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Non-empirical improvement of PBE and its hybrid PBE0 for general description of molecular properties

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Imposition of the constraint that, for the hydrogen atom, the exchange energy cancels the Coulomb repulsion energy yields a non-empirical re-parameterization of the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA) exchange-correlation energy functional, and of the related PBE hybrid (PBE0). The re-parameterization, which leads to an increase of the gradient contribution to the exchange energy with respect to the original PBE functional, is tested through the calculation of heats of formation, ionization potentials, electron affinities, proton affinities, binding energies of weakly interacting systems, barrier heights for hydrogen and non-hydrogen transfer reactions, bond distances, and harmonic frequencies, for some well known test sets designed to validate energy functionals. The results for the re-parameterized PBE GGA, called PBEmol, give substantial improvement over the original PBE in the prediction of the heats of formation, while retaining the quality of the original PBE functional for description of all the other properties considered. The results for the hybrids indicate that, although the PBE0 functional provides a rather good description of these properties, the predictions of the re-parameterized functional, called PBEmolβ0, are, except in the case of the ionization potentials, modestly better. Also, the results for PBEmolβ0 are comparable to those of B3LYP. In particular, the mean absolute error for the bond distance test set is 17% lower than the corresponding error for B3LYP. The re-parameterization for the pure GGA (PBEmol) differs from that for the hybrid (PBEmolβ0), illustrating that improvement at the GGA level of complexity does not necessarily provide the best GGA for use in a hybrid. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.3691197]

I. INTRODUCTION

The Kohn-Sham version[1] of density functional theory (DFT) (Ref. 2) has become a very important tool for electronic structure calculations of molecules and solids.[3–7] At present, although the exact form of the exchange-correlation (XC) energy density functional remains unknown, there are several types of approximations that have proved, in general, to be quite useful for the description of a wide variety of systems and properties. Among these, the most prominent are the local spin density approximation (LSDA), generalized gradient approximations (GGA), meta-GGAs, and hybrids (both global and range-separated).[5,7] In order of increasing complexity, these correspond to the first four rungs of Perdew's ladder of functionals.[8]

Further refinement of functionals more complicated than LSDA is of continuing importance. Both computational cost and basic insight benefit from improved accuracy at any given rung. There is a conceptual challenge and opportunity as well. Though the rungs are defined by increasing structural complexity, there is no guarantee that even a very successful approximation for a given rung actually exhausts the accuracy limits of that rung.

Here we consider those issues in the context of seeking improvements via re-parameterization of a particular form of a GGA exchange-correlation functional. This has long been an active area, not only because GGAs in themselves have proven to be very useful in terms of the good balance they provide between computational effort and accuracy for both molecules and solids, but also because GGAs are an important component of higher-rung functionals. Such is the case, for example, for the global hybrid functionals[9–11] in which a fixed fraction of exact exchange is combined with a GGA.

In the development of XC functionals, semi-empirical and non-empirical approaches have been followed.[7] In the semi-empirical approach, some of the parameters in the functional are fixed through the use of experimental or computed data. Usually this is done by minimizing the mean absolute error of one or more properties predicted by the proposed functional for the systems in a selected training set. In contrast, the non-empirical philosophy fixes the parameters solely from

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physical and mathematical information. Such non-empirical approaches are dominated by constraint satisfaction.[6]

Among the GGA functionals, the Perdew-Burke-Ernzerhof (PBE)[12] GGA was constructed non-empirically to satisfy several constraints. It has seen wide use in the study of a great variety of molecular and extended systems. For molecular systems, PBE leads to an accuracy in the prediction of properties such as ionization potentials, electron affinities, and bond distances, which is similar to that obtained through semi-empirical functionals. However, PBE yields large errors in the prediction of atomization energies, in comparison with the results obtained from empirical functionals.[13]

A global hybrid, associated with PBE, and free from adjustable parameters, has been proposed.[13,14] Denoted PBE0, this hybrid gives an accuracy comparable to that obtained from semi-empirical hybrids, including atomization energies.

In the construction of the PBE functional, there are no constraints explicitly related to the self-interaction error (SIE), yet SIE is a very important influence upon adequate description of thermochemistry and kinetics.[15–22] Thus, the object of the present work is to obtain some of the parameters in the PBE exchange-correlation functional by constraining them to correction of the SIE for the case of the hydrogen atom, and to test the new parameterization in both the GGA and in the corresponding global hybrid.

An important matter of context is that Zhang and Yang proposed a modified version of PBE (revPBE)[23] in which the functional form is kept, and only the value of the parameter κ (related to the Lieb-Oxford bound,[24,25] see below) is changed with respect to PBE. That change leads to an improvement of the atomization and total energies. In revPBE, the value of the parameter κ was determined by fitting exchange-only total atomic energies of some rare gases (from He to Ar) to exact exchange-only results from the optimized exchange potential method. Thus, revPBE is, in the present context, semi-empirical.

