Seeking for reliable double-hybrid density functionals without fitting parameters: The PBE0-2 functional

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Without the use of any empirical fitting to experimental or high-level \textit{ab initio} data, we present a double-hybrid density functional approximation for the exchange-correlation energy, combining the exact Hartree-Fock exchange and second-order Møller-Plesset (MP2) correlation with the Perdew-Burke-Ernzerhof (PBE) functional. This functional, denoted as PBE0-2, is shown to be accurate for a wide range of applications, when compared with other functionals and the \textit{ab initio} MP2 method. The qualitative failures of conventional density functional approximations, such as self-interaction error and noncovalent interaction error, are significantly reduced by PBE0-2.

I. INTRODUCTION

Over the past two decades, Kohn-Sham density functional theory (KS-DFT) \cite{Kohn65} has become a very popular electronic structure method for molecular and solid-state systems, due to its computational efficiency and reasonable accuracy. Although the exact exchange-correlation (XC) density functional \( E_{xc}[\rho] \) in KS-DFT remains unknown, accurate approximations to \( E_{xc}[\rho] \) have been continuously developed to extend the applicability of KS-DFT to a wide range of systems \cite{Levy96}.

The hierarchy of approximations to \( E_{xc}[\rho] \) has been formulated as a \textit{Jacob’s ladder} connecting the earth (Hartree theory) to the heaven (chemical accuracy) \cite{Perdew92}. The first rung of the ladder is the local density approximation (LDA) \cite{Kohn65,Perdew81}, representing the XC energy density by the local density. Going beyond the LDA, there has been an increasing interest in the “parameter-free” functionals developed by Perdew and co-workers, such as PBE \cite{Perdew96} and TPSS \cite{Vosko80}, demonstrating the usefulness of these functionals. As LDA, PBE, and TPSS belong to the first, second, and third rungs of the ladder, respectively, they systematically improve upon the description of short-range XC effects by climbing up the ladder (with slightly increasing computational costs). However, due to the lack of accurate treatment of nonlocal XC effects, these semilocal functionals (first three rungs) can lead to significant errors, characterized by self-interaction error (SIE), noncovalent interaction error (NCIE), and static correlation error (SCE), in situations where these failures occur \cite{Perdew96,Jung06}.

The SIEs of density functional approximations (DFAs) can be reduced by hybrid DFT methods (fourth rung) \cite{Adamo03}, combining a fraction of the exact Hartree-Fock (HF) exchange with a semilocal functional. As the fraction of HF exchange included in a hybrid functional can be rationalized by perturbation theory arguments \cite{Adamo04}, the PBE-based hybrid functional PBE0 \cite{Adamo03}, has gradually gained its popularity. In view of the successive evolution of the PBE-based functionals: LDA (first rung) \( \rightarrow \) PBE (second rung) \( \rightarrow \) TPSS (third rung) \( \rightarrow \) PBE0 (fourth rung) \( \rightarrow \) ? (fifth rung), naturally, the question is, what could be a functional on the fifth rung (highest rung) of the ladder? In this work, we propose a PBE-based double-hybrid functional (fifth rung), and demonstrate its superiority to the functionals on the first four rungs of the ladder, for a wide range of applications.

II. THE PBE0-2 FUNCTIONAL

The SIEs and NCIEs associated with DFAs can be simultaneously reduced by double-hybrid methods (fifth rung) \cite{Curtiss00,Perdew08}, combining a fraction of HF exchange and a fraction of second-order Møller-Plesset (MP2) correlation \cite{Curtiss01} with a semilocal functional. Accordingly, a PBE-based double-hybrid functional is given by

\[
E_{xc} = a_x E_{xc}^{HF} + (1-a_x) E_{xc}^{PBE} + (1-a_c) E_{xc}^{PBE} + a_c E_{xc}^{MP2},
\]

where \( E_{xc}^{HF} \) is the HF exchange, \( E_{xc}^{PBE} \) is the PBE exchange, \( E_{xc}^{PBE} \) is the PBE correlation, and \( E_{xc}^{MP2} \) is the MP2 correlation (a perturbative term evaluated with the orbitals obtained using the first three terms of the energy). In this work, the two mixing parameters, \( a_x \) and \( a_c \), are determined by physical arguments (i.e., without the use of any empirical fitting to experimental or high-level \textit{ab initio} data).

