

Switching between OPTX and PBE exchange functionals

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Abstract. We report here a study into what causes the dramatic differences between OPBE and PBE for reaction barriers, spin-state energies, hydrogen-bonding and $\pi - \pi$ stacking energies. It is achieved by the implementation of a new functional that switches smoothly from OPBE to PBE at a predefined point P of the reduced density gradient s . By letting the point P run as function of the reduced density gradient s , with values from $s = 0.1$ to $s = 10$, we can determine which part of the exchange functional determines its behavior for the different interactions. Based on the thus obtained results, we have created a new exchange functional that shows the good results of OPBE for reaction barriers and spin-state energies, and combines it with the good respectively reasonable results of PBE for hydrogen-bonding and $\pi - \pi$ stacking. In summary, the new functional combines the best of OPBE with the best of PBE.

1. Introduction

In the past few years, it has been shown [1–6] that early GGA functionals like BP86 [7,8] and the non-empirical PBE [9] are quite reliable in many aspects, but have problems with reaction barriers [10] and spin ground-states of transition metal (TM) complexes [11,12]. Surprisingly enough, these latter problems are dramatically reduced when using the recently developed optimized exchange (OPTX) functional [13] by Handy and Cohen, to give the OPBE functional [14]. In fact, it was very recently [12] shown that this latter functional is the only DFT functional able to correctly predict the spin ground-state for a diverse set of TM complexes. In a recent study [15], we tried to establish what is the origin of this different behavior of e.g. the OPBE vs. the PBE functional, which differ only in their formulation for the exchange energy. In that study, we removed the non-empirical constraints [9] that were imposed on the PBEx functional, and vice versa, imposed them on the OPTX functional. Although our study [15] made it clear that OPTX benefits from not having the constraints imposed, we did not find a rationale for the apparent successes of OPBE for reaction barriers [10] and spin-state energies [12].

Here we report our second attempt for trying to understand the differences in the behavior between the OPBE and PBE functionals by specifically looking at the form of the exchange functional. In particular, we have looked at a number of typical systems (spin-state energies [11,12], S_N2 reaction barriers [10],

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$\pi - \pi$ stacking [16], hydrogen-bonding [2,15]) and investigated which part of the exchange functional is responsible for the differences between OPBE and PBE. In order to do so, we have implemented a new switched functional that goes smoothly from OPTX to the PBEx functional at a predefined point P of the reduced density gradient s , with the use of a switching function (see below). Here we let the point P run from $s = 0.1$ to $s = 10$ atomic units, where s is the usual reduced density gradient ($s = |\nabla\rho|/2\rho k_F$; $k_F^3 = [3\pi^2 \cdot \rho]$). The switching function q_{sw} is taken from the CHARMM force field [17] and is defined as:

$$\begin{aligned} q_{sw} &= 1 & s < a \\ q_{sw} &= \frac{(b+2s-3a)(b-s)^2}{(b-a)^3} & a < s < b \\ q_{sw} &= 0 & s > b \\ a &= P - 0.1 & b &= P + 0.1 \end{aligned}$$

The enhancement factor for the switched exchange functional then has the form:

$$F_{sw}(s) = q_{sw} \cdot F_{OPTX}(s) + (1 - q_{sw}) \cdot F_{PBEx}(s) \quad (1)$$

Therefore, suppose we want to know the energy for the switched functional with $P = 5.0$. This means that up to $s = 4.9$ the enhancement factor is that of OPTX, after $s = 5.1$ it is equal to the PBEx enhancement factor, and inbetween 4.9 and 5.1 it goes smoothly from one to the other. By letting the point P go from 0.1 to 10.0 atomic units, we will obtain a straightforward answer to the question which factor determines the good or bad behavior for e.g. spin-states or reaction barriers.

2. Computational details

All DFT calculations were performed with a locally adapted version of the Amsterdam Density Functional (ADF, version 2006.01) [18,19] program developed by Baerends et al. The MOs were expanded in a large uncontracted set of Slater-type orbitals (TZ2P, QZ4P) [20], which are respectively of triple- ζ quality augmented by two sets of polarization functions, and of quadruple- ζ quality augmented by four sets of polarization functions. An auxiliary set of s , p , d , f , and g STOs was used to fit the molecular density and to represent the Coulomb and exchange potentials accurately in each SCF cycle. All energies were calculated post-SCF on orbitals/densities that were obtained mainly with LDA; the issue of self-consistency was previously found to be negligible (0.1–0.3 kcal·mol⁻¹) [21,22].