Several other GGAs have been motivated as modifications or extensions of PBE. Though those efforts share the non-empirical philosophy, they use different expressions for the XC energy functional.[26–32] Given the popularity of the PBE functional, it is worthwhile to focus on the specific task of determining a near-optimal parameterization for a large class of systems (here, molecules).

II. THEORY

A. Context

The PBE exchange energy functional, in the spin restricted case, is expressed in the form[12]

$$E_X^{PBE} = \int d\mathbf{r}\, \rho(\mathbf{r})\, \varepsilon_X^{\mathrm{unif}}(\rho)\, F_X^{PBE}(s), \tag{1}$$

where $\rho(\mathbf{r})$ is the electron number density, $\varepsilon_X^{\mathrm{unif}}(\rho)$ is the exchange energy density of a uniform electron gas, and $F_X^{PBE}(s)$ is the PBE exchange enhancement factor, given by

$$F_X^{PBE}(s) = 1 + \kappa - \frac{\kappa}{1 + \frac{\mu s^2}{\kappa}}. \tag{2}$$

Here $s = |\nabla\rho(\mathbf{r})|/(2\,k_F\,\rho(\mathbf{r}))$ is the exchange dimensionless reduced density gradient, $k_F = (3\,\pi^2\,\rho(\mathbf{r}))^{1/3}$, and $\kappa = 0.804$ and $\mu = 0.21951$ are constants. (Unless noted otherwise, we use Hartree atomic units.)

The PBE correlation energy is given by

$$E_C^{PBE} = \int d\mathbf{r}\, \rho(\mathbf{r})\, [\varepsilon_C^{\mathrm{unif}}(r_s, \zeta) + H(r_s, \zeta, t)], \tag{3}$$

where $\varepsilon_C^{\mathrm{unif}}(r_s, \zeta)$ is the correlation energy density of the uniform electron gas, $H(r_s, \zeta, t)$ is a function that takes into account the gradient contribution to the correlation energy,[12] $r_s = (3/4\pi\,\rho(\mathbf{r}))^{1/3}$, $\zeta = (\rho_\uparrow(\mathbf{r}) - \rho_\downarrow(\mathbf{r}))/\rho(\mathbf{r})$, $t = |\nabla\rho(\mathbf{r})|/2\,\phi\,k_s\,\rho(\mathbf{r})$, with $\phi(\zeta) = [(1+\zeta)^{2/3} + (1-\zeta)^{2/3}]/2$, $k_s = \sqrt{4\,k_F/\pi}$, and $\rho_\uparrow$, $\rho_\downarrow$ are the spin-up and spin-down number densities.

The PBE functional satisfies several constraints.[12] Under uniform scaling of the electron density, $\rho\,(\mathbf{r}) \to \lambda^3\,\rho(\lambda\,\mathbf{r})$, the exchange contribution scales like λ, leading to the correct uniform gas limit. PBE-X also obeys the spin scaling relationship $E_X[\rho_\uparrow, \rho_\downarrow] = (E_X[2\,\rho_\uparrow] + E_X[2\,\rho_\downarrow])/2$. In addition, it satisfies the upper bound $E_X < 0$, and the local Lieb-Oxford (LO) lower bound, $\varepsilon_X(\mathbf{r}) \geq -1.68\,\rho^{4/3}(\mathbf{r})$ for all $\mathbf{r}$. LO bound satisfaction is achieved by fixing the parameter κ to the value 0.804. With respect to the sum rule for the exchange hole, Kurth, Perdew, and Blaha[33] have argued that the PBE functional essentially satisfies that rule, because PBE-X is quite similar to the analytical fit to a numerical GGA[34] by Perdew and co-workers.[35,36] The numerical GGA, in turn, was built with real space cutoffs, that were set, among other things, to impose the exchange hole sum rule.

Under uniform scaling of the electron density, the C contribution of PBE scales[37] correctly to a constant in the limit $\lambda \to \infty$, and satisfies the upper bound $E_C \leq 0$. Also, the sum rule for the C hole may be assumed to be essentially satisfied by the PBE functional, for the same reasons mentioned for the X hole. In addition, in the rapidly varying limit, $t \to \infty$, the correlation energy vanishes, and in the slowly varying limit, $t \to 0$, one recovers the second-order gradient expansion,

$$H \to (e^2/a_0)\,\beta\,\phi^3\,t^2, \tag{4}$$

where $\beta \approx 0.066725$.[38]

In the slowly varying limit, the X enhancement factor adopts the form

$$F_X^{PBE}(s) \to 1 + \mu\,s^2. \tag{5}$$

In the original PBE functional this fact plays an important role, since the value of μ was set so that the second-order term of the correlation energy given in Eq. (4) cancels the second-order term of the exchange energy given in Eq. (5), that is,

$$\mu = \pi^2\,\beta/3. \tag{6}$$

This was done in order to retain the LSDA linear response, because it provides an excellent description for small density variations around the uniform electron gas. Thus, from Eq. (6) and for $\beta_{PBE} = 0.066725$, one gets $\mu_{PBE} = 0.21951$.

