

# Analysis of the effect of changing the $a_0$ parameter of the Becke3-LYP hybrid functional on the transition state geometries and energy barriers in a series of prototypical reactions

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A series of eleven gas-phase chemical reactions have been examined to assess the dependence of transition state geometries and energy barriers, as well as energy differences between reactants and products, on the  $a_0$  B3LYP functional parameter. Throughout the study we have changed the  $a_0$  parameter from 0.1 to 0.9 and for the  $a_c$  and  $a_x$  parameters we have followed the relationships  $a_x = 1 - a_0$  and  $a_c = a_x$ . By comparing with the QCISD transition state geometries and energy barriers, our systematic study allows us to identify the influence of the  $a_0$  parameter in the reactions studied. In general, B3LYP calculations with the original parameters underestimate energy barriers, this trend being corrected when the  $a_0$  parameter increases. Our study also shows that the fraction of Hartree–Fock exchange needed to predict accurate barrier heights differs from the optimal fraction needed to predict thermochemical properties and geometries.

## 1. Introduction

Quantum chemistry has developed into a powerful, must-have tool for penetrating the complexities of reaction mechanisms. Among the different methodologies available to quantum chemists, density functional theory (DFT)<sup>1–5</sup> within the Kohn and Sham formulation<sup>3</sup> has become increasingly popular in the last decade for the study of chemical reactions.<sup>6–22</sup> It has been demonstrated that the gradient corrected exchange and correlation functionals in DFT [the so-called generalized gradient approximation (GGA)<sup>23–25</sup>] give results with comparable and frequently even higher accuracy than *ab initio* calculations in the study of chemical reactivity.<sup>7,9,10,15–22</sup> Even more accurate results can usually be achieved using hybrid functionals.<sup>9,12,14,18,20–22</sup> These hybrid methods based on the adiabatic connection formula<sup>26</sup> combine, in variable proportions, local and gradient corrected exchange and correlation functionals with the exact Hartree–Fock (HF) exchange.

Currently, a widely used hybrid scheme for the exchange–correlation functional is Becke’s three-parameter method, which was originally formulated as:<sup>27</sup>

$$E_{XC} = E_X^{LSDA} + a_0(E_X^{\text{exact}} - E_X^{LSDA}) + a_x \Delta E_X^{\text{B88}} + a_c \Delta E_C^{\text{PW91}}, \quad (1)$$

the  $E_X^{\text{exact}}$ ,  $E_X^{LSDA}$ ,  $\Delta E_X^{\text{B88}}$ , and  $\Delta E_C^{\text{PW91}}$  terms being the HF exchange energy based on Kohn–Sham orbitals, the uniform electron gas exchange–correlation energy, Becke’s 1988 gradient correction for exchange,<sup>23</sup> and the 1991 Perdew and Wang’s gradient correction to correlation,<sup>28</sup> respectively. Commonly, this procedure is referred to as the B3PW91 method. The coefficients  $a_0$ ,  $a_x$ , and  $a_c$  were determined by Becke<sup>27</sup> by a linear least-squares fit to 56 experimental atomi-

zation energies, 42 ionization potentials, and 8 proton affinities. The values thus obtained were  $a_0 = 0.20$ ,  $a_x = 0.72$ , and  $a_c = 0.81$ . The so-called B3LYP functional is probably even more popular than the B3PW91 method. In the Gaussian 98<sup>29</sup> implementation, the expression used is similar to eqn. (1) with some minor differences:<sup>30</sup>

$$E_{XC} = E_X^{LSDA} + a_0(E_X^{\text{exact}} - E_X^{LSDA}) + a_x \Delta E_X^{\text{B88}} + E_C^{\text{VWN}} + a_c(\Delta E_C^{\text{LYP}} - E_C^{\text{VWN}}). \quad (2)$$

In this equation, Perdew and Wang’s correlation functional originally used by Becke is replaced by the Lee–Yang–Parr (LYP)<sup>24</sup> one. Since the LYP functional already contains a local part and a gradient correction, one has to remove the local part to obtain a coherent implementation. This can be done in an approximate way by subtracting  $E_C^{\text{VWN}}$  from  $\Delta E_C^{\text{LYP}}$ . Note that in the Gaussian 98 implementation the VWN functional is the one derived by Vosko *et al.* from a fit to the random phase approximation<sup>31</sup> results.

