

The Universal Behavior of Parameter-Free Hybrid and Double-Hybrid Models

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Abstract

ABSTRACT 1: It is suggested here that the ultimate accuracy of DFT methods arises from the type of hybridization scheme followed. This idea can be cast into a mathematical formulation utilizing an integrand connecting the non-interacting and the interacting particle system. We consider two previously developed models for it, dubbed as HYB0 and QIDH, and assess a large number of exchange-correlation functionals against the AE6, G2/148, and S22 reference datasets. An interesting consequence of these hybridization schemes is that the error bars, including the standard deviation, are found to markedly decrease with respect to the pure (non-hybrid) case. This improvement is substantially better than variations due to the underlying density functional used. We thus finally hypothesize about the universal character of the HYB0 and QIDH models.

ABSTRACT 2: The hybrid HYB0 and double-hybrid QIDH models, derived previously within the adiabatic connection formalism, are used here with a number of exchange-correlation density functionals to assess their global performance against challenging reference datasets. The systematic improvement observed, on both the average error and the standard deviation over the set of density functionals considered, when this hybridization hierarchy is applied, highlight its robustness and prompted us to speculate about its general applicability.

Computational chemistry has reached such a degree of maturity and performance that many-electron properties of systems extending to hundreds of atoms can be predicted with great accuracy. This remark is especially verified for Density Functional Theory (DFT) due to its excellent trade-off between accuracy and cost, which thus allows for a fine description of covalent and noncovalent electron interactions occurring in biological or chemical systems. Part of this success comes from the steady and step-by-step development of novel density-functionals (DFs), and the special efforts done by the community to overcome some well-known and all-pervasive weaknesses such as the self-interaction error,¹ or the ‘soft- or non-binding’ behavior of van der Waals’ complexes.^{2–4}

Historically, an important breakthrough started in the nineties with the audacious idea to cast semilocal density-functionals (GGA, meta-GGA) into hybrids by combining exact-like and approximate density-based exchange together with a correlation energy functional.^{5–8} Going from the semilocal to the hybrid density-functional approximation enhanced the nonlocal character of the exchange part and succeeded to decrease by a factor of two the errors previously found on covalent or short-range properties. This hybridization mechanism is justified by a rigorous formalism known as the adiabatic connection model:⁹

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

where E_{xc} represents the exchange-correlation contribution to the total Kohn-Sham (KS) energy, and \mathcal{W}_α stands for the exchange-correlation integrand. The coupling-constant integrand, once its conveniently defined, allows for connecting the noninteracting ($\alpha = 0$) to the fully interacting system ($\alpha = 1$), supposing that the upper limit is ideally described by a pure exchange-correlation density-functional, while the lower limit tends to the exact-exchange energy, usually computed as the Hartree-Fock (HF) exchange term from the KS orbitals.

Several hybrid schemes were consequently formulated starting from this adiabatic-connection model. Most of them are empirically parameterized to minimize errors on reference datasets, and generally outperform within their specific domain of activity. On the contrary, other hybrid

forms adopt a more general scheme, avoid parameterization and derive from physical hypothesis and constraints applied to the exchange-correlation integrand \mathcal{W}_α . For instance the PBE0 hybrid density-functional is obtained after approximating \mathcal{W}_α by a polynomial of the coupling-constant integrand α .⁷ The reliability of this nonempirical approach was systematically studied,^{10,11} and leads to what we call here the HYB0 model:

$$E_{xc}^{\text{HYB0}}[\rho] = a_0 E_x^{\text{HF}} + (1 - a_0) E_x^{\text{DF}}[\rho] + E_c^{\text{DF}}[\rho], \quad (2)$$

where E_x^{HF} denotes the Hartree-Fock-like (also termed exact-like) exchange, while E_x^{DF} and E_c^{DF} stand for the exchange and correlation density-functional energy terms respectively ($a_0 = 1/4$ fixes the fraction of exact-like exchange).