Recently, Perdew *et al.*[39] have discussed the dilemma that arises from the weight given to the gradient dependence in

GGA functionals, when one is designing an XC energy functional that could lead to a reasonable description of finite and extended systems. The heats of formation of molecules are improved when the gradient contribution to the exchange energy is increased, and worsened when it is decreased,[40] while lattice parameters of solids and surface energies exhibit the opposite tendencies. Thus, since PBE cannot fulfill both requirements simultaneously, those authors[39] proposed a modified PBE, specifically parameterized to constraints relevant for solids, called PBEsol, which reduces to the second-order gradient expansion for slowly varying densities.[41] That is, in PBEsol $\mu = \mu_{\mathrm{GEA}} = 10/81 \approx 0.12346$ and $\beta_{PBEsol} = 0.046$. This latter value is obtained through the fitting of the jellium surface exchange-correlation energy.

Later, Zhao and Truhlar[27] arrived at the same conclusion with respect to the connection between the value of μ and the behavior of lattice constants and atomization energies, and found, additionally, that the value of μ also correlates with the behavior of the cohesive energies of solids, reaction barrier heights, and non-hydrogenic bond distances in small molecules.

B. Alternative analysis

Since early in DFT, cancellation of SIE has been known to be important.[42] However, at the lower rungs of the XC ladder, it is impossible to satisfy all of the rigorous constraints that are, in principle, applicable. See, for example, Ref. 32 for discussion and references. In particular, the PBE parameterization could not impose a SIE correction and simultaneously retain all the constraints those authors deemed significant.

Although Coulomb self-interaction is conceptually simple, the description of this contribution for a many-electron system in terms of the electronic density remains unknown. However, in the case of a one-electron system, with$\rho_1(\mathbf{r})$ the one-electron density, the exact exchange energy must cancel the Coulomb repulsion energy,

$$E_X[\rho_1] = -J[\rho_1], \tag{7}$$

and the correlation energy vanishes

$$E_C[\rho_1] = 0. \tag{8}$$

It is worth mentioning that cancellation of the self-coulomb energy against self-exchange for the hydrogen atom fixes one of the parameters in the meta-GGA functionals TPSS (Ref. 43) and revTPSS (Ref. 44) in which PBE is embedded.

Thus, one can follow an alternative approach to parameterizing the PBE-XC form by making use of Eq. (7) and the hydrogen atom density for $\rho_1(\mathbf{r})$ to fix the value of μ. Then one determines β from Eq. (6) to achieve cancellation of the second-order gradient term in order to retain the LSDA linear response. Since the Coulomb repulsion energy evaluated for the ground state electron density of the hydrogen atom, $\pi^{-1}e^{-2r}$, is $5/16 = 0.31250$ hartree, one can evaluate the exchange energy with Eqs. (1) and (2) for this density, and fix the value of μ so that $E_X[\rho_1]$ is equal to -0.31250 hartree. With a numerical procedure implemented in Mathematica, the solution of this equation leads to $\mu_{xH} = 0.27583$, which is 26% larger than $\mu_{PBE} = 0.21951$, and considerably larger (123%) than $\mu_{GE} = 10/81 \approx 0.12346$.

From Eq. (6) this one-electron SIE-correction procedure leads to $\beta_{xH} = 0.08384$, a value about 25% larger than the value $\beta_{PBE} = 0.066725$ of the original PBE, and considerably larger than the value $\beta_{PBEsol} = 0.046$ used in PBEsol. It is important to mention that the correlation gradient coefficient $\beta_{PBE} = 0.066725$, was derived by Ma and Brueckner in the high density limit,[38] and a value about 17% higher was derived also for that limit by Langreth and Vosko.[45] With respect to the latter, Perdew *et al.*[44] have argued in favor of the Ma and Brueckner value for PBE, TPSS,[43] and rev-TPSS,[44] because the difference with the Langreth and Vosko value comes from a long-range contribution to the gradient expansion of the correlation hole that would not be present in the PBE-C functional, due to the underlying real-space cutoff used in its construction. Nevertheless, the value derived in the present work is rather close to that of Langreth and Vosko. Moreover, it has the advantage that, as in the original PBE functional, when added to the X functional, the second-order gradient terms cancel each other, so that the LSDA linear response is retained.