The B3LYP method has normally been used with the same three parameters derived originally for the B3PW91 functional. However, some authors have already explored the possibility of changing the values originally derived by Becke to improve the results for a particular property or class of molecules. Latajka and coworkers<sup>32</sup> were the first who proposed to change the  $a_0$  parameter from 0.20 to 0.35 in the B3P86<sup>27,33</sup> functional to better describe the structural properties of hydrogen-bonded complexes. Later, it was reported<sup>34</sup> that a more accurate infrared signature of these hydrogen-bonded systems can be achieved by using the parameters  $a_0 = 0.322$ ,  $a_x = 1$ , and  $a_c = 0.67$ . On the other hand, Chermette *et al.*<sup>35</sup> carried out a specific parametrization of the B3LYP functional for  $H_{2n+1}^+$  clusters using the  $H_5^+$  system as reference. The  $a_0 = 0.559$  and  $a_x = 0.493$  ( $a_c$  was fixed to 1.0) parameters in eqn. (2) give the B3LYP geometry that better matches a

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coupled cluster with single, double and noniterative estimation of triple substitutions, (CCSD(T)), optimized structure of this  $\text{H}_5^+$  cluster.

More recently, Abu-Awwad and Politzer<sup>36</sup> analyzed 12 parameter combinations of the B3LYP coefficients to find a parameter set (PS) that provides orbital energies that can be taken as reasonable approximations to the ionization potentials. They concluded that, despite the fact that there is no single parameter combination that can be identified as the optimum,  $a_0 = 0.4$  seems to be the best option to get accurate ionization potentials. Further, Csonka and coworkers,<sup>37</sup> by analyzing the influence of the three parameters of the B3LYP method on the H–H equilibrium bond length, concluded that the experimental H–H distance could be reproduced with appropriate selection of these parameters, although an infinite number of solutions exist.

Finally, it is worth noting that the B3LYP hybrid functional has been recently reparametrized for a series of small molecules to reproduce high-level *ab initio* densities by means of quantum molecular similarity techniques.<sup>38,39</sup> The authors concluded that the three Becke parameters are not universal, different molecules having quite different optimum parameters. However, for most molecules the optimum parameters governing the amount of gradient corrections for exchange and correlation have similar values ( $a_c \approx a_x$ ), while the optimum  $a_0$  and  $a_x$  are related through the expression  $a_0 \approx 1 - a_x$ , *i.e.*, the larger the exact exchange included, the smaller the GGA exchange correction needed.

A number of workers have examined transition states (TS) in different chemical reactions using DFT.<sup>6–22</sup> These studies have outlined the need for using GGA functionals for accurate transition state calculations.<sup>7,9,10,15–22</sup> Moreover, these and additional<sup>12,40</sup> works have shown that, as a general trend, the HF barriers are usually too high and the DFT ones are somewhat underestimated, particularly those involving radical reactions. Hybrid functionals combining DFT treatments of exchange and correlation with HF exchange usually lead to better results, probably due to cancellation of errors.<sup>9,12,14,18,20–22,41</sup> Indeed, for the simple  $\text{H} + \text{H}_2 \rightarrow \text{H}_2 + \text{H}$  reaction, increasing the fraction of exact HF exchange in hybrid schemes (as in the B3(H) method,<sup>35</sup> with  $a_0 = 0.559$ ,  $a_x = 0.493$  and  $a_c = 1$ , or in Becke's half-and-half<sup>42</sup> linear interpolation of the adiabatic connection integral (BH&HLYP)<sup>14,35</sup> with  $a_0 = 0.5$ ,  $a_x = 0.5$ , and  $a_c = 1$ ) leads to a considerable improvement in the energy barrier. Moreover, Durant<sup>14</sup> found, for a series of seven reactions involving a small number of atoms, that the performance of the BH&HLYP functional is the best in calculating energy barriers when compared to other hybrid functionals with smaller  $a_0$  parameter that systematically underestimate the barriers. Likewise, preliminary results by Jursic point out that a better agreement with experimental barriers is obtained by increasing the  $a_0$  parameter.<sup>21</sup> More recently, Truhlar *et al.*<sup>22</sup> have studied a variety of hybrid DFT methods to determine how accurately these hybrid DFT methods predict some saddle point geometries and reaction barrier heights. They<sup>22</sup> have concluded that the MPW1K hybrid density functional, derived from the mPW1PW91 ( $a_0 = 0.25$ ), is the most accurate functional for the studied reactions.

Therefore, these findings seem to indicate that the  $a_0$  parameter, which reflects how much exact exchange should be included in the description of a particular system, is crucial in the calculation of the energy barrier.<sup>15</sup> To study this issue further, we have undertaken a systematic study of the effect of the  $a_0$  parameter on the transition state geometries and energy barriers for eleven widely studied chemical reactions, representative of some important classes of reactions. The results have been compared with the HF and the singles and doubles quadratic configuration interaction (QCISD)<sup>43</sup> transition state geometries and energy barriers.