If both empirical and nonempirical approaches largely succeed to reduce self-interaction errors, and also perform well for properties out of stable equilibrium regions,¹² most of them fail to describe noncovalent or long-range interactions which drive van der Waals complexes. To alleviate this drawback of common functionals, a possible remedy consists in going a step further in the theoretical developments by increasing the physical constraints on the exchange-correlation integrand, and/or by enhancing the nonlocal character of the density-functional by an hybridization of the correlation part. The resulting density-functional approximation is called ‘double-hybrid’ (DH), in analogy to the previous ‘hybrid’ notation introduced time ago. The concept of DHs was introduced by the pioneering work of Ernzerhof in 1996,¹³ used by Truhlar in 2004 with the multi-coefficient protocols,¹⁴ and finally popularized by Grimme in 2006 with the advent of the so-called B2-PLYP.¹⁵

We note that some tentatives of rationalization aim at explaining the origin of these latter models.^{16–22} Here again, the justification of this additional hybridization starts from the adiabatic connection model (Eq. (1)). At the lower limit ($\alpha \rightarrow 0$), \mathcal{W}_α tends to the exact-exchange energy at zeroth-order of α , and its derivative to the second-order Görling-Levy energy^{23,24} (GL2) at first-

order of α :

$$\mathcal{W}_0[\rho] = E_x^{\text{HF}}, \quad \left. \frac{\partial \mathcal{W}_\alpha[\rho]}{\partial \alpha} \right|_{\alpha=0} = 2E_c^{\text{GL2}}, \quad (3)$$

where the GL2 energy term is generally approximated by the second-order perturbation theory (PT2) energy term although computed from the singly exchange-hybridized Kohn-Sham orbitals ($E_c^{\text{GL2}} \approx E_c^{\text{PT2}}$). Recently some of us derived a novel double-hybrid model from a quadratic approximation of the coupling integrand (Eq. (1)). The model is denoted as QIDH²² and stands as:

$$E_{xc}^{\text{QIDH}}[\rho] = a_0 E_x^{\text{HF}} + (1 - a_0) E_x^{\text{DF}}[\rho] + \frac{1}{3} E_c^{\text{PT2}} + \left(1 - \frac{1}{3}\right) E_c^{\text{DF}}[\rho], \quad (4)$$

where E_c^{PT2} represents the second-order perturbation correlation energy and $a_0 = 3^{-1/3}$ fixes now the fraction of exact-exchange. Double-hybrids bring a dynamical correlation contribution which is of high interest to accurately model potential energy surfaces around the bonding region. Moreover at large interatomic distances, this nonlocal correlation corrects for the premature vanishment of the DF correlation term, and helps the density-functional to recover the binding behavior of weakly-interacting systems.

These hybrid and double-hybrid models (HYB0 and QIDH respectively) are thus rooted on the same nonempirical grounds and can be viewed as two different routes to improve performances by increasing the theoretical constraints. In our previous investigations,^{22,25,26} we tested the relevance of these two models (HYB0 and QIDH) on a large number of ground- and excited-state properties, choosing the PBE parameter-free functional to estimate the density-based energy terms.

In this Letter, we want to go a step further and demonstrate the universal range of our models. With this aim, we chose a representative panel of ten pure density-functionals (Table 1), which are then hybridized and double-hybridized in order to assess the relevance of the HYB0 and QIDH models. Note that every of the models out of the selection made were built with different empirical or nonempirical backgrounds, and are known to perform differently to estimate covalent or

noncovalent properties.

Therefore, to illustrate the impact of the pure DFs within the HYB0 and QIDH models, we first focus on the evaluation of atomization energies. Atomization reactions are an excellent indicator on how well is behaving a DF within the covalent region. To test this type of property, we first select the AE6 small but representative dataset.²⁷ This set reports six reference atomization reactions of organic systems, and is widely used by the community to train and test density-functionals in a cost-effective fashion. We also select the extended G2/148 dataset^{28–30} which deals with first and second row-based systems, and includes a collection of 148 accurate reference atomization energies relatively free from experimental error bars.

Figure 1 reports the AE6 and G2/148 mean absolute deviations (MADs) averaged over the ten pure as well as with the two HYB0 and QIDH hybridized models (See Figures S1 and S2 in the Supporting Information for more details). Note that black bars measure the standard deviation of each MAD collection.