3. Results and discussion

We start our inquiry of the differences between OPBE and PBE for the performance for the energy landscapes of bimolecular nucleophilic substitution (S_N2) reactions [23]. We have recently compared DFT functionals with high-level CCSD(T) data from the literature [10], and observed that the most honest comparison could be made for a subset of reactions (**A2–A6** from that paper), where large basis sets were used both in the reference CCSD(T) data and in our DFT data. For this subset, PBE gave an overall performance for the energy (P_E , the average of four mean absolute deviations; see ref. [10] for details) of 4.01 kcal·mol⁻¹, while OPBE performs much better with a value of only 2.12 kcal·mol⁻¹. This reduction results mainly from the deviation for the central barrier, which is ca. twice as small for OPBE as for PBE. Shown in Fig. 1 is the switched functional (see Eqs (1) and (2) above) as function of

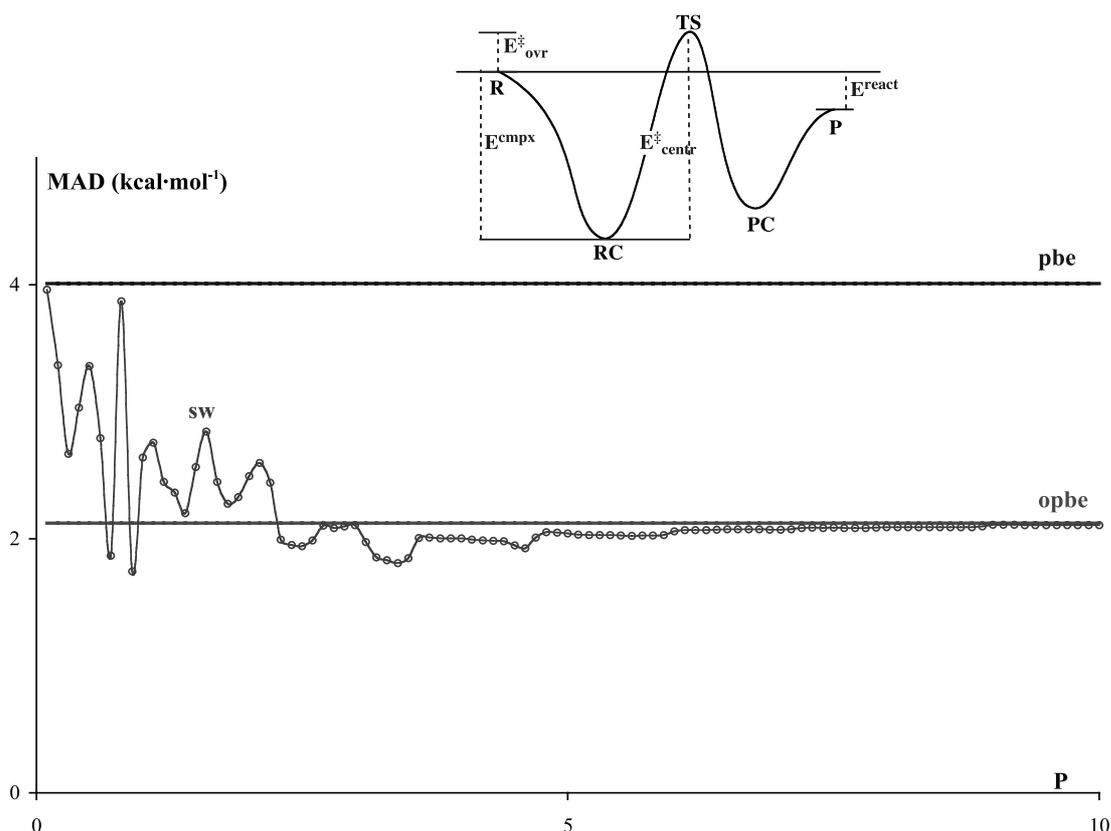


Fig. 1. Switched result for overall performance P_E (mean absolute deviation, $\text{kcal}\cdot\text{mol}^{-1}$) of S_N2 reactions.

point P (the point where the switching takes place). From this figure, it becomes clear that only the part up to $s = 2.5$ is vitally important for the S_N2 reactions. This can be seen as follows. When P equals 2.5 (indicated in the figure with the vertical line), the enhancement factor of the switched functional corresponds to OPBE only up to $s = 2.4$, and to PBE afterwards. Yet its performance is very similar to the OPBE result already, and changes only slightly for larger P values. Large fluctuations are seen for smaller P values, with especially oscillating behavior for $P < 1$.