## 2. Method of calculation

We have performed all calculations discussed below on eleven chemical reactions for all species involved (reactants, transition states, and products) with the Gaussian 98 set of programs.<sup>29</sup> Full geometry optimizations with no symmetry restrictions have been performed for all species. We have confirmed that the correct minima or saddle points at the potential energy hypersurface (PES) were found by making sure that all reactant and product optimized geometries have no corresponding negative Hessian matrix eigenvalues, while our TS were indeed found to possess a single negative eigenvalue.

### Density functional calculations

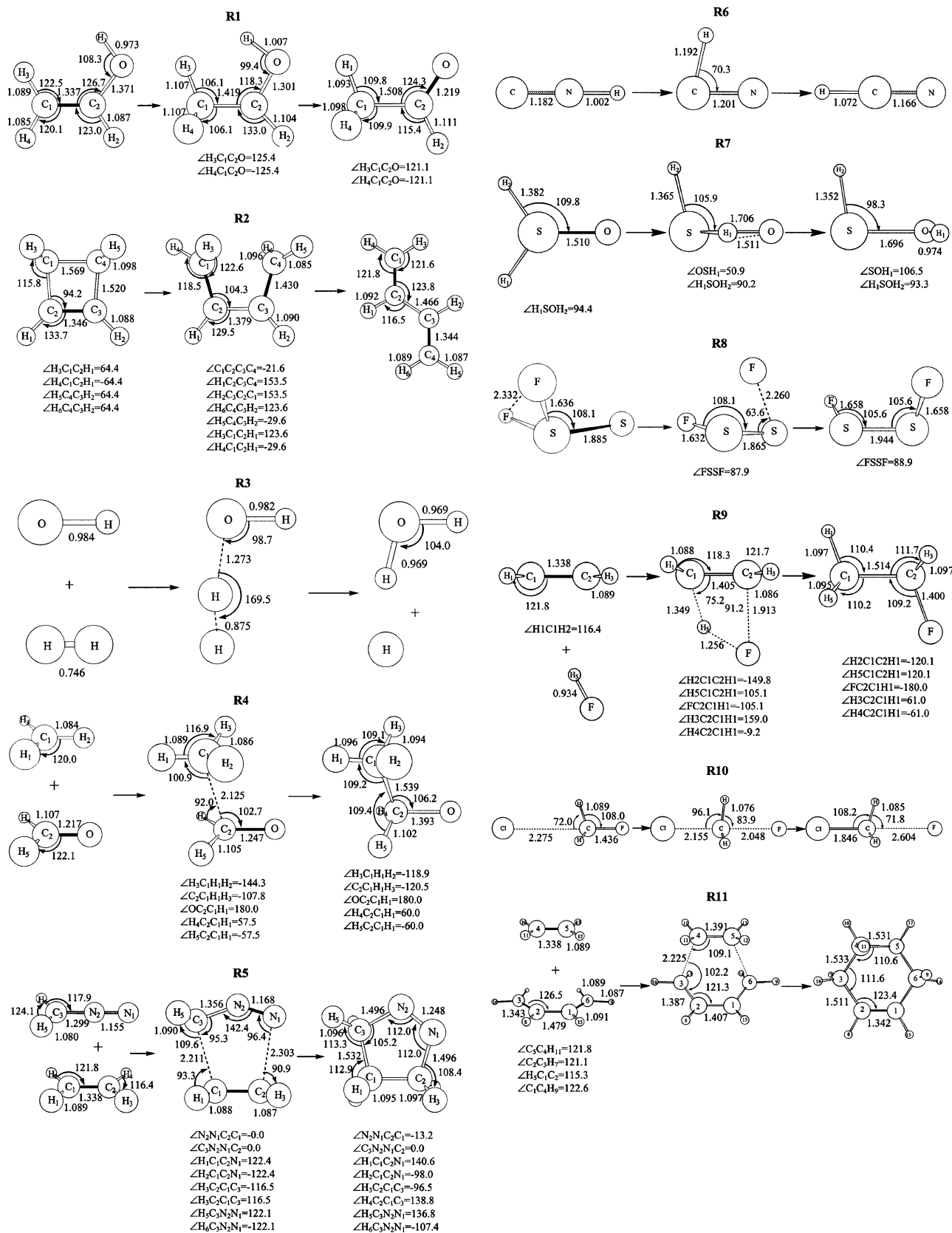
Becke's three parameter functional B3LYP,<sup>27,30</sup> as given by eqn. (2), was employed throughout our DFT calculations. Large integration grids were used to minimize the sensitivity of calculations on the grid size. We have made use of the Gaussian 98 program feature that allows one to vary the B3LYP standard Becke's PS through internal options.<sup>44</sup> In Table 1, we show the different PSs  $\{a_0, a_x, a_c\}$  employed. PS number one corresponds to Becke's original B3LYP parameter values.<sup>27</sup> The other sets are dependent on the chosen values for  $a_0$ , which were varied by 0.100 increments in the interval  $0.100 \leq a_0 \leq 0.900$ , with fixed  $a_x = 1 - a_0$  and  $a_c = a_x$ . The  $a_x = 1 - a_0$  relationship has already been used in some hybrid functionals<sup>45,46</sup> such as the recent B1 method,<sup>46</sup> that in addition takes  $a_c = 1$  and  $a_0 = 0.16$  or 0.28 depending on the choice of the GGA. We also found in previous reports<sup>38,39</sup> that the  $a_x = 1 - a_0$  and  $a_c = a_x$  relations between the B3LYP parameters are, on average, the optimal ones to minimize the difference between the actual B3LYP density and the QCISD one in a series of small molecules, and for this reason the  $a_x = 1 - a_0$  and  $a_c = a_x$  relationships will be maintained throughout this work. However, neither the choice that we have employed here nor other possible alternative relations among the three parameters should be considered as universal.<sup>39,45</sup>