Independently of the semilocal DF and of the dataset chosen, a general improvement of the performances is observed going from the pure to the hybrid and double-hybrid models. In average over the ten DFs, the HYB0 hybridization largely decreases the error by 4.7 kcal mol⁻¹ on the G2/148, while the QIDH hybridization reduces it further by about 6.0 kcal mol⁻¹. For the AE6 the general improvement is slightly smaller when going from the pure to the QIDH model (~ 5.0 kcal mol⁻¹). Apart from this global overview on atomization energy estimations, the validity of each model might be better appreciated according to the standard deviation of the performances. Indeed the standard deviation represents how far the performances are spread around the average of the MADs of the series. As a consequence of it, the smaller the standard deviation is, the more robust the nonempirical hybrid model becomes. For the G2/148 dataset, the standard deviation of the pure DFs is relatively important and reaches 10.0 kcal mol⁻¹. This large deviation is due to the inclusion within the collection of the PBEsol semilocal DF (See Figure S2 in the Supporting Information). This nonempirical density-functional is particularly accurate for the estimation of lattice constant parameters or cohesive energies in case of periodic system calculations,^{31,32} but is rather

inaccurate for atomization energies of molecules. Going from pure to the HYB0 or QIDH models, the standard deviation decreases by 4.8 kcal mol⁻¹ and 5.3 kcal mol⁻¹ respectively. The standard deviations measured on the AE6 dataset confirm this trend. As global overview on atomization energies, these results clearly show that starting from a disperse collection of performances, the level of hybridization tends to minimize the spreading of the MADs, thus validating the consistency of the hybrid and double-hybrid nonempirical models followed here.

Furthermore we choose to test the universal range of the two hybridized models for weak interactions which are also another workhorse for current methods. This property is of high interest because many of the DFs fail to correctly describe the London interactions (induced dipole — induced dipole interaction) governing the binding of some van der Waals complexes. As a test case we focus on the S22 dataset^{33,34} (noted S22/full) which involves seven H-bonded dimers (S22/HB subset), seven dispersion-dominant interacting dimers (S22/DD subset), and eight mixed interacting complexes (S22/MX subset). Figure 1 summarizes the averaged performances of the investigated models (See Figures S3 and S4 in the Supporting Information for individual details and Figure S5 for basis set convergence tests).

As regards its average performance, the simple hybridization scheme does not bring a large improvement for weak interaction estimations. Of course hybrids based on the HYB0 model perform efficiently for H-bond interactions but still suffer from the lack of nonlocal correlation, which is an essential component to estimate dispersion interactions. The double hybridization scheme largely improves the average performances, and even reaches the chemical accuracy threshold (defined as an error less than 1.0 kcal mol⁻¹ for all types of noncovalent interactions). Concerning the consistency of the two hybrid models employed so far, we remark that the standard deviation goes from 0.8 kcal mol⁻¹ for pure DFs to 0.6 kcal mol⁻¹ for HYB0 and 0.2 kcal mol⁻¹ for QIDH. The global improvement of the average performances and the decrease of the standard deviations of the series when going from nonhybridized to double hybridized approaches show once again the consistency of the models.

Until now we evaluated the average impact of the ten tested semilocal DFs on the performances

of the HYB0 and QIDH models, and found it small as compared to the large MAD spreading obtained in case of the pure density-functionals. We will now focus on the best DF candidate to fit with the two hybrid models. Figure 2 illustrates this point, and compares the performances of the best hybridized models with the one obtained with our previous tests (employing PBE) on covalent and noncovalent properties. Globally speaking, the only slight improvement ($\sim 1.0 \text{ kcal mol}^{-1}$) is obtained when the PBEh semilocal DF is plugged into the HYB0 model on the AE6 and G2/148 datasets. Considering numerical and basis set convergence errors, the other performance increases are not largely relevant.