Based on the double-hybrid approximations proposed by Sharkas, Toulouse, and Savin \cite{Sharkas05}, and the closely related work of Brémond and Adamo \cite{Adam09}, Toulouse \textit{et al.} \cite{Toulouse12} have proposed the linearly scaled one-parameter double-hybrid (LS1DH) approximation (see Eq. (10) of Ref. \cite{Toulouse12}), showing the relationship between the mixing parameters, \( a_x \) and \( a_c \), in a double-hybrid functional,

\[
a_c = (a_x)^3.
\]
Applying Eq. (2) to Eq. (1), only one of the mixing parameters needs to be determined.

Functionals on the first four rungs of the ladder fail to describe long-range van der Waals (vdW) interactions in regions where there is no overlap of the subsystems, due to the lack of long-range correlation effects. This problem can be greatly reduced by the DFT-D (KS-DFT with empirical dispersion corrections) schemes or by a fully nonlocal density functional for vdW interactions (vdW-DF), showing generally acceptable performance on several noncovalent systems.

By contrast, the MP2 correlation in a double-hybrid functional is itself fully nonlocal, and thus responsible for describing long-range vdW interactions. To determine the fraction of MP2 correlation in Eq. (1), consider the two limiting cases where the functional is itself fully nonlocal, and thus responsible for describing long-range vdW interactions (vdW-DF) or by a fully nonlocal density functional for vdW interactions (vdW-DF), showing generally acceptable performance on several noncovalent systems.

Our resulting PBE-based double-hybrid functional, defined in Eqs. (1) and (3), is denoted as PBE0-2, where the “0” refers to no fitting parameters, and the “2” refers to the post-KS treatment for the MP2 correlation.

By contrast, the mixing parameters are adopted in PBE0-DH, another PBE-based double-hybrid functional (also based on Eqs. (1) and (2)), wherein a half-and-half mixing of the PBE and HF exchange functionals is employed. Therefore, a comparison between the performance of PBE0-2 and PBE0-DH is particularly important, as it shows the significance of the physical arguments used in determining the mixing parameters.

\[ a_c = 1/2, \quad a_x = (1/2)^{1/3} \approx 0.793701. \]  

Our resulting PBE-based double-hybrid functional, defined in Eqs. (1) and (3), is denoted as PBE0-2, where the “0” refers to no fitting parameters, and the “2” refers to the post-KS treatment for the MP2 correlation.

III. RESULTS

For a comprehensive comparison of different functionals, we examine the performance of PBE0-2, other PBE-based functionals (LDA, PBE, TPSS, PBE0, and PBE0-DH), three popular functionals (B3LYP (a hybrid functional), B2PLYP (a double-hybrid functional), and B2PLYP-D3 (a double-hybrid functional with empirical dispersion corrections)), and the ab initio MP2 method, on various test sets involving the 223 atomization energies (AEs) of the G3/99 set, the 40 ionization potentials (IPs), 25 electron affinities (EAs), and 8 proton affinities (PAs) of the G2-1 set, the 76 barrier heights of the NHTBH38/04 and HTBH38/04 sets, the 8 proton affinities (PAs) of the G2-1 set, LDA performs poorly, while all the other functionals perform similarly to MP2. For the barrier heights of the NHTBH38/04 and HTBH38/04 sets, the interaction energies of the weakly bound systems are computed with the counterpoise correction for the basis set superposition errors (BSSE).

As shown in Table I for the AEs of the G3/99 set, B2PLYP and B2PLYP-D3 have the best performance (partly due to the fact that this test set overlaps with their training sets). PBE0-2 performs similarly to PBE0-DH, PBE0, TPSS, and B3LYP, and significantly outperforms LDA, PBE, and MP2. For the IPs, EAs, and PAs of the G2-1 set, LDA performs poorly, while all the other functionals perform similarly to MP2. For the barrier heights of the NHTBH38/04 and HTBH38/04 sets, PBE0-2, PBE0-DH, B2PLYP, and B2PLYP-D3 have comparable performance, and are the best functionals here. For the noncovalent interactions of the S22 and S66 sets, B2PLYP-D3 performs the best (mainly due to the empirical dispersion corrections). PBE0-2 performs similarly to MP2, and significantly outperforms all the other functionals.