### Ab initio calculations

To compare with the different PS-B3LYP calculations, we have performed HF and QCISD *ab initio* calculations for all species, employing the same basis set throughout (see below). As discussed in the Introduction, the HF energy barriers are usually too high (as compared to QCISD or experimental values), while B3LYP (with Becke's original PS) tend to be too low. We would expect to find a compromise in the PS values (since the  $a_0$  parameter controls how much exact HF exchange is included) and underscore whether the B3LYP hybrid functional with a specific PS may reproduce QCISD quality results for these reactions, but with a fraction of the computational cost.

**Table 1** Parameter sets employed for the B3LYP calculations. The parameter set 1 corresponds to the original Becke3-LYP parameter set<sup>27</sup>

Parameter set	$a_0$	$a_x$	$a_c$
1	0.200	0.720	0.810
2	0.100	0.900	0.900
3	0.200	0.800	0.800
4	0.300	0.700	0.700
5	0.400	0.600	0.600
6	0.500	0.500	0.500
7	0.600	0.400	0.400
8	0.700	0.300	0.300
9	0.800	0.200	0.200
10	0.900	0.100	0.100



**Fig. 1** The eleven chemical reactions studied in this work, with their labeling scheme (R1,R2,...,R11) and the QCISD/6-31G\* optimized geometries for all reactants, transition states, and products, except for R10 where the 6-31+G\* basis set was employed. Distances and angles are given in Å and degrees, respectively.

### Basis sets

In all calculations, both DFT (B3LYP) and *ab initio* (HF and QCISD), the chosen basis set was the 6-31G\* polarization-function augmented split-valence basis set.<sup>47</sup> Polarization func-

tions are especially needed to correctly describe polar neutral molecules and diffuse functions when charges and/or long-range interactions are present. Therefore, this basis set was employed throughout this work, except in reaction (R10), where, since anionic species are involved, we augmented the

**Table 2** Activation barriers (kcal mol<sup>-1</sup>) for each reaction at the B3LYP/6-31G\* level of calculation, considering the different parameter sets, at the HF/6-31G\* level, and at the QCISD/6-31G\* level. For R3, values in parentheses correspond to the activation barriers calculated at the same levels of theory but with the 6-311++G(3df,3pd) basis set

Parameter set	Reaction										
	1	2 <sup>a</sup>	3 <sup>b</sup>	4	5 <sup>c</sup>	6	7	8	9	10 <sup>d</sup>	11 <sup>e</sup>
1	65.1	35.6	3.2 (0.9)	1.5	14.3	33.4	41.9	50.6	36.1	0.3	18.5
2	63.9	33.2	2.1 (0.1)	1.4	14.2	32.5	40.4	47.0	34.6	0.0	18.8
3	65.4	35.2	4.8 (2.3)	2.5	15.8	33.5	42.1	50.0	37.7	0.3	20.7
4	66.8	37.1	7.5 (4.7)	3.4	17.5	34.5	43.8	53.0	40.6	0.9	22.7
5	68.0	39.1	10.2 (7.1)	4.2	19.1	35.5	45.5	56.1	43.3	1.6	24.7
6	69.0	41.0	12.8 (9.6)	4.9	20.7	36.6	47.4	59.2	45.7	2.2	26.6
7	69.9	42.8	15.3 (12.0)	5.4	22.4	37.6	49.2	62.3	47.9	2.8	28.5
8	70.7	44.7	17.7 (14.4)	5.9	24.0	38.7	51.2	65.4	49.9	3.3	30.4
9	71.4	46.6	20.1 (16.7)	6.2	25.7	39.8	53.1	68.4	51.7	3.7	32.3
10	72.0	48.4	22.4 (19.0)	6.4	27.4	40.9	55.1	71.3	53.2	4.1	34.1
HF	69.8	46.9	26.7 (23.7)	8.9	32.2	39.8	53.8	72.5	57.1	3.0	41.1
QCISD	70.1	39.4	12.9 (7.0)	7.0	18.0	34.7	42.8	52.3	47.7	5.0	26.5