The hybridization of the nonempirical PBE semilocal density-functional with the HYB0 and QIDH models appears thus as a good compromise for covalent and noncovalent interactions but the question still remaining is whether the PBE0 and PBE-QIDH performances are equivalent to those of standard and/or more modern hybrids and double-hybrids. Figure 3 compares our models with fully empirical hybrids (global³⁵⁻³⁷ and range-separated³⁸⁻⁴⁰) and double-hybrids^{15,41} deriving from pure GGA, meta-GGA, nonseparable gradient approximation NGA and meta-NGA. Empirical density-functionals like mPW2-PLYP, B2-PLYP, ω B97X and B3LYP are particularly efficient to estimate atomization energies of the reactions included in the G2/148 dataset. These reference reactions are part of the training sets used during their parameterizations: a considerable advantage which helps them to perform under $3.0 \text{ kcal mol}^{-1}$. PBE0 and PBE-QIDH are on the line of the other modern hybrids for covalent properties (error spread between 4.0 and $5.0 \text{ kcal mol}^{-1}$). For weak interaction purposes, PBE-QIDH reveals its challenging character as the best double-hybrid candidate. PBE0 performs better than the global-hybrids of its generation (*e.g.* B3LYP), but still stays behind the M06 and M06-HF for this type of properties.

In this Letter, we demonstrated the universal behavior of the nonempirical HYB0 hybrid and QIDH double-hybrid models. Their performances, when they are coupled with a selection of ten semilocal density-functionals, were thoroughly tested through the evaluation of covalent and noncovalent properties of the most interest, and showed that the influence of the density-based exchange-correlation energy terms on the performances of the hybrid models is statistically small

by comparison with the one obtained with pure density-functionals (nonhybridized). This investigation validated the (statistical relevant) improvement going from the HYB0 to the QIDH model raised in our previous studies, and showed that the PBE semilocal density-functional is a good candidate for them. Finally we also compared the performances of our models with standard and modern empirical density-functionals. The PBE-QIDH double-hybrid is on the line with the best performing density-functionals for noncovalent interaction purposes, but stays in the average for covalent interaction estimates.

Computational Methods

All the computations were done with the Gaussian program package.⁴² The semilocal density-functionals, in any of their respective single and double hybridization forms, which were not commercialized with Gaussian'09 were fully implemented within the software. An ultrafine integration grid was set for meta-GGA-based computations. The Ahlrichs quadruple- ζ and the Pople triple- ζ 6-311+G(3df, 2pd) basis sets were used to evaluate atomization energies of systems included in the AE6²⁷ and G2/148^{28–30} datasets respectively, while the Dunning triple- ζ *cc-pVTZ* basis set was employed to compute the weakly binding energies of complexes involved in the S22 dataset.³³

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Table 1: List and nature of the semilocal exchange-correlation density-functionals considered in this work.

DF	type	comments ^a
PBE ⁴³	GGA	built from first-principles ($\kappa = 0.804$, $\mu = 0.219$)
PBEsol ³¹	GGA	μ is reoptimized; relevant for solids ($\kappa = 0.804$, $\mu = 0.123$)
revPBE ⁴⁴	GGA	κ is reoptimized using reference values ($\kappa = 1.227$, $\mu = 0.219$)
APBE ⁴⁵	GGA	built from first-principles ($\kappa = 0.804$, $\mu = 0.260$)
PBEsol ⁴⁶	GGA	built from first-principles ($\kappa = 0.804$, $\mu = 0.276$)
TCA ⁴⁷	GGA	built from first-principles ($\kappa = 0.804$, $\mu = 0.219$)
PBEh ⁴⁸	GGA	modeling of the exchange hole
PW91 ⁴⁹	GGA	modeling of the exchange-correlation hole
TPSS ⁵⁰	meta-GGA	additional constraints imposed
BLYP ^{51,52}	GGA	parameterized using reference values

^a The symbols κ and μ refers to the Lieb-Oxford bound and to the effective gradient coefficient for exchange respectively.

