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Optimized GGA Functional for Proton Transfer Reactions[†]

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In this article, a modified version of the gradient-corrected BP86 functional is presented. Such a functional, called mBP86, has been obtained by a reparameterization of the Becke's 1988 exchange functional on the activation barriers of selected proton transfer reactions. Whereas standard GGA methods usually underestimate these values, the mBP86 model shows a significant improvement. As a "side effect", several other chemical properties, including atomization and reaction energies, are also better described and are included so that the mBP86 can be considered to be a general improvement over the parent BP86 functional. Next, the proposed approach has been used to simulate proton transfer reaction in malonaldehyde and in the protonated imidazole dimer by first-principles molecular dynamics. These simulations indicate that this modified functional provides energy and structure evolution very close to the popular B3LYP functional. More generally, our results suggest that the mBP86 can be a cheap, yet reliable, alternative for large scale simulation of proton transfer carried out using approaches where the popular hybrid functionals cannot easily be routinely used.

1. Introduction

The quest for better exchange−correlation functionals in the Kohn−Sham (KS) approach to the density functional theory (DFT)[1] has led to models that provide very accurate results for a large number of physicochemical properties. Improved numerical performances have been obtained not only by working on the analytical expression but also by enlarging the number of variables in the functional form well beyond those present in the local or generalized gradient approximations (GGA), that is, the electron density (ρ) and its gradient ($\nabla\rho$). So, for instance, hybrid approaches contain a fraction of Hartree−Fock (HF) exchange, whereas meta-GGA functionals include the kinetic electron density (τ) contribution.

Another important mainstream is the treatment of DFT as a parametrized approach. Here different functionals are mixed, in a judicious way, to obtain the best numerical performances for a defined training set. (See, for instance, refs 2−4). Such an ensemble could be composed of different properties to cover the largest possible spectrum of chemical applications, but thermochemistry (atomization energies, ionization potentials, reaction barriers) still plays a dominant role.

As a matter of fact, all of the most accurate models require the inclusion of contributions (as HF exchange), which are not always easily accessible for all computational approaches or code implementation. For instance, whereas hybrid functionals were already implemented several years ago in codes for periodic systems using localized (Gaussian) basis,[5] they were only recently introduced to approaches based on plane waves.[6] The same holds for first-principles molecular dynamics (MD) approaches, such as the Car−Parrinello dynamics, where the evaluation of exact exchange is computationally very demanding.[7] Finally, it must be also noted that GGA approaches can be significantly faster than hybrids, so that it has been recently suggested that they can also be used to accelerate SCF convergence in time-demanding methods.[8] All of these examples underline the need for a reliable and efficient treatment of exchange and correlation energies at the GGA level, that is, with models based on only the electron density and its gradient.

It is common practice to split any functional into an exchange and a correlation part, the first one giving the largest (about the 90%) contribution of the total exchange−correlation energy. In the panoply of the exchange functionals available in literature, the one proposed by Becke more than 20 years ago is certainly one of the most popular.[9] It is based on a simple expression for the corresponding energy

$$E_X = E_X^{\mathrm{LDA}} - \beta \sum_{\sigma} \int \rho_{\sigma}^{4/3} \frac{x_{\sigma}^2}{1 + \gamma x_{\sigma} \sinh^{-1} x_{\sigma}} \, \mathrm{d}^3 r \tag{1}$$

where x_σ is the ratio $x_\sigma = |\nabla\rho_\rho|/\rho_\sigma^{4/3}$. The values of β and γ are not independent because if the correct behavior of the exchange-energy density, U_x, is required,[10] then γ must be equal to 6β. Albeit this last parameter can be theoretically determined because it corresponds to the second-order expansion coefficient (this expansion is obtained from the truncation of the Svendsen−von Barth[11] expansion), values obtained by fitting procedures provide more accurate numerical results for atoms and molecules, leading to typical β values that are about twice the theoretical value.[12] In particular, β was determined in the original approach using as training set the exact exchange energies of six noble gas atoms. The obtained β value (0.0042) provides excellent results for a wide variety of chemical problems, notably when the B exchange is used with GGA correlation functionals such as that of Perdew (P86)[13] or that developed by Lee, Yang, and Parr[14] (LYP, leading to the well-known BP86 and BLYP approaches, respectively). However other choices for β are possible, especially if a strong theoretical justification is not requested (or searched). For instance, Lee and Zhou[15] used a fitting over all neutral atoms with nuclear charge $Z =$ 1 to 54 and 86, obtaining a β value that differs from Becke's