Thus, one can see that incorporation of the one-electron SIE-correction constraint using the ground state density of the hydrogen atom leads to an augmentation of the gradient contribution, which, in principle, might be expected to lead to a better description of the heats of formation for molecules. We call this new parameterization PBEmol, because as in PBEsol, only the values of the parameters associated with the second-order gradient expansion are changed.

Note that the PBE correlation energy functional does not satisfy Eq. (8). The value obtained with $\beta_{xH} = 0.08384$ for the hydrogen atom electron density is equal to -0.004876 hartree, while with $\beta_{PBE} = 0.066725$ the value is equal to -0.005976 hartree. Thus, there is a noticeable decrease in the error (almost 20%) obtained with the value of β that comes from the value of μ that cancels correctly the self-interaction in the hydrogen atom.

To have the total electron-electron interaction energy in the hydrogen atom equal to zero, one could combine Eqs. (7) and (8) in the form $J[\rho_1] + E_X[\rho_1] + E_C[\rho_1] \cong 0$. When one fixes the value of μ through this approximate expression, with β for the correlation energy determined through μ, using Eq. (6), one finds that $\mu \approx 0.22536$, a value that is rather close to $\mu_{PBE} = 0.21951$. Therefore, this procedure should not be expected to improve on the description of molecular properties with respect to the original PBE. In addition, it is appropriate to emphasize that the correct description of one-electron systems requires the satisfaction of Eqs. (7) and (8) separately.

The non-empirical constraint satisfaction procedure to fix the parameters present in an approximate functional, necessarily involves choices. Considering that neither PBE nor PBEsol are one-electron self-interaction free, in the present work, we propose an alternative non-empirical parameterization of the PBE functional where $\kappa$is fixed through the enforcement of the local Lieb-Oxford bound, μ is set to satisfy Eq. (7) for the hydrogen atom, and β is determined from Eq. (6) to recover the linear response of LSDA. Thus, the proposed parameterization implies that Eq. (7) is partially satisfied, while Eq. (8) is not satisfied.

To fulfill Eq. (8) one could abandon the PBE correlation and combine the PBEmol exchange with a correlation energy functional that vanishes for one-electron systems. In the meta-GGA correlation functionals[43,44,46] based on PBE, this is achieved by introducing a dependence in the Kohn-Sham orbitals through the kinetic energy density τ, so that the combination of this correlation with PBEmol would not preserve the basic features of a GGA type functional. An alternative to satisfy Eq. (8) is to use the semi-empirical GGA correlation LYP,[47] a combination that is not explored further in the present work to preserve the non-empirical nature of the proposed exchange-correlation energy functional evaluated here.

III. RESULTS AND DISCUSSION

To test the behavior of PBEmol and the corresponding PBEmol-hybrid, which will be discussed later, with the values of μ and β just determined, we have done calculations for several molecular properties, using specifically designed test sets in each case.

A. Properties and test sets

We follow a common approach to validate the proposed XC functionals by calculating thermochemical, kinetic, and structural properties for specific molecular datasets that are composed of systems for which there is accurate experimental or theoretical information.

To establish the thermochemical accuracy of the different functionals,[48] we calculated the standard heat of formation ($\Delta_f H^0_{298}$) for 223 molecules that comprise the G3/99 test set,[49] following the procedure established by Curtiss *et al.*[50] In it, as a first step, the 223 molecular geometries are determined with the B3LYP hybrid functional[9,10,47,51,52] and the 6-31G(2df,p) basis set,[53] and the harmonic frequencies are scaled by a factor of 0.9854. Then, the molecular standard heat of formation is calculated from experimental atomic data, and from the total molecular energy at the previously calculated geometry and the total atomic energies, both determined with the specific functional one is testing and with a specific basis set. We have used the Def2-TZVPP basis set[54] for all the functionals.

Ionization potentials, electron affinities, and proton affinities were also calculated. For the first two, the datasets[55,56] IP13/3 and EA13/3, which consist of six atoms and seven molecules, were used as test sets. For the molecules, the calculations were done adiabatically with the geometries reported in Ref. 57. On the other hand, for the proton affinities, the test set PA8 (Refs. 58 and 59) of eight molecules that belong to the G2/97 dataset[50,60,61] was used, with the geometries of the anions and neutral species of MP2(full)/ 6-31G(2df,p) calculations reported in Ref. 62. For the latter three properties, the calculations were done with the 6-31++G(d,p) basis set.