The same trends can be seen for the central barrier of the S_N2 reactions (see Fig. 2). Interestingly enough, quite low deviations are seen for P values of 0.7 and 0.9, for both the central barrier and the overall performance P_E .

We now turn to spin-state energies [11,12,24], in particular those of the high-spin compound $\text{Fe}(\text{N}(\text{CH}_2\text{-o-C}_6\text{H}_4\text{S})_3)(1\text{-Me-imidazole})$. Experimentally, and with the OPBE functional [11], it has a high-spin sextet ground-state. In contrast, the PBE functional erroneously predicts a low-spin ground-state for this complex [11], already by looking at vertical spin-state energies. E.g., OPBE predicts a vertical ΔE_{LH} splitting of $+12.3 \text{ kcal}\cdot\text{mol}^{-1}$, while PBE gives $-4.4 \text{ kcal}\cdot\text{mol}^{-1}$. The results for the switched functional (see Fig. 3) show that this difference is determined by a very narrow region, i.e. only by the region where $s \leq 1$.

All the rest of the s range seems to be irrelevant for the spin-state energies of PBE and OPBE. This therefore begs the question: is this a general trend or is it typical for only these two systems?

In order to further investigate this, we also looked at hydrogen-bonding (Fig. 4) and $\pi - \pi$ stacking

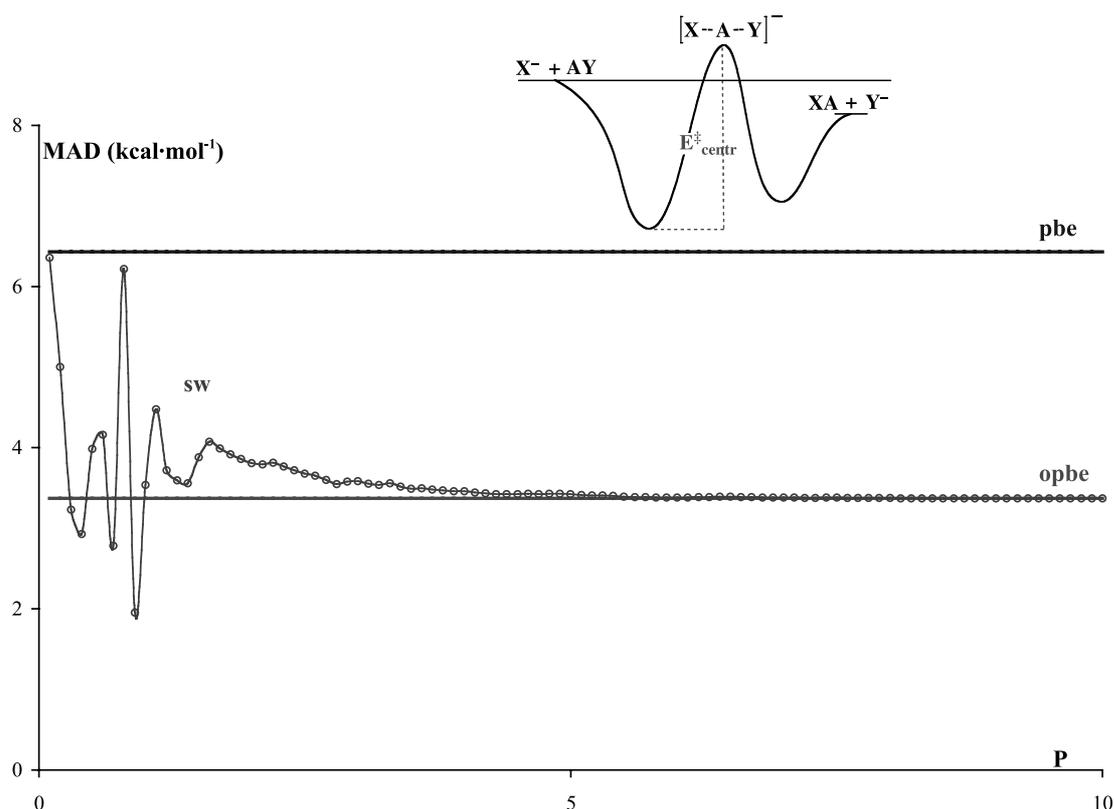


Fig. 2. Switched result for central barrier (mean absolute deviation, $\text{kcal}\cdot\text{mol}^{-1}$) of S_N2 reactions.