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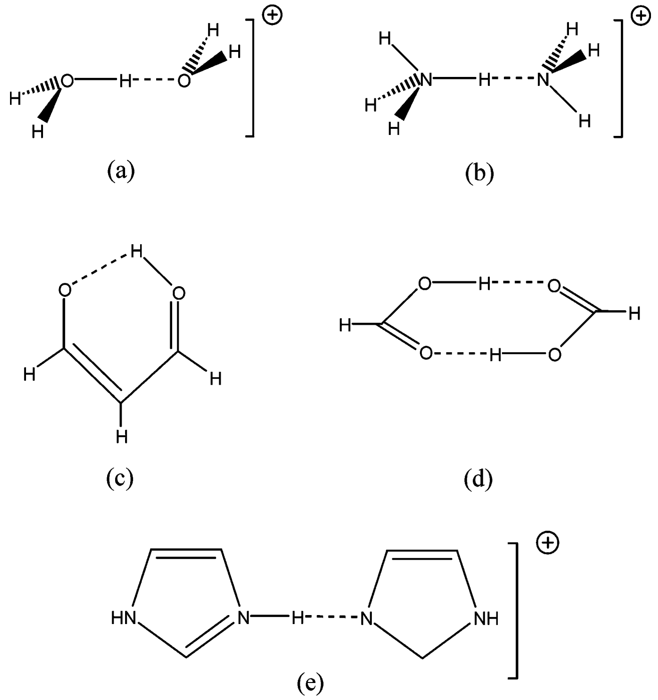

Figure 1. Sketches of the considered molecules: (a) protonated water dimer, $H_5O_2^+$; (b) protonated ammonia dimer, $N_2H_7^+$; (c) malonaldehyde; (d) formic acid dimer; (e) protonated imidazole dimer.

value only in the fifth decimal. On the contrary, Pople and coworkers[4] found a smaller value (0.035) when optimizing an enlarged set including 56 atomization energies, 40 ionization potentials, 25 electron affinities, and 8 proton affinities.

In the past, we have shown that a reparametrization of a given exchange functional on chemical systems or properties could lead to a significant improvement of its numerical performances, even for properties other than those considered in the training sets. This is the case, in particular, for the mPW91 exchange functional,[16] which provides enhanced results for kinetics[17] or of the mPBE approach.[18]

In this article, we propose a reparametrization of the B88 exchange functional by a fitting procedure on selected proton transfer (PT) reactions. Beyond the intrinsic interest in chemical and biological systems, such reactions indeed constitute a severe challenge for DFT methods, which usually provide very low activation energies that are quite far from a realistic description. (See, for instance, refs 19 and 20.) Such a fault can be traced back to the self-interaction error,[21,22] but on one side, corrected methods are expensive or numerically unstable, and on the other, methods working on error compensation, such as hybrid functionals, often require the inclusion of other variables and, therefore, belong to the above-mentioned categories.

Four simple and representative systems have been retained: protonated water ($H_5O_2^+$) and ammonia ($N_2H_7^+$) dimers, malonaldehyde, and formic acid dimer. (See Figure 1.) The obtained modified-B88 (mB) functional, coupled to the common P86 correlation functional, has been then applied to some standard tests concerning atomization energies and kinetics to show its improved performances over the parent approach and its general purpose nature. Finally, first-principles MD calculations, based on the atom-centered density matrix propagation (ADMP) method[23] have been carried on two models systems, namely malonaldehyde and the protonated imidazole dimer. (See Figure 1.) Such a dynamics approach allows for a direct comparison of trajectories and properties obtained with GGA functionals, which are used in the many MD approaches based on plane waves, and those computed with hybrid functionals. Our results show that in these MD simulations, the mBP86 functional provides energy and structure evolutions equivalent to those obtained with the reference B3LYP approach.