Here, we calculate the interaction energy curves for the parallel-displaced (in Fig. 1) and T-shaped (in Fig. 2) configurations of the benzene dimer as functions of the intermonomer distance R (defined in Ref. [27]), where the optimized geometries and reference values are taken from the S66 \times 8 set [37]. Overall, the predicted interaction energy curves of B2PLYP-D3 and PBE0-2 are the closest ones to the reference curves (within an error of 1 kcal/mol). LDA predicts too short equilibrium distances, and all the other functionals predict severely underbinding or even repulsive curves. MP2 incorrectly predicts the parallel-displaced configuration to be more stable than the T-shaped one.

The isodesmic reaction energies of n-alkanes to ethane have been known to give systematic errors in conventional DFT calculations. The considered bond separation reaction,

\[ \text{CH}_3(\text{CH}_2)_m\text{CH}_3 + m\text{CH}_4 \rightarrow (m+1)\text{C}_2\text{H}_6 \]  

was first proposed by Redfern et al. to show the errors of B3LYP systematically increase as the number of chain units in n-alkanes, m, increases. To assess how PBE0-2 improves upon this problem, we calculate the isodesmic reaction energies of n-alkanes to ethane, where the optimized geometries and reference values are taken from Ref. [40]. As shown in Fig. 3, the predicted reac-
FIG. 1. Interaction energy curve for the parallel-displaced configuration of the benzene dimer as a function of the intermonomer distance $R$ (defined in Ref. [37]), where $R_0$ is the equilibrium distance.

FIG. 2. Same as Fig. 1 but for the T-shaped configuration.

FIG. 3. Errors for isodesmic reaction energies of $n$-alkanes to ethane.

FIG. 4. Dissociation curve of $\text{He}^+_2$. Zero level is set to $E(\text{He}) + E(\text{He}^+)$ for each method.
TABLE I. Mean absolute errors (in kcal/mol) of 10 methods for various test sets (see text for details).

| System     | LDA | PBE | TPSS | PBE0 | PBE0-DH | PBE0-2 | B3LYP | B2PLYP | B2PLYP-D3 | MP2 |
|------------|-----|-----|------|------|---------|--------|-------|--------|-----------|-----|
| G3/99 (223)| 121.26 | 21.51 | 5.30 | 6.29 | 5.11   | 5.82   | 5.48 | 3.97   | 2.98      | 9.18   |
| IP (40)    | 5.73  | 3.45 | 3.59 | 3.17 | 3.01   | 1.09   | 4.69 | 2.56   | 2.44      | 5.48   |
| EA (25)    | 5.03  | 2.41 | 2.61 | 3.55 | 3.01   | 1.81   | 3.79 | 2.35   | 2.35      | 3.95   |
| PA (8)     | 5.91  | 1.60 | 1.81 | 1.14 | 0.96   | 0.61   | 1.16 | 1.18   | 1.13      | 0.96   |
| NHTBH (38) | 12.62 | 8.62 | 9.16 | 3.63 | 1.57   | 4.56   | 2.19 | 2.44   | 3.38      | 3.88   |
| HTBH (38)  | 17.95 | 9.67 | 8.68 | 4.60 | 2.01   | 4.69   | 2.17 | 2.45   | 2.44      | 5.48   |
| S22 (22)   | 2.03  | 2.72 | 3.56 | 2.46 | 1.78   | 0.61   | 3.90 | 2.25   | 0.22      | 0.89   |
| S66 (66)   | 1.85  | 2.23 | 3.09 | 2.10 | 1.58   | 0.67   | 3.33 | 1.96   | 0.21      | 0.45   |

FIG. 5. Same as Fig. 4, but for Ar$^+$. Performance. As PBE0-2 contains a very large fraction ($\approx 79\%$) of HF exchange and a large fraction (50\%) of MP2 correlation, the SIE and NCIE associated with PBE0-2 are significantly reduced, reflecting its superior performance for self-interaction problems and noncovalent interactions, respectively. However, due to the perturbative treatment of nonlocal correlation, the SCE of PBE0-2 can be enormous in situations where strong static correlation effects are pronounced $^{[2, 8]}$. It remains challenging to develop a generally accurate density functional resolving all the qualitative failures of semilocal approximations at a reasonable computational cost.

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