(Fig. 5) with the switched functional. For the hydrogen-bonding, we investigated four systems (the dimers of ammonia, water, formic acid, and formamide, where we took the geometry from ref. [25]) but show here only the results for the ammonia dimer; the plots of the switched functional for the other three dimers have different energy scales (e.g. formic acid dimer has an interaction energy of $-18.6 \text{ kcal}\cdot\text{mol}^{-1}$ instead of the -3.2 for the ammonia dimer), but similar trends. For all four cases does the switched result approach the OPBE result at a P value of ca. 5 (see e.g. Fig. 4).

For the $\pi - \pi$ stacking, we looked at the anti-parallel stacked cytosine dimer for which a CCSD(T) energy is available [26] to compare with. Similar as for the hydrogen-bonding, the switched results start to approach the OPBE data at a P value of ca. 5 (see Fig. 5).

From these latter two figures, it is clear that the onset of going from PBE to the OPBE result by the switched functional is later (i.e. at larger P values) than for the S_N2 energy profiles (Fig. 2) or the spin-state energies (Fig. 3). But in this case, this is not particularly bad because OPBE is not performing very well for these weak hydrogen-bonding and $\pi - \pi$ stacking interactions. In fact, OPBE gives repulsive interactions [2,16] while they should be attractive.

Interestingly enough, the results for the switched functional show that for a P value of ca. 0.9, the weak interactions still resemble the good PBE performance. Together with the results already obtained for the S_N2 energy profile and the spin-state energy, we therefore reach the conclusion that it should be possible to create a new functional that:

- gives the same good performance for S_N2 energy profile as OPBE

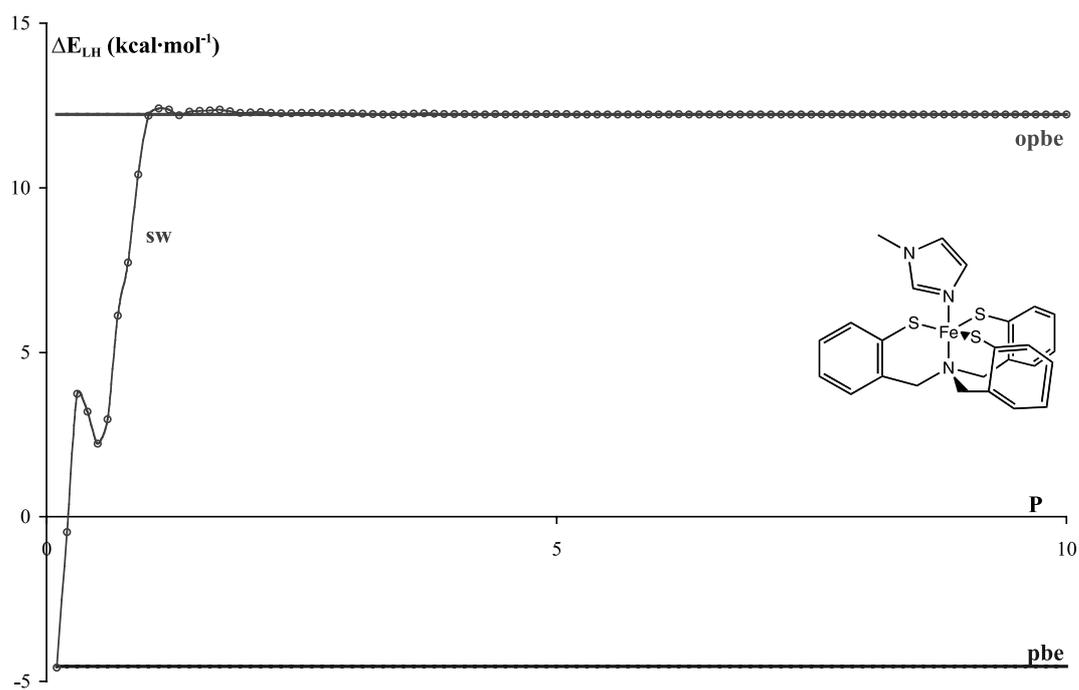


Fig. 3. Spin-state energy ΔE_{LH} ($E_{\text{doub}} - E_{\text{sextet}}$, $\text{kcal}\cdot\text{mol}^{-1}$) for high-spin iron complex.