2. Computational Details

All of the calculations were performed with a locally modified version of the Gaussian package.[24] DFT calculations have been carried out using the B88 exchange functional in GGA schemes, coupled to the P86 or the LYP correlations, or in hybrid approaches such as B3LYP and B3P86.[25] Some MP2 calculations have been also carried out for PT reactions to obtain reference post-HF values.

First-principles MD simulations have been carried out within the ADMP formalism.[23] Here the fictitious mass of the electron was set to 0.2 amu. We monitored the stability of the simulations by checking at each step the idempotency of the density matrix (within a 10^{-12} a.u. threshold for the rms) and the so-called 'adiabaticity index' (ref 23) within a 10^{-4} threshold. The dynamic simulations were performed with an initial nuclear kinetic energy equal to 600 μhartrees for the PT in malonaldehyde and 200 μhartrees for the imidazole dimer, for a total simulation time equal to 55 fs for the malonaldehyde and 44 fs in the imidazole dimer case. The velocity–Verlet algorithm[26] was employed for the integration of equations of motion using a time step of 0.055 fs for malonaldehyde and 0.040 fs for the imidazole dimer.

Several basis sets have been used, all belonging to the Pople's basis family. For the four PT reactions belonging to the "training set", a double-ζ quality Pople basis set has been used, with polarization functions on all of the atoms and with diffuse functions on all of the non-H atoms, namely, 6-31+G(2d,p). The same basis set was used for all of the ADMP simulations. Atomization energies have been computed using the 6-311+G (3df,2p) basis set, with single-point energy calculations on the geometries used by Pople and coworkers in their systematic study of some thermodynamic properties.[27] For the elementary transformations belonging to Truhlar's B6H[28] and NHTBH38/04[29] databases, the 6-311+G(3df,2p) basis set was also used.

3. Results and Discussion

3.1. Parameterization Set and Static Benchmarks. As mentioned above, four simple systems undergoing PT have been chosen as the training set, namely, $H_5O_2^+$, $N_2H_7^+$, malonaldehyde, and formic acid dimer. Such systems have been largely studied at DFT levels, and it has been shown that the hybrid B3LYP approach provides results close to those obtained with the MP2 model. (See, for instance, refs 19, 30, and 31).

The BP86 mean absolute error (MAE), evaluated with respect to the MP2 values, for the activation energies of the PT reaction as a function of the β parameter in Becke exchange, is reported in Figure 2. From this plot, it clearly appears that the original β value (0.0042) provides a quite large error, the MAE being 4.2 kcal/mol (Table 1), which is higher than the 1.8 kcal/mol given by the reference B3LYP approach. However, lower errors are obtained for a relative large range of β, between 0.0011 and 0.0022, the corresponding MAE varying between 2.2 and 2.5 kcal/mol. Therefore, any value in this interval leads to a significant improvement, giving MAE that is significantly smaller than that obtained with the original parameter (−50%). Of course, other properties could be affected by the choice of β, and a cross check is to reduce the interval. A natural choice

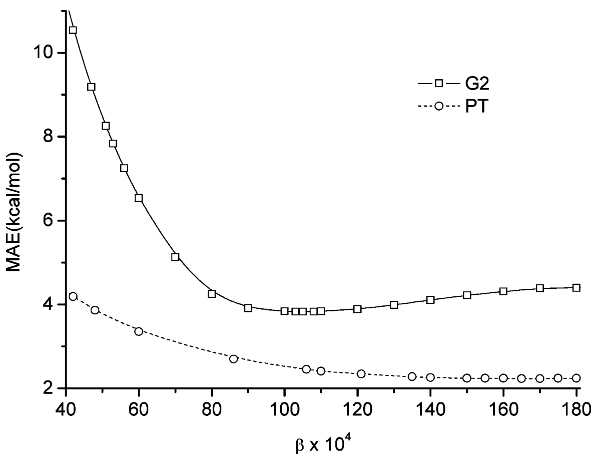

Figure 2. Mean absolute error (MAE, kcal/mol) for proton transfer activation barriers (PT) and atomization energies (G2) as a function of the parameter β in the Becke 88 exchange functional.