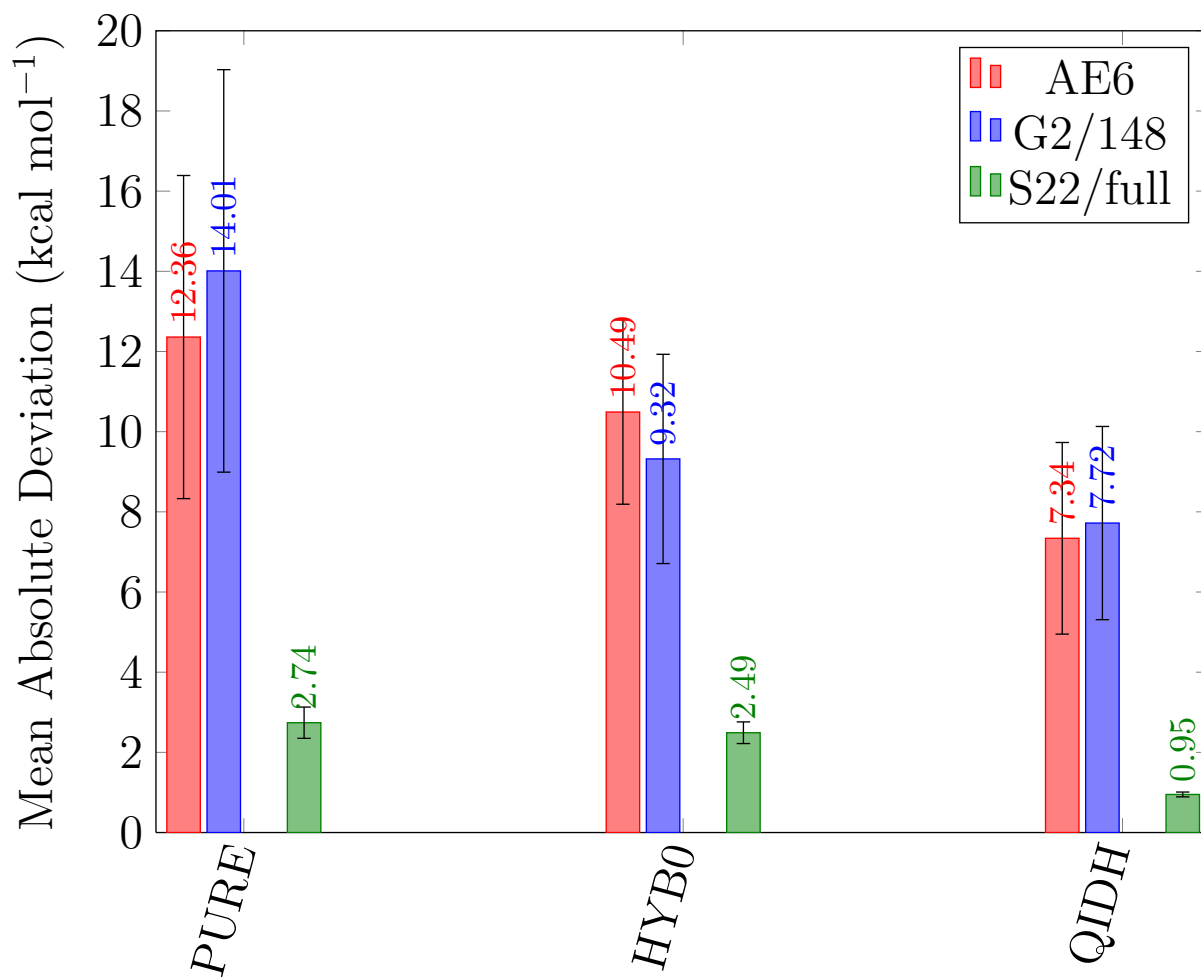


Figure 1: Averages over the ten mean absolute deviations for the pure density-functionals and the hybridized HYB0 and QIDH variants. Black error bars represent the standard deviation of the series. The performances are evaluated on the AE6 (red) and G2/148 (blue) atomization energy datasets, and on the S22/full (green) nonbonded interaction dataset. All the reactions of the AE6, G2/148 and S22/full test sets are evaluated with the def2-QZVP, 6-311+G(3df, 2pd) and *cc-pVTZ* basis sets respectively.