Another important test category is the binding energy for weakly interacting systems. For it, we did calculations for the set of 31 cases comprised of the HB6/04,[63] CT7/04,[63] DI6/04,[63] WI7/05,[64] and PPS5/05[64] test sets. These correspond to six hydrogen bonding dimers, seven charge-transfer complexes, six dipole interaction complexes, seven dispersion-interacting systems, and five $\pi - \pi$ stacking complexes, respectively. In this case, the calculations also were done with the 6-31++G(d,p) basis set

To test the performance of these functionals in chemical reactions, we have considered the barrier heights of 38 cases that correspond to the forward and backward transition states of 19 hydrogen transfer reactions and 19 non-hydrogen transfer reactions contained, respectively, in the test sets HTBH38/04 and NHTBH38/04.[57,64–66]

To analyze the capabilities of these functionals to describe molecular geometries, we have made use of the T-96R test set[48] that consists of 96 chemical species, whose bond distances are given in Ref. 67.

Finally, we have also considered the harmonic vibrational frequencies using the T-82F test set[48] with 82 molecules, whose experimental values were taken from Refs. 67–69.

The Def2-TZVPP basis set was used for the barrier heights, bond distances, and vibrational frequencies. All the calculations were done with a developmental version of NWCHEM 6.0.[70]

B. GGA results

Since the only change we have made to the PBE functional involves values of some of the parameters that characterize it, we did comparison calculations with the PBEsol and the revPBE functionals. Those also differ from PBE only in parameterization, not in form. In Table I, one can see the values of the parameters μ, β, and κ for the exchange functionals of PBE form studied in this work. Additionally, we have considered RPBE,[26] which is a non-empirical GGA functional with a different form than PBE that recovers the gradient expansion form given in Eq. (5), lies very close to revPBE for $s = 0$ up to $s \approx 3.0$, and has the same asymptotic limit of PBE, so it provides an interpolation between revPBE and PBE.

We have also done calculations with the meta-GGA revTPSS functional.[44] Since it belongs to the next rung up in Perdew's ladder,[8] it provides a reference for the improvement achieved by the GGA functionals.

The mean absolute errors (MAEs) for the different PBE-like functionals and for the different properties considered in this work are presented in Table II, together with the results for the non-empirical RPBE and revTPSS functionals. The individual deviations for each system and the XC functionals considered in this work can be found in the supplementary material.[71]

TABLE I. Parameters for the PBE-like exchange functionals considered in this work.

Parameters	PBEsol	PBE	revPBE	PBEmol
μ	0.12346	0.21951	0.21951	0.27583
β	0.046	0.06673	0.06673	0.08384
κ	0.804	0.804	1.245	0.804

TABLE II. Mean absolute errors (MAE) for the PBE-like functionals and the meta-GGA functional rev-TPSS, for several properties. All energies are in kcal/mol, bond distances are in Å, and frequencies in cm^{-1}.

	MAE					
Property	PBE	PBEsol	revPBE	PBEmol	RPBE	revTPSS
Heats of formation	21.21	57.44	10.73	9.80	13.00	4.55
Ionization potentials	3.47	2.63	3.00	3.97	3.00	3.06
Electron affinities	2.64	2.63	2.48	2.81	2.49	2.45
Proton affinities	1.39	2.87	1.29	1.18	1.31	1.80
Binding energies of weakly interacting systems	1.64	2.25	1.63	1.52	1.52	1.41
Reaction barrier heights						
Hydrogen transfer forward	9.49	13.05	6.66	7.82	6.50	6.63
Hydrogen transfer backward	9.72	12.82	7.13	8.29	7.04	7.72
Non-hydrogen transfer forward	10.38	11.69	8.97	9.74	9.03	11.18
Non-hydrogen transfer backward	9.96	10.76	8.76	9.62	8.81	10.08
Bond distances	0.0179	0.0147	0.0244	0.0194	0.0258	0.0204
Frequencies	43.30	44.70	48.77	43.56	50.67	39.58

With respect to the heats of formation, one sees that the GGA that leads to the best description is PBEmol, with a substantial improvement over the original PBE, and modest improvement over revPBE. For this property RPBE improves upon PBE, but it is worse than PBEmol. However, the best GGA MAE is still more than twice the meta-GGA MAE for this property.

For the ionization potentials, revPBE and RPBE lead to a moderately better description than PBEmol. The advantage of revPBE and RPBE is about 13% for the electron affinities, but revPBE and RPBE are 9% and 11%, respectively, worse than PBEmol for the proton affinities, and revPBE is 7% worse for the weakly interacting system binding, while RPBE is equal. For barrier heights, the PBEmol MAE is 18%–20% worse than RPBE for hydrogen transfer reactions, for which revPBE is similar to RPBE, and 8%–10% worse than revPBE for the non-hydrogen cases, for which RPBE is also similar to revPBE. However, for bond distances PBEmol is 25% and 33% better than revPBE and RPBE, respectively, and only 8% worse than the original PBE. For frequencies the story is similar.