<sup>a</sup> Experimental activation barrier is 32.9 kcal mol<sup>-1</sup>.<sup>20</sup> <sup>b</sup> Experimental activation barrier is 4.0 ± 0.3 kcal mol<sup>-1</sup>.<sup>21</sup> <sup>c</sup> CCSD(T)/6-31G\*//QCISD/6-31G\* energy barrier is 13.8 kcal mol<sup>-1</sup>.<sup>62</sup> <sup>d</sup> For this reaction, diffuse functions were used (6-31+G\*). <sup>e</sup> Experimental activation barriers are 23.6<sup>20</sup> and 25.1 ± 2<sup>21,41a</sup> kcal mol<sup>-1</sup>.

basis with diffuse functions, *i.e.*, the 6-31+G\* basis set was employed there. These basis sets are well known<sup>48</sup> to provide adequate numerical precision for the calculation of geometrical parameters and energetics of the chemical species studied here. Furthermore, several authors have found a small dependence of calculated B3LYP barrier heights and transition state geometries on the basis set size.<sup>11,14,19</sup> So, in our opinion the conclusions reached using the 6-31G\* should not be altered significantly by the use of larger basis sets.<sup>22</sup> Nevertheless, in order to check this last statement, the energy barrier and energy difference of one of the reactions studied (R3) have been calculated employing the 6-311++G(3df,3pd) basis set.<sup>48</sup>

### 3. Results and discussion

We assess the dependence on the different B3LYP PSs of some features of the PES, such as energy differences between reactants and products and energy barriers between reactants and transition states, of eleven prototypical chemical reactions, chosen from a sample of representative classes of chemical reactions. These reactions, with their labeling scheme (R1, R2, ..., R11) and their QCISD/6-31G\* optimized geometries for reactants, TS, and products are shown in Fig. 1.

In all these reactions, the reactants and products were arbitrarily defined so that the reactions are always exothermic. Under this criterion, the TS tends to have reactant-like character.<sup>49</sup> These reactions were also chosen since there are previous studies on them (see references for each reaction), although here we compare with our own computed HF and QCISD results. Hence we have the following reactions grouped by classes:

(a) Tautomerism reaction (R1: Vinyl alcohol conversion to acetaldehyde)<sup>12,50–53</sup>

(b) Electrocyclic ring-opening TS (R2: Cyclobutene conversion to *trans*-buta-1,3-diene)<sup>12,20,21,54–59</sup>

(c) Radical reactions (R3: OH + H<sub>2</sub> → H<sub>2</sub>O + H),<sup>12,21,22,60</sup> (R4: Formaldehyde plus methyl radical converted to ethoxyl radical)<sup>12</sup>

(d) 1,3-dipolar cycloaddition (R5: Diazomethane plus ethylene cycloaddition)<sup>61–64</sup>

(e) Intramolecular rearrangements (R6: HNC → HCN),<sup>6,7,9,21,49,65–68</sup> (R7: Thioxonium ylide conversion to

hydrogen thioperoxide, H<sub>2</sub>SO → HSOH),<sup>9,49,65,69</sup> (R8: Difluoride thiosulfoxide rearrangement to difluoride disulfide, F<sub>2</sub>SS → FSSF)<sup>9,49,70</sup>

(f) Electrophilic addition (R9: HF + C<sub>2</sub>H<sub>4</sub> → C<sub>2</sub>H<sub>5</sub>F)<sup>65,71,72</sup>