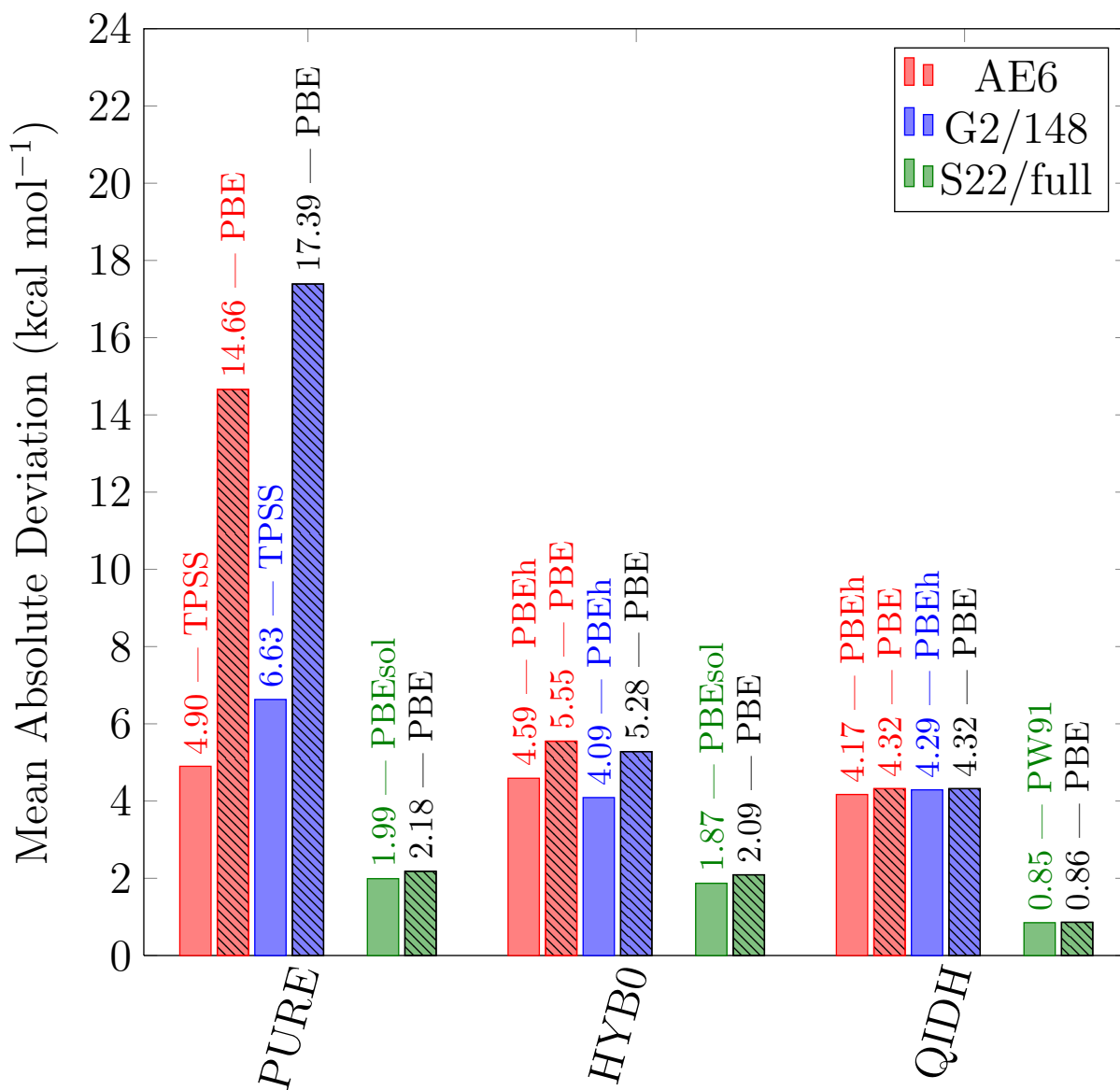


Figure 2: Best (filled-color) and PBE-based density-functional (black-dashed) mean absolute deviations for the AE6 (red), G2/148 (blue) and S22/full (green) test sets. All the reactions of the AE6, G2/148 and S22/full datasets are evaluated with the def2-QZVP, 6-311+G(3df, 2pd) and *cc-pVTZ* basis sets respectively.

