reactions are evaluated with the quadruple- ζ def2-QZVP basis set.

perturbation is fixed to 1/3, and the proportion of exact exchange can vary between 2/3 and 1. This quadratic integrand double-hybrid is coupled with PBE and TPSS semilocal functionals, and the amount of exact exchange is set to decrease the SIE of many-electron systems. The overall performances of QIDH are close to that of PBE0-DH but improve the SIE treatment. We hope that this study will stimulate the new development of parameter-free DHs through the AC exchange and correlation integrand.

Computational details: All the computations were done with the Gaussian program package⁴⁷ except for the PCONF, WATER27, IDISP, ISOL22, and the excitation subsets. These last five datasets were computed with the Orca software⁴⁸ making use of the RI-MP2^{49–51} approach. An ultrafine integration grid is set for TPSS-based DHs computations. As recommended by Grimme,¹³ the large Ahlrichs' type quadruple- ζ basis set def2-QZVP⁵² is used to compute the GMTKN30 database.¹³ Particularly for electron affinities and binding energies of water (subsets G21EA and WATER27), diffuse s and p functions are taken from the Dunning *aug-cc-pVQZ*⁵³ and added to def2-QZVP to obtain the *aug-def2-QZVP* basis. Vertical excitation energies are obtained using the Tamm-Dancoff approach and with the def2-TZVPP basis set. Note that these excitation energies (Ω_{DH}) are obtained⁵⁴ as $\Omega_{\text{DH}} = \Omega_{\text{GH}} + a_c \Delta_{(\text{D})}$, where $\Delta_{(\text{D})}$ is a CIS(D)-like correction,⁵⁵ scaled by a_c , and added to the excitation energy computed with a GH.

To give a more representative view of the performances of the investigated DHs, the 31 subsets of the GMTKN30 are clustered according to the eight tested properties. Atomization and decomposition cluster groups together the MB08-165, W4-08, and W4-08WOMR subsets. Adiabatic process cluster brings together G21EA, G21IP, and PA subsets. Self-interaction error cluster is composed by the SIE11 subset. Barrier cluster assembles BHPERI and BH76 subsets. Reaction cluster gathers together BH76RC, RSE43, O3ADD6, G2RC, AL2X, NBPRC, ISO34, ISOL22, DARC, ALK6, and BSR36 subsets. Difficult cases cluster is composed by the DC9 subset. Weak interaction cluster groups together the IDSIP, WATER27, SS2, ADIM6, RG6, and HEAVY28 subsets. Conformer cluster brings together PCONF, ACONF, SCONF, and CYCONF subsets. For a more complete description of all the subsets the reader is oriented to the GMTKN30 reference.¹³

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