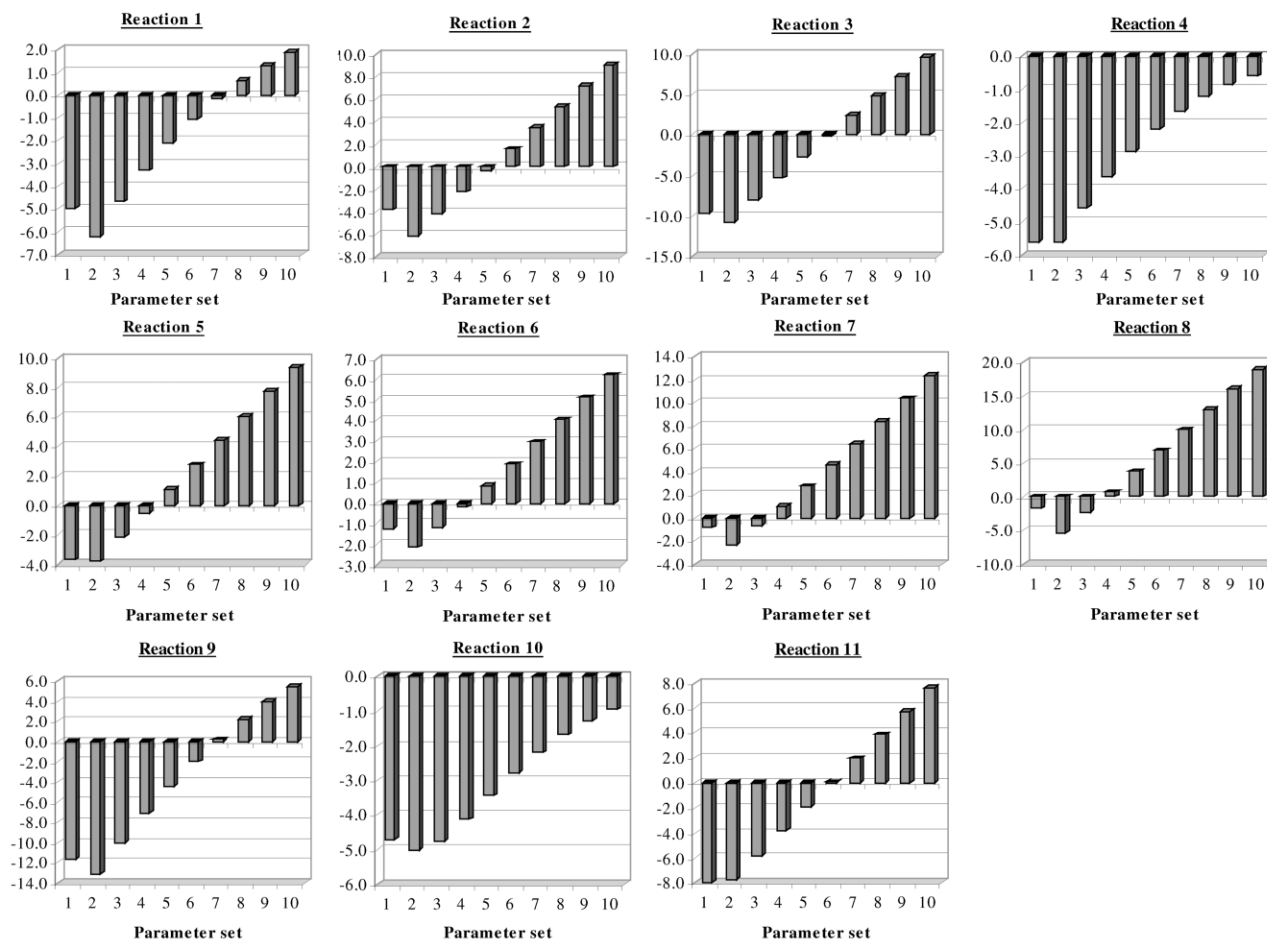
(g) S<sub>N</sub>2 Nucleophilic substitution (R10: CH<sub>3</sub>Cl + F<sup>-</sup> → Cl<sup>-</sup> + CH<sub>3</sub>F)<sup>65,73–79</sup>

(h) Diels–Alder cycloaddition (R11: *cis*-buta-1,3-diene plus ethylene to yield cyclohexene, C<sub>2</sub>H<sub>4</sub> + C<sub>4</sub>H<sub>6</sub> → C<sub>6</sub>H<sub>10</sub>).<sup>10,12,20,21,41,65,80–83</sup>

#### Energy barriers

Table 2 lists the energy barriers from reactants (in kcal mol<sup>-1</sup>) for all the eleven chemical reactions studied, computed with the B3LYP hybrid functional with 10 different PSs. HF and QCISD results with the same basis set are also shown for comparison. Taking the QCISD results as the reference, the HF energy barriers are systematically overestimated, with the exception of reactions R1 and R10 for which HF performs surprisingly well. Remarkably, for all eleven reactions the B3LYP energy barriers are underestimated by 0.9 to 11.6 kcal mol<sup>-1</sup> with respect to the QCISD values. However, for the R2 and R3 reactions, for which experimental values are available, the B3LYP/6-31G\* method performs considerably better than QCISD/6-31G\*, although the reverse is true for R11. As expected, increasing *a*<sub>0</sub> leads in all cases to an increase in the energy barrier. In most reactions (R2, R5, R6, R7, R8, and R11), the increase in the energy barrier is monotonic with the *a*<sub>0</sub> value. As an example, each increase of *a*<sub>0</sub> by 0.1 enlarges the energy barrier of R2 by about 1.9 kcal mol<sup>-1</sup>. For other reactions (R1 and R9), the increase of the energy barrier is usually larger for smaller *a*<sub>0</sub> values. For instance, in the R1 reaction, the energy barrier increases by 1.5 kcal mol<sup>-1</sup> when going from *a*<sub>0</sub> = 0.1 to *a*<sub>0</sub> = 0.2, while the change from *a*<sub>0</sub> = 0.8 to *a*<sub>0</sub> = 0.9 produces an increase of only 0.6 kcal mol<sup>-1</sup>. R3, R4, and R10 are intermediate cases.