Since the results for the heats of formation, whose improvement was one of our main goals, are better for PBEmol than revPBE, by almost 1 kcal/mol in MAE and better than the original PBE by more than a factor of two in MAE, we argue that PBEmol is a serious candidate GGA of PBE form for general purpose use with finite systems. The argument is strengthened in that revPBE depends upon an empirical determination of the value of the parameter, whereas PBEmol retains the non-empirical nature of PBE by fixing the values of μ, β, and κ through constraint satisfaction.

With respect to RPBE, which is also a non-empirical functional, the results indicate that PBEmol provides a better description of heats of formation and distances, while RPBE provides a better description of the barrier heights.

Also, in the same vein, one sees that the meta-GGA revTPSS provides a great improvement in the heats of formation with respect to the GGA functionals, by reducing the MAE to 4.55 kcal/mol. However, revTPSS does not yield a systematic improvement in other properties and, in fact, worsens some.

For insight into parameter dependence, we also did calculations with the one-electron SIE-corrected value of $\mu_{xH} = 0.27583$ for the exchange energy, combined with the original values $\beta_{PBE} = 0.066725$ and with $\beta_{PBEsol} = 0.046$ for the correlation energy for all the datasets. The MAEs deteriorate for both combinations. In fact, the trend in the results including the ones with $\beta_{xH} = 0.08384$, indicate that the lower the value of this parameter, the worse the description of all the properties, including the heats of formation. For the G3/99 data set with $\mu_{xH} = 0.27583$, the MAE for $\beta_{PBE} = 0.066725$ is 10.21 kcal/mol, and for $\beta_{PBEsol} = 0.046$ is 14.30 kcal/mol. Thus, it seems that the cancellation of the second-order terms of the gradient expansion to retain the LSDA linear response is important for the description of molecular properties.

It is appropriate to mention that when one makes use of $\mu = 0.22536$ and $\beta = 0.06850$ (determined from Eq. (6) for this value of μ), which correspond to the approximation given by the combination of Eqs. (7) and (8), namely, $J[\rho_1] + E_X[\rho_1] + E_C[\rho_1] \cong 0$, one obtains, as discussed above, a similar description to that of the original PBE for the properties considered. For the G3/99 data set, one obtains a MAE of 19.35 kcal/mol. This suggests that the independent satisfaction of Eqs. (7) and (8) is more important than the cancellation of their sum.

In summary, PBEmol exhibits major improvement over PBE for heats of formation and rather good overall performance among functionals of the PBE form. Apparently, the one-electron SIE correction is a major factor in constraining the GGA rung of Jacob's ladder, at least for finite systems.

C. Results for PBE-type hybrids

Global hybrid functionals, in which a fraction of exact exchange is mixed with GGA XC, were introduced by Becke[9] from considerations of the adiabatic connection formula. In

TABLE III. Mean absolute errors (MAE) for the PBE-like hybrid functionals, B3LYP, and M06-2X for several properties. All energies are in kcal/mol, bond distances are in Å and frequencies in cm^{-1}.

	MAE						
Property	PBEsol0	PBE0	PBEβ0	PBEmol0	PBEmolβ0	B3LYP	M06-2X
Heats of formation	32.31	5.72	9.09	11.28	5.65	5.69	2.52
Ionization potentials	3.08	3.44	5.13	3.56	5.33	4.76	3.01
Electron affinities	2.67	2.91	2.77	3.18	2.78	3.26	2.84
Proton affinities	2.11	1.16	1.13	1.10	1.11	1.31	2.06
Binding energies of weakly interacting systems	1.52	1.05	1.14	0.95	1.00	1.17	0.62
Reaction barrier heights							
Hydrogen transfer forward	6.73	4.05	4.36	2.79	3.26	4.29	1.04
Hydrogen transfer backward	7.19	4.90	5.08	3.79	4.13	4.65	1.38
Non-hydrogen transfer forward	7.77	6.68	7.13	6.10	6.66	7.81	1.76
Non-hydrogen transfer backward	7.25	6.22	6.41	5.71	6.00	6.67	1.92
Bond distances	0.0128	0.0103	0.0097	0.0095	0.0090	0.0108	0.0155
Frequencies	53.53	45.19	44.05	42.94	41.80	35.23	70.13

this context, he proposed a hybrid with three parameters,[10]