TABLE 1: Mean Absolute Errors for the Atomization Energies of the G2-55 and G2-148 Sets (Thermochemistry, kilocalories per mole), Bond Lengths of the G2-32 Set (Structures, angstroms), and Proton Transfer Reactions (PT, kilocalories per mole)

	thermochemistry		structures	
	G2−55	G2−148	G2−32	PT barrier[a]
BP86	10.54	20.16	0.014	4.19 (−4.19)
BLYP	4.70	7.12	0.014	2.97 (−2.97)
mBP86	3.84	7.72	0.010	2.41 (−2.41)
B3P86	7.86	17.72	0.009	2.82 (−2.82)
B3LYP	2.32	3.09	0.007	1.77 (−1.77)

[a] In parentheses are reported the mean signed errors.

is to introduce a second training set composed of the atomization energies of 55 molecules belonging to the G2 set, an ensemble already used in functional testing.[16,27] In this case, the MAE on the computed energy presents a shallow minimum in a closer interval, β ranging between 0.0010 and 0.0011. (See Figure 2.) Balancing the two behaviors, it appears that $\beta = 0.0011$ represents an appropriate compromise between good kinetics for PT, that is, a significant improvement on the activations barriers for PT reactions (that is our main target), and thermodynamics, the G2 results being largely better than the original value. The B88-derived exchange functional using this value will be denoted in the following as modified-Becke (mB).

In Table 1 are reported the results obtained for the thermochemistry, structures, and PT barriers, obtained with five functionals based on the B exchange, namely, BP86, BLYP, mBP86, B3P86, and B3LYP. This latter functional, B3LYP, can be considered to be the reference, and is the most widely used in chemistry and provides the best results on all of the considered cases. As expected, mBP86 provides better results than BP86 for all of these tests, with very significant improvements: the error for PT reactions decreases by 43%, and the errors in the G2 sets are divided by nearly a factor of 3. The mBP86 functional also gives better results than BLYP for PTs (2.4 vs 3.0 kcal/mol) and for the small G2 set. (The error is 22% smaller with respect to BLYP error.) Furthermore, it describes in a more balanced way small and large G2 sets. Surprisingly, mBP86 is also better than the hybrid B3P86 functional by a factor of nearly two, and it is relatively close to the values obtained with B3LYP. As recently suggested,[32,33] these numerical results indicate that, at least for some chemical systems, GGA functionals can work as well (if not better) as hybrid ones, thus filling the gap between different rungs on the Perdew functional ladder.[34]

TABLE 2: Mean Absolute Errors and, In Parentheses, Mean Signed Errors (kilocalories per mole) for the Activation Barriers of Some Simple Reactions

method	H trans[a]	HA trans[b]	uni and assoc[b]
BP86	9.46(−9.46)	15.56(−15.56)	3.95(−3.52)
BLYP	8.00(−8.00)	14.70(−14.70)	3.58(−3.47)
mBP86	6.31(−6.06)	12.69(−12.69)	3.08(−2.74)
B3P86	6.19(−6.19)	9.17(−9.17)	2.87(−1.41)
B3LYP	4.89(4.89)	8.54(−8.54)	2.02(−1.52)

[a] Hydrogen transfer reaction (H trans). [b] Heavy atoms transfer reactions (HA trans) and unimolecular and association reactions (uni and assoc) from the B6H and NHTBH38/04 databases.[29,30]

Because improved energetic are often obtained at the detriment of structural parameters (for instance, ref 35), geometrical optimizations have also been carried on the G2−32 set, a reduced set containing only 32 molecules.[16] Again, mBP86 performs better than BP86 and BLYP, and it is equivalent to B3P86.

Table 2 collects the results obtained for the two benchmark databases for kinetics, recently designed by Truhlar and coworkers (denoted as B6H and NHTB38/04), including hydrogen and heavy-atoms transfers as well as unimolecular and association reactions.[28,29] Also, for these tests, the mBP86 constitutes a significant improvement on BP86 for all of the considered reactions barriers, the errors being reduced by 33% for H transfers, 18% for heavy atoms, and 22% for the unimolecular and association processes. As before, mBP86 is very close to the B3P86 hybrid.

In summary, these benchmarks indicate that mBP86 represents a significant improvement over two of the most common GGA functionals (BP86 and BLYP) and that it could provide results close to, and sometime better than, those obtained with the related B3P86 hybrid functional.