Although for each reaction there are always some PSs yielding B3LYP results better than HF results and some quite close to the QCISD result, apparently there is not a single universal PS which is the best (closest to QCISD) for *all* the eleven reactions. This certainly happens because we have considered all sort of reactions, some involving radicals, intramolecular rearrangements, *etc.* However, it is apparent that there are some PS best combinations for a specific class of reaction. This is



**Fig. 2** Difference between the energy barrier provided by each parameter set at the B3LYP/6-31G\* level of theory and that obtained by the QCISD/6-31G\* method, for each of the reactions studied. For reaction R10 the 6-31+G\* basis set was employed.

seen better graphically in Fig. 2, where the energy barrier difference between the B3LYP and QCISD results for all reactions and PS combinations are displayed. It can be observed that there are some groupings or classes of reactions that perform better at the B3LYP level with certain parameter combinations:

(a) Reactions R1, R2, R3, R9, and R11 yield best results with PSs 5, 6, and 7 ( $0.4 < a_0 < 0.6$ ). These reactions include a tautomerism reaction, an electrocyclic ring-opening, and electrophilic and Diels–Alder addition type of reactions, as well as the radical reaction R3. The fact that the energy barrier in R3 requires an  $a_0$  value of 0.5 is in agreement with the result by Durant,<sup>14</sup> who found that the BH&HLYP method with  $a_0 = 0.5$  provides better energy barriers than the B3LYP functional for a series of small radical reactions.

(b) Reactions R5, R6, R7, and R8 yield best results with PSs 3 and 4 ( $0.2 < a_0 < 0.3$ ). This group includes the intramolecular rearrangement reactions.

(c) Reactions R4 and R10 yield best results with PS 10 ( $a_0 = 0.9$ ) and are overall the worst performers. In this group there is one radical reaction and a nucleophilic substitution.

It can be observed that all reactions (even R4 and R10) with their best PS yield B3LYP results that are off from the QCISD results by only a few tenths of kcal mol<sup>-1</sup> on average. It is worth noting that, between PS 1 and PS 3 the main difference is the  $a_x$  parameter. For most reactions, PS 3 with  $a_x = 0.800$  yields better energy barriers than PS 1 with  $a_x = 0.720$ . This seems to corroborate the fact that the choice of the common  $a_x = 1 - a_0$  relation works well, the presence of the  $E_X^{\text{exact}}$  term reducing the need for the GGA correction  $E_X^{\text{B88}}$  to approximately the same extent.

On the whole, in all the reactions studied the B3LYP energy barrier is somewhat underestimated and this can be corrected by the use of an  $a_0$  value larger than that used in the original Becke's formulation ( $a_0 = 0.2$ ).<sup>27</sup> Therefore, calculation of energy barriers should be carried out with a functional that includes a larger fraction of HF exchange, instead of using the original B3LYP functional. Other possible functionals that already include a larger amount of HF exchange could be the mPW1PW91 ( $a_0 = 0.25$ )<sup>84</sup> and the BH&HLYP ( $a_0 = 0.50$ ). In particular, Truhlar *et al.*<sup>22</sup> have shown that the BH&HLYP functional performs better than the B3LYP method for calculating energy barriers.

Finally, as mentioned above, reaction R3 has also been studied with the 6-311++G(3df,3pd) basis set to discuss the effect of the basis set on energy barriers. The values of the energy barriers obtained for R3 with each method and with the 6-311++G(3df,3pd) basis set have been incorporated in Table 2 in parentheses. With the larger basis set, the QCISD energy barrier (7.0 kcal mol<sup>-1</sup>) is much closer to the experimental result (4.0 kcal mol<sup>-1</sup>)<sup>21</sup> while the B3LYP energy barrier decreases and gets worse. In general, the B3LYP/6-311++G(3df,3pd) energy barriers are between 2.0 and 3.5 kcal mol<sup>-1</sup> smaller than those calculated with the 6-31G\* basis set. Nevertheless, in both cases, the increase in the  $a_0$  parameter has the effect of increasing the energy barrier. When compared to QCISD, the best PS corresponds to  $a_0 = 0.4$  for the 6-311++G(3df,3pd) basis set and to  $a_0 = 0.5$  for the 6-31G\* basis set. However, as far as the effect of increasing the  $a_0$  parameter in energy barriers is concerned, the conclusions obtained with the two different basis sets are quite similar.