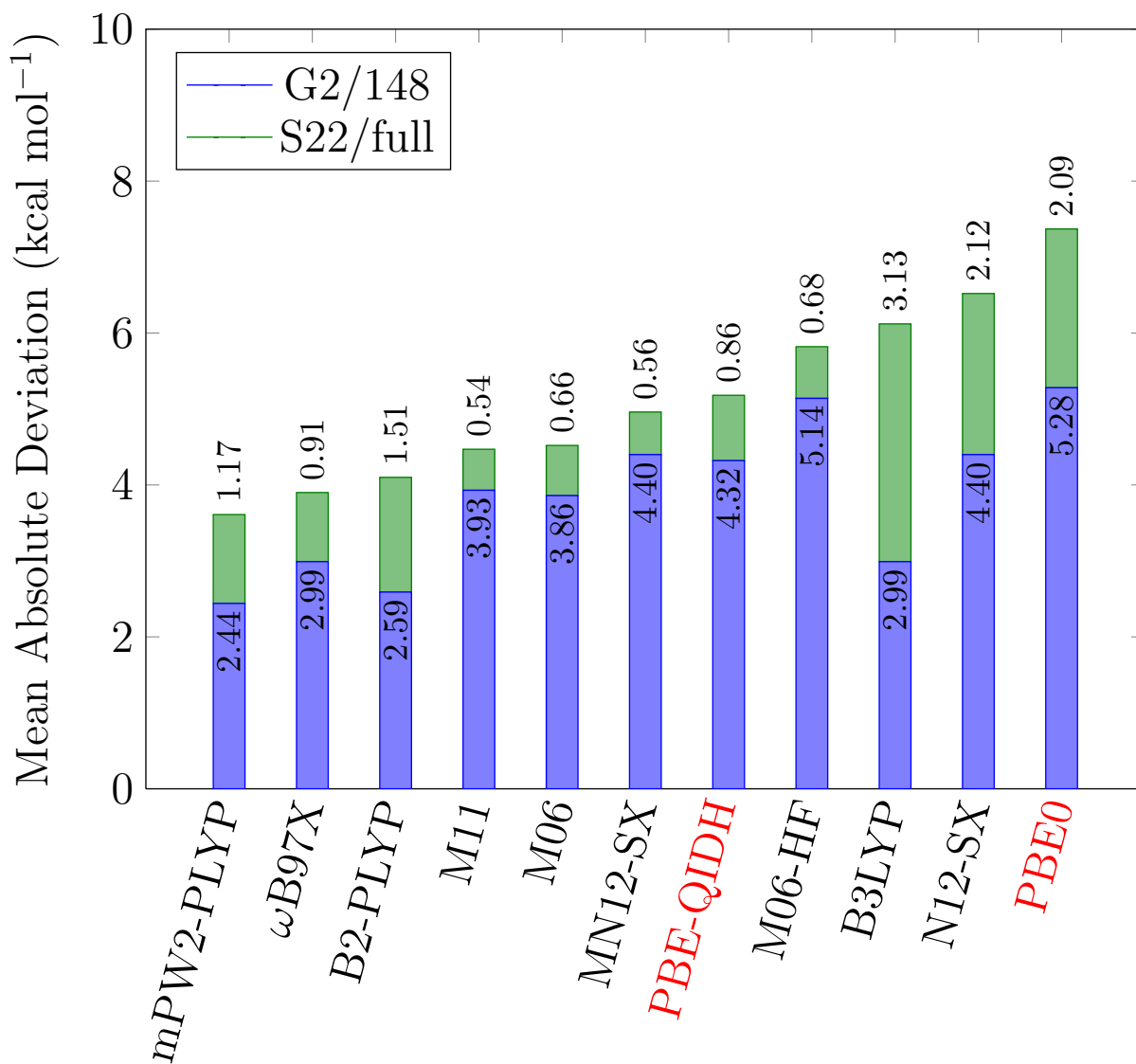


Figure 3: Cumulative mean absolute deviations for the PBE-based HYB0 and QIDH models (red fonts), and for some standard and modern density-functionals. The performances are evaluated on the G2/148 (blue) atomization energy dataset and on the S22/full (green) nonbonded interaction dataset. All the reactions of the G2/148 and S22/full test sets are evaluated with the 6-311+G(3*df*, 2*pd*) and *cc-pVTZ* basis sets respectively.

Supporting Information Available

Individual performances of the investigated density-functionals are given in Supporting Information. This material is available free of charge via the Internet at <http://pubs.acs.org/>.

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Graphical TOC Entry