$$E_{XC}^{\mathrm{hyb}} = E_{XC}^{\mathrm{LSD}} + a_0\left(E_X^{\mathrm{exact}} - E_X^{\mathrm{LSD}}\right) + a_X\left(E_X^{\mathrm{GGA}} - E_X^{\mathrm{LSD}}\right) + a_C\left(E_C^{\mathrm{GGA}} - E_C^{\mathrm{LSD}}\right), \tag{9}$$

where E_{XC}^{GGA} is a generalized gradient approximation and E_{XC}^{LSD} is its local spin density part. In subsequent work,[11] the functional given by Eq. (9) was simplified by setting $a_X = 1 - a_0$ and $a_C = 1$, leading to a hybrid with just one adjustable parameter,

$$E_{XC}^{\mathrm{hyb}} = E_{XC}^{\mathrm{GGA}} + a_0\left(E_X^{\mathrm{exact}} - E_X^{\mathrm{GGA}}\right). \tag{10}$$

Perdew, Ernzerhof, and Burke[72] later presented an argument based on Görling-Levy perturbation theory[73,74] that suggests that $a_0 \approx 1/4$. With this value, a hybrid based on PBE GGA XC, E_{XC}^{GGA}, and free from adjustable parameters, was proposed.[13,14] As noted earlier, this hybrid is known as PBE0.[14]

Thus motivated, we also have analyzed the PBE0-type hybrids corresponding to PBEmol and PBEsol, which we denote as PBEmol0 and PBEsol0. Additionally, we have also considered two other hybrids which result from modification of the gradient contribution to the correlation energy in PBE0 and PBEmol0 based on Eq. (6). That is, if one assumes that, in the slowly varying limit, the gradient portion of exchange that enters into Eq. (10) must cancel the gradient portion of correlation, then one needs to multiply the value of β by 3/4. In the case of PBE, in the hybrid PBE0, $\mu = \mu_{PBE} = 0.21951$ and $\beta = \beta_{PBE} = 0.066725$. However, in the hybrid we denote as PBEβ0, $\mu = \mu_{PBE} = 0.21951$, but $\beta = (3/4)\beta_{PBE} = 0.050044$. Correspondingly for the case of PBEmol, the hybrid PBEmol0 has $\mu = \mu_{xH} = 0.27583$ and $\beta = \beta_{xH} = 0.08384$, while the hybrid PBEmolβ0 has $\mu = \mu_{xH} = 0.27583$ but $\beta = (3/4)\beta_{xH} = 0.06288$.

Note that in either case, with the full β or with β multiplied by 3/4, the homogeneous electron gas limit is recovered, because the gradient terms vanish in this limit, and the exact exchange piece of Eq. (10) becomes equal to the LSD part contained in E_X^{GGA}.

To assess the performance of these five, constraint-based PBE-based hybrids, we have done calculations for the same test sets used for the GGA functionals. The results are reported in Table III, where we have included, for comparison, results from the popular B3LYP hybrid,[9,10,47,51,52] which, as previously mentioned, contains three calibrated parameters. We have also incorporated calculations with the M06-2X hybrid.[75] This empirical hybrid provides a reference for any improvement achieved, since the 32 adjustable parameters that it contains were fixed to minimize the error with respect to the test sets for ionization potentials, electron affinities, proton affinities, binding energies of weakly interacting systems, and the barrier heights for hydrogen and non-hydrogen transfer reactions that we are considering, together with a test set for atomization energies and various other test sets for other properties.

The results indicate that although PBE0, which uses the original parameters of PBE, provides a rather good description of these properties, the predictions of PBEmolβ0 are, except in the case of the ionization potentials, modestly better. Note, particularly, the improvements in the MAEs of the forward and backward hydrogen transfer reactions, and for the bond distances and frequencies. Also, the results for non-empirical PBEmolβ0 are comparable to those of the semi-empirical B3LYP, except for the ionization potentials and the frequencies. A relevant aspect is the fact that, although B3LYP is known to yield a rather good description of molecular geometries, there is a considerable improvement, about 17% reduction in the MAE, in the prediction of bond distances in favor of PBEmolβ0. Perhaps even more interestingly, the heat of formation and ionization potential MAEs for PBEmolβ0 are within a factor of two of the corresponding MAEs from M06-2X, while the PBEmolβ0 MAEs for bond lengths and frequencies are better than those from M06-2X. Considering that M06-2X is heavily parameterized for thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements, this is encouraging progress towards finding the real accuracy level of the hybrid functional rung without empiricism.

In general, the results indicate that the PBEmolβ0 hybrid provides a modest but useful improvement over PBE0 and B3LYP. Since all the parameters in PBEmolβ0 are determined through constraint satisfaction, rather than fitting, it seems to be a strong candidate hybrid functional for general use in the calculation of a wide variety of molecular properties.