3.2. First-Principles Molecular Dynamics. The main aim of the present article was to define a GGA functional that, albeit through an ad hoc parametrization, could provide accurate simulations for PT reactions. Indeed, the correct reproduction of activation barrier is not, by itself, a guarantee for the proper description of the time evolution of the total energy. Therefore, to assess the mBP86 functional, ADMP simulation has been carried out for PT in malonaldehyde. Such a molecule can be considered to be a challenging system because the motion of the proton is coupled to a rearrangement of the π electronic system. In this case, the underestimation of the activation barrier is augmented by the excessive degree of electronic conjugation in the molecular backbone provided by DFT methods.[19] One of the roles of the HF exchange in the hybrid scheme is precisely to correct this DFT overdelocalization. As a consequence, a hybrid functional such as B3LYP provides accurate activation energies and the overall potential energy surface for PT in such a molecule.[19,31]

The results of the simulations, collected in Figure 3, represent the relative energy (ΔE) evolution from the transition state to the energy minimum. The energy profiles obtained with the five considered functionals have very similar shapes: at first, there is a slight increase in the energy to reach a maximum at $t = 6.5$ fs. Then, a global decrease in the energy occurs, leading to a minimum at slightly different times (between 36.3 and 37.9 fs, Table 3). Afterwards, some fluctuations around this equilibrium point are present, characterized by a succession of small rises and

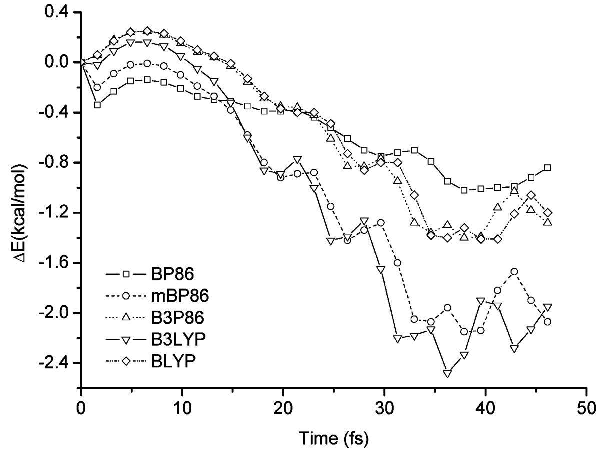

Figure 3. Time evolution of the energy for proton transfer reaction in malonaldehyde during ADMP simulations.

TABLE 3: Energy (ΔE, kilocalories per mole) and Time (t_{min}, femtosecond) of the Minima in the First-Principles Dynamics Simulations of Proton Transfer in Malonaldehyde and Imidazole Dimer

	BP86	BLYP	mBP86	B3P86	B3LYP
malonaldehyde					
t_{min}	37.9	39.6	37.9	37.9	36.3
ΔE	1.02	1.41	2.15	1.40	2.48
protonated imidazole dimer					
t_{min}	0.0	34.0	32.5	32.5	31.0
ΔE	0.0	0.10	0.23	0.06	0.26

decreases in the energy up to the end of the simulation. It is remarkable that the minimum is reached at approximately the same time, independently of the functional used to study the trajectory. However, ΔE values are quite different: BP86 and B3P86 both significantly underestimate the stabilization of the minimum with respect to the saddle point (but B3P86 less than BP86), whereas B3LYP and mBP86 give very close energy evolutions. This last result must be emphasized: the two curves are almost superposed, even if the energy maxima are generally reached 1.6 fs later when mBP86 is used.

To evaluate the transferability of the mBP86 functional, another PT simulation, considering a system not belonging to the training set, was undertaken: the protonated imidazole dimer. (See Figure 1e.) Beyond the intrinsic interest of this system as a model for charge carrier migration in fuel-cell membranes,[36] such a dimer shows a very low activation barrier, as illustrated by the data in Table 3 and the plots in Figure 4. As for malonaldehyde, the MD starting point corresponds to the TS structure, where the transferred proton is shared by two nitrogens of the two imidazole molecules. Such a structure is a minimum at the BP86 level, with the energy increasing along the simulation (up to +0.1 kcal/mol, Figure 4). The inclusion of exact exchange improves the situation, and a shallow energy minimum (ΔE = −0.06 kcal/mol) is obtained at the B3P86 level after 32.5 fs. The mBP86 functional provides, as before, results that are very close to those obtained with the B3LYP functional. Moreover, The B3LYP and mBP86 curves are again almost overlaid and quite different from those provided by the other methods, and both methods give a net minimum of −0.2 kcal/mol. As already discussed in the calibration part, a better energy landscape should not imply a worsening of the structural parameters. The monitoring of the time evolution of crucial bonds confirms the reliability of mBP86. In Figure 5 is reported the evolution of the NH bond for the chosen functionals. Once again, the agreement between mBP86 and B3LYP should be underlined, thus showing that the proposed approach gives a correct energy landscape that is also in zones of the PES far from the minima.