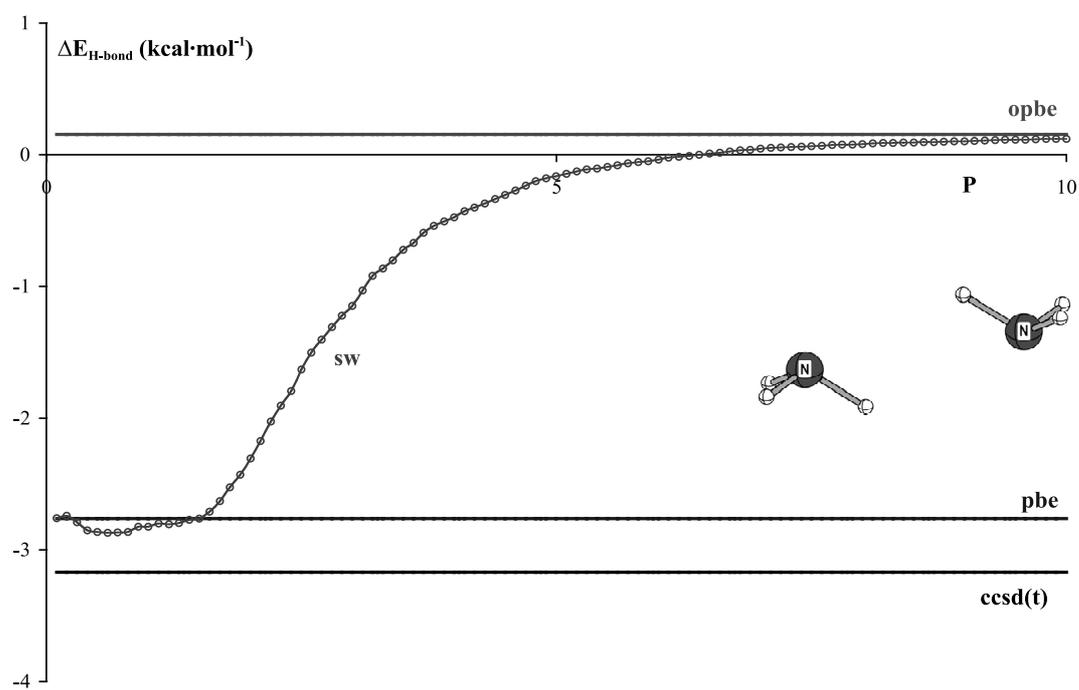


Fig. 4. Hydrogen-bond energy ($\text{kcal}\cdot\text{mol}^{-1}$) for ammonia dimer.