With respect to the modification of the gradient contribution to the correlation energy, as an alternative approach[76] to the one given above, one could consider that in a hybrid, in the small gradient limit there are two contributions, one from the GGA exchange portion, and another from the exact exchange portion. Assuming that the latter becomes equal to the gradient expansion approximation in the small gradient limit, Eq. (5) adopts the form

$$F_X^{PBE}(s) \to 1 + \left(\frac{1}{4}\,\mu_{\text{GEA}} + \frac{3}{4}\,\mu_{\text{GGA}}\right) s^2 + \dots, \qquad (11)$$

and using Eq. (6) one finds that $\beta = 3\,((1/4)\mu_{\text{GEA}} + (3/4)\mu_{\text{GGA}})/\pi^2$. Since $\mu_{\text{GEA}} = 10/81$, through this procedure one is led to a parameterization in which $\beta = 0.05942$ for PBEβ0 and $\beta = 0.07226$ for PBEmolβ0. Using these values of β one finds that in the case of PBEβ0, the MAE for the heats of formation is reduced to a value of 7.15 kcal/mol, the MAE for the ionization potentials is reduced to a value of 4.04 kcal/mol, and all the other properties remain basically the same. In the case of PBEmolβ0, the MAE for the heats of formation is increased to a value of 7.90 kcal/mol, the MAE for the ionization potentials is decreased to a value of 4.37 kcal/mol and all the other properties remain basically the same. Thus, at least for the heats of formation it seems that the value of β obtained from the assumption that, in the slowly varying limit, the gradient portion of exchange that enters into Eq. (10) must cancel the gradient portion of correlation, leads to a better description. However, certainly the relationship between β and μ in a hybrid is a matter that requires further studies.

IV. FINAL REMARKS

The study presented in this work is complementary to the development of PBEsol,[39] and to the work of Zhao and Truhlar,[27] in the sense of highlighting the importance of the gradient coefficients μ and β for the PBE-X and C, respectively. The present results indicate that larger values are more appropriate for finite systems, while the PBEsol finding is that lower values are more appropriate for extended ones. Such larger values follow from enforcement of the constraint that the one-electron SIE be corrected for the hydrogen atom. Incorporated through the value of the parameter μ of the PBE functional, and the corresponding modification of the value of β for the cancellation of the gradient terms in the slowly varying limit, this constraint seems to be important to improve the description of molecular properties. Thus, just as PBEsol is recommended for solid state calculations, we recommend PBEmol as the GGA of PBE form for molecular calculations and PBEmolβ0 as the PBE-based non-empirical hybrid XC functional for molecules. As an insight into further improvement in XC functional, we point out that the difference between the PBEmol and PBEmolβ0 parameterizations illustrates that a good stand-alone GGA does not necessarily correspond to the optimal ingredient GGA for a hybrid.

Observe that the self-consistent Kohn-Sham solution for the hydrogen atom, using the PBEmol exchange-correlation functional with a particular basis set, leads to Coulomb and exchange energies that do not fulfill Eqs. (7) and (8), because the electron density obtained is not equal to the exact ground-state electron density, which was the one used to set the value of $\mu_{xH} = 0.27583$. For example, one finds that the sum of the Coulomb and the exchange energies for the Def2-TZVPP basis set is equal to -0.00132 hartree and for the 6-31++G(d,p) basis set is equal to -0.00204 hartree, instead of being equal to zero. This situation implies that an alternative approach to the one presented here, could consist in a basis set dependent PBE functional, in which the value of μ is fixed through Eq. (7) for the electron density that corresponds to a particular basis set. We are at present investigating this aspect.

Finally, we note that, in other work,[29,32] we have given two simple replacement forms for the PBE-X functional. Both of them yield substantial improvement in the MAE of heats of formation. We have under investigation the issue of re-parameterization of those forms with the one-electron SIE correction given here.

Note added in proof. After this manuscript was accepted, we became aware of the work developed in Refs. 77 and 78. In Ref. 77 the authors made use of the asymptotic expansions of the semiclassical neutral atom to derive a non-empirical value of μ equal to 0.260, and fixed β through Eq. (6) for this value of μ. The calculations for the test sets reported in this work for these values of μ and β, keeping $\kappa = 0.804$, lead to a MAE of 10.74 kcal/mol for the heats of formation, which is 1 kcal/mol above the value obtained for PBEmol. The results for all other properties are practically the same. In Ref. 78 the authors performed a two-dimensional scan of the parameters μ and κ, with β fixed through Eq. (6). They found that a larger value of μ leads to a better description of molecular properties, in agreement with our own finding in the present work.

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