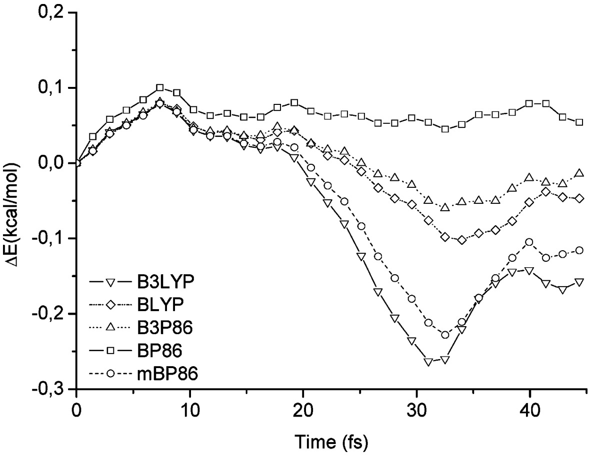

Figure 4. Time evolution of the energy for proton transfer reaction in the protonated imidazole dimer during ADMP simulations.

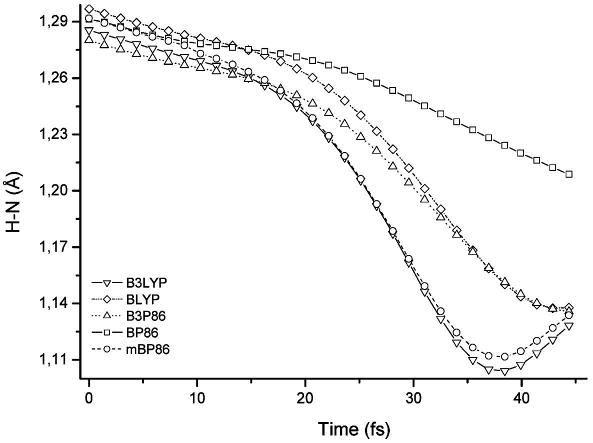

Figure 5. Time evolution of the N−H bond during the proton transfer reaction in the protonated imidazole dimer.

The fact that this last PT reaction does not belong to the original training set prompts us to assume that mBP86 describes such a process intrinsically better than the parent BP86, and it provides results, in terms of both energy and structure, similar to those obtained with the reference B3LYP functional. In other terms, the mBP86 functional represents a cheap yet robust way to improve first-principles MD simulations significantly and reaches higher numerical accuracy in the PES description.

4. Conclusions

This new parametrization of the Becke's 1988 functional, leading to the pure GGA mBP86, gives a significant improvement for the activation barriers of PT reactions. The obtained results are very close to those provided by the B3LYP approach, de facto still the reference in the DFT world. As a "side effect", an amelioration of the thermochemistry for the G2 sets and some kinetic tests has been found so that the mBP86 can be considered to be a general improvement over the parent BP86 functional. Next, the ADMP simulations on malonaldehyde and imidazole dimer have confirmed that mBP86 leads to performances closer to B3LYP, in terms of both energy and structure time evolution. Accordingly, we have designed a pure GGA functional that behaves almost as well as the popular B3LYP hybrid functional within both static and dynamic approaches.

From a more general point of view, there are two major outcomes of this work. First of all, we have shown how through a chemically oriented reparameterization of classical functional better performances could be achieved. Second, the obtained functional, mBP86, is competitive with the hybrid B3LYP approach for the study of PT reactions. The possibility of very easily implementing this new functional in most of the usual codes, even for the ones for which HF exchange is not available, and to use it for first-principles dynamics seems to constitute a more than interesting advantage.

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