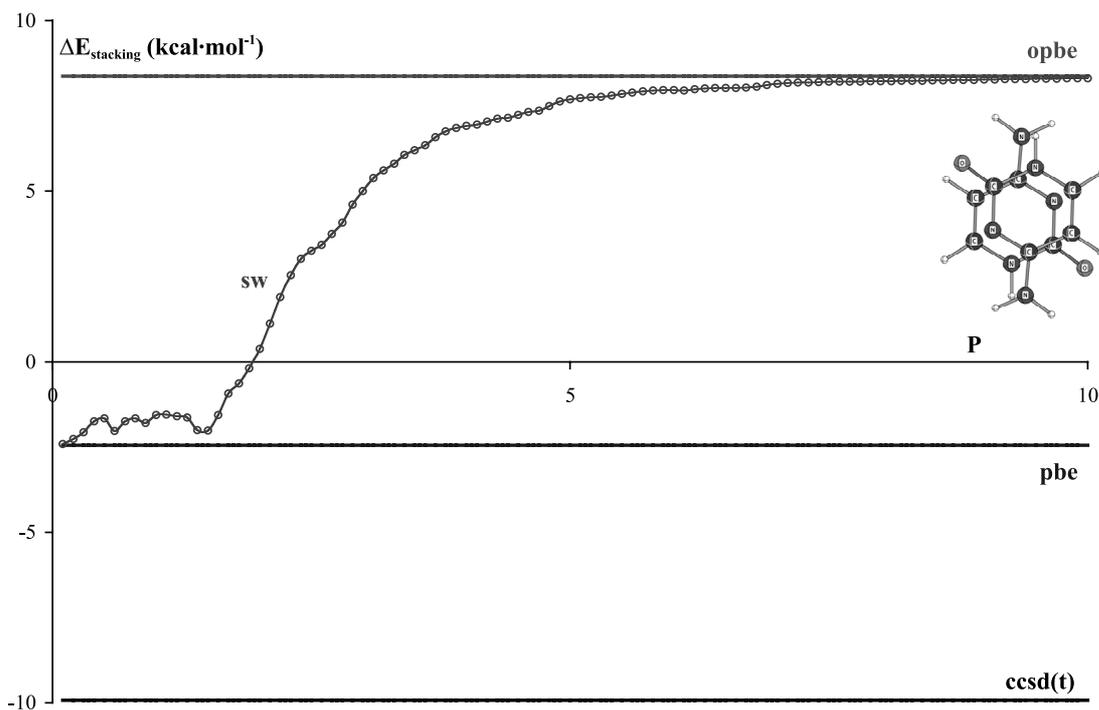


Fig. 5. Stacking energy ($\pi - \pi$, kcal·mol⁻¹) for cytosine dimer.

- gives the same good performance for spin-state energies as OPBE
- gives the same good performance for hydrogen-bonding as PBE
- gives the same reasonable performance for $\pi - \pi$ stacking as PBE

For this new functional, one might simply take the switching function and use it with an appropriate P value (e.g. 0.9) for this new functional. However, even though the switching is smooth, it might still lead to numerical instabilities. It would therefore be better to have an analytical formula that transforms the OPTX formula for small s into the PBE formula for larger s .

Based on the formulations of the enhancement factors and their plot as function of s (see Fig. 6), it should be noticed that the main effect of the OPTX formula is that it provides an almost horizontal profile up to $s \approx 0.5$. The same effect can be obtained by slightly adapting the PBE formulation for the exchange enhancement factor (the original PBE formula [9] has the values $A = 1.0$, $B \approx 0.219515$, $C = B/0.804$, $D = E = 0.0$):

$$F_{new}(s) = A + \frac{Bs^2}{1 + Cs^2} - \frac{Ds^2}{1 + Es^4}$$

For the new functional, the factor A should be equal to that of OPTX (1.05151), the factor C is determined by factors A and B and the Lieb-Oxford bound ($A + B/C = 1.804$) [9], while the factors B , D , and E are free to minimize the difference between F_{new} and F_{optx} ($s \leq 0.7$) and F_{pbex} ($s \geq 0.9$). After minimization, this results then in the following values for the new functional: $A = 1.05151$, $B = 0.191458$, $C = 0.254433$, $D = 0.180708$, $E = 4.036674$. The graphical representation of this new functional is also shown in Fig. 6. With this new functional, the results for the S_N2 energy profile, spin-state energies, hydrogen-bonding energy and $\pi - \pi$ stacking are very promising (see Table 1). I.e.,

Table 1
Performance of DFT functionals for different interactions
(kcal·mol⁻¹)

	CCSD(T)	PBE	OPBE	new
<i>MAD S_N2^a</i>				
ΔE_{react}	0.0	0.34	0.31	0.32
ΔE_{cmpx}	0.0	1.49	3.54	1.61
$\Delta E_{\text{centr}}^{\ddagger}$	0.0	6.43	3.37	3.75
$\Delta E_{\text{ovr}}^{\ddagger}$	0.0	7.78	1.26	4.17
P_E	0.0	4.01	2.12	2.46
<i>Spin-state^b</i>				
ΔE_{LH}	–	–4.40	12.29	9.38
<i>Stacking^c</i>				
ΔE_{int}	–9.93	–2.45	+8.38	–1.67
<i>H-bonding^d</i>				
ammonia	–3.17	–2.76	+0.15	–2.82
water	–5.02	–4.85	–1.52	–4.89
formic acid	–18.61	–18.23	–10.82	–18.52
Formamide	–15.96	–14.79	–7.82	–15.06

a) mean absolute deviations (MAD) for energy profiles of S_N2 reactions (see ref. [10] for details); b) vertical spin-state energy for high-spin state compound (see text and ref. [11]), no CCSD(T) energy available to compare with; c) $\pi - \pi$ stacking energy for anti-parallel cytosine dimer, CCSD(T) value and geometry taken from ref. [26]; d) hydrogen-bonding interactions for dimers, reference CCSD(T) energy and geometries taken from ref. [25].

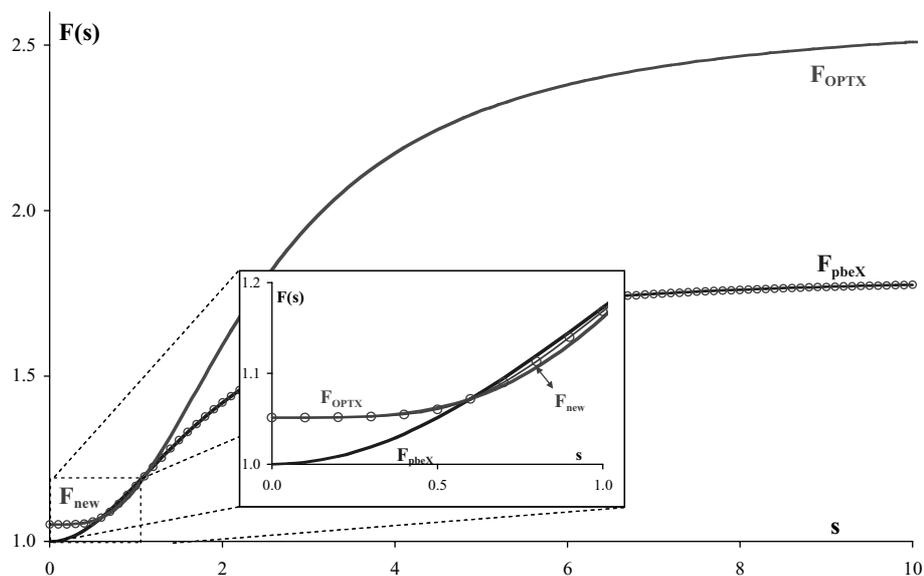


Fig. 6. Enhancement factors for OPTX, PBE and new functional.

the new functional retains all of the good behavior of OPBE (barriers, spin-state) and PBE (H-bonds), and does not suffer from their bad performances. We are currently in the process of optimizing the abovementioned parameters for further improvement of these results.

4. Conclusions

Based on switching between the OPBE and PBE functionals, we have identified which regions of the exchange formulations are responsible for the different performance of these functionals for a number of different interactions. It was shown that by switching between OPBE and PBE at around $s \approx 1$, we might obtain a new and improved functional that would combine the good qualities of the two functionals. Based on this result, we have proposed a small correction of the PBE exchange formulation that mimics the effect of the OPTX functional at small values of s . This small correction indeed functions very well for all interactions studied here, i.e. the energy profiles of S_N2 reaction, spin-state energies of iron complexes, hydrogen bonding interactions and $\pi - \pi$ stacking energies. That is, we have created a new functional that combines the best of OPBE and PBE.

Acknowledgments

We thank the HPC-Europa program of the European Union, the Netherlands Organization for Scientific Research (NWO), and the Spanish MEC (project nrs. CTQ2005-08797-C02-01/BQU, CTQ2008-03077/BQU and CTQ2008-06532/BQU) for financial support.

References

- [1] M. Swart, C. Fonseca Guerra and F.M. Bickelhaupt, *J Am Chem Soc* **126** (2004), 16718.
- [2] T. van der Wijst, C. Fonseca Guerra, M. Swart and F.M. Bickelhaupt, *Chem Phys Lett* **426** (2006), 415.
- [3] C. Fonseca Guerra and F.M. Bickelhaupt, *Angew Chem Int Ed* **38** (1999), 2942.
- [4] C. Fonseca Guerra, F.M. Bickelhaupt, J.G. Snijders and E.J. Baerends, *Chem -Eur J* **5** (1999), 3581.
- [5] C. Fonseca Guerra, F.M. Bickelhaupt, J.G. Snijders and E.J. Baerends, *J Am Chem Soc* **122** (2000), 4117.
- [6] F.M. Bickelhaupt and E.J. Baerends, in: *Reviews in Computational Chemistry*, (Vol. 15), Wiley-VCH: New York, 2000, p. 1.
- [7] A.D. Becke, *Phys Rev A* **38** (1988), 3098.
- [8] J.P. Perdew, *Phys Rev B* **33** (1986), 8822.
- [9] J.P. Perdew, K. Burke and M. Ernzerhof, *Phys Rev Lett* **77** (1996), 3865.
- [10] M. Swart, M. Solà and F.M. Bickelhaupt, *J Comput Chem* **28** (2007), 1551.
- [11] M. Swart, A.R. Groenhof, A.W. Ehlers and K. Lammertsma, *J Phys Chem A* **108** (2004), 5479.
- [12] M. Swart, *J Chem Theor Comp* **4** (2008), 2057.
- [13] N.C. Handy and A.J. Cohen, *Molec Phys* **99** (2001), 403.
- [14] M. Swart, A.W. Ehlers and K. Lammertsma, *Molec Phys* **102** (2004), 2467.
- [15] M. Swart, M. Solà and F.M. Bickelhaupt, in: *Handbook of Computational Chemistry Research*, F. Columbus, ed., Nova Science: Hauppauge, USA, 2009, accepted.
- [16] M. Swart, T. van der Wijst, C. Fonseca Guerra and F.M. Bickelhaupt, *J Mol Model* **13** (2007), 1245.
- [17] B.R. Brooks, R.E. Brucoleri, B.D. Olafson, D.J. States, S.J. Swaminathan and M. Karplus, *J Comput Chem* **4** (1983), 187.
- [18] E.J. Baerends, J. Autschbach, A. Bérces, F.M. Bickelhaupt, C. Bo, P.L. de Boeij, P.M. Boerrigter, L. Cavallo, D.P. Chong, L. Deng, R.M. Dickson, D.E. Ellis, L. Fan, T.H. Fischer, C. Fonseca Guerra, S.J.A. van Gisbergen, J.A. Groeneveld, O.V. Gritsenko, M. Grüning, F.E. Harris, P. van den Hoek, C.R. Jacob, H. Jacobsen, L. Jensen, G. van Kessel, F. Kootstra, E. van Lenthe, D.A. McCormack, A. Michalak, J. Neugebauer, V.P. Osinga, S. Patchkovskii, P.H.T. Philipsen, D. Post, C.C. Pye, W. Ravenek, P. Ros, P.R.T. Schipper, G. Schreckenbach, J.G. Snijders, M. Solà, M. Swart, D. Swerhone, G. te Velde, P. Vernooijs, L. Versluis, L. Visscher, O. Visser, F. Wang, T.A. Wesolowski, E. van Wezenbeek, G. Wiesenekker, S.K. Wolff, T.K. Woo, A.L. Yakovlev and T. Ziegler, ADF 2006.01; SCM: Amsterdam, The Netherlands, 2006.
- [19] G. te Velde, F.M. Bickelhaupt, E.J. Baerends, C. Fonseca Guerra, S.J.A. van Gisbergen, J.G. Snijders and T. Ziegler, *J Comput Chem* **22** (2001), 931.
- [20] E. van Lenthe and E.J. Baerends, *J Comput Chem* **24** (2003), 1142.
- [21] G.T. de Jong, D.P. Geerke, A. Diefenbach and F.M. Bickelhaupt, *Chem Phys* **313** (2005), 261.

- [22] G.T. de Jong, D.P. Geerke, A. Diefenbach, M. Solà and F.M. Bickelhaupt, *J Comput Chem* **26** (2005), 1006.
- [23] S. Shaik, H.B. Schlegel and S. Wolfe, *Theoretical aspects of physical organic chemistry: the S_N2 reaction*, Wiley: New York, 1992.
- [24] M. Güell, J.M. Luis, M. Solà and M. Swart, *J Phys Chem A* **112** (2008), 6384.
- [25] P. Jurecka, J. Sponer, J. Cerny and P. Hobza, *Phys Chem Chem Phys* **8** (2006), 1985.
- [26] P. Jurecka, J. Sponer and P. Hobza, *J Phys Chem B* **108** (2004), 5466.