**Table 3** Energy difference (kcal mol<sup>-1</sup>) between products and reactants for each reaction at the B3LYP/6-31G\* level of calculation, considering the different parameter sets, at the HF/6-31G\* level, and at the QCISD/6-31G\* level of calculation. For R3, values in parentheses correspond to the energy differences calculated at the same levels of theory but with the 6-311++G(3df,3pd) basis set

Parameter set	Reaction										
	1	2 <sup>a</sup>	3 <sup>b</sup>	4	5 <sup>c</sup>	6	7	8	9	10 <sup>d</sup>	11 <sup>e</sup>
1	-15.3	-11.8	-6.5(-12.9)	-18.9	-37.0	0.3	-16.6	-25.3	-30.6	-26.7	-47.0
2	-15.7	-13.6	-5.8(-12.4)	-16.3	-31.9	-17.2	-23.9	0.7	-29.3	# <sup>f</sup>	-41.6
3	-15.7	-12.9	-4.6(-11.0)	-17.2	-34.3	-16.7	-25.3	-0.1	-29.2	-26.7	-43.5
4	-15.8	-12.3	-3.4(-9.5)	-18.3	-36.7	-16.2	-26.5	-1.0	-29.3	-28.3	-45.5
5	-15.9	-11.7	-2.3(-8.1)	-19.6	-39.1	-15.7	-27.5	-1.8	-29.4	-29.7	-47.4
6	-15.9	-11.2	-1.2(-6.7)	-20.9	-41.6	-15.2	-28.3	-2.7	-29.6	-31.0	-49.4
7	-16.0	-10.7	-0.1(-5.3)	-22.2	-44.0	-14.6	-29.0	-3.5	-29.8	-32.2	-51.3
8	-16.0	-10.2	1.0(-3.9)	-23.6	-46.5	-14.1	-29.5	-4.3	-30.1	-33.3	-53.3
9	-16.0	-9.7	2.0(-2.6)	-25.1	-48.9	-13.6	-29.9	-5.0	-30.5	-34.3	-55.2
10	-16.1	-9.3	3.1(-1.3)	-26.5	-51.4	-13.0	-30.2	-5.7	-31.0	-35.4	-57.1
HF	-17.0	-12.6	0.1(-4.2)	-21.7	-42.6	-12.5	-32.4	-6.3	-26.7	-38.2	-46.7
QCISD	-16.0	-10.2	-10.5(-14.0)	-16.2	-42.5	-17.2	-29.0	-1.3	-25.1	-24.5	-50.6

<sup>a</sup> Experimental reaction energy is  $-11.4 \pm 0.5$  kcal mol<sup>-1</sup>.<sup>20</sup> <sup>b</sup> Experimental reaction energy is  $-14.6 \pm 3$  kcal mol<sup>-1</sup>.<sup>21</sup> <sup>c</sup> CCSD(T)/6-31G\*\*/QCISD/6-31G\* reaction energy is  $-41.6$  kcal mol<sup>-1</sup>.<sup>62</sup> <sup>d</sup> For this reaction, diffuse functions were used (6-31+G\*). <sup>e</sup> G2M reaction energy is  $-41.3$  kcal mol<sup>-1</sup>.<sup>41a</sup> <sup>f</sup> For this set of parameters we have not obtained an energy difference between products and reactants because it has not been possible to locate the minimum corresponding to reactants.

### Energy differences

Table 3 lists the energy differences between reactants and products (in kcal mol<sup>-1</sup>) for all the eleven chemical reactions computed using the B3LYP hybrid functional with 10 different PSs. HF and QCISD results with same basis set are also included for comparison.

Taking the QCISD results as reference, the B3LYP errors appear slightly smaller for reaction energies than for energy barriers. This is not at all surprising if one considers that the B3LYP parameters were optimized using thermochemical data of equilibrium species. The effect of increasing  $a_0$  on the reaction energies is less clear than it was for energy barriers. For most reactions, the increase in the  $a_0$  parameter leads to an increase in the exothermicity of the reactions. However, the opposite behavior is found for R2, R3, and R6. To our knowledge, experimental reaction energies are only available for R2 and R3. For R2, both the QCISD and B3LYP methods yields quite good results. For R3, the B3LYP result is about 5 kcal mol<sup>-1</sup> off from the experimental value. However, calculation of this reaction energy with the 6-311++G(3df,3pd) basis set yields  $-12.9$  kcal mol<sup>-1</sup>, a value quite close to the experimental result.<sup>21</sup>

Once more, it can be observed that there are some groupings or classes of reactions that perform better at the B3LYP level with certain parameter combinations for the energy differences, although they are not always exactly the same ones as for the activation barriers.

(a) Reactions R1 and R2 yield best results with PS 8 ( $a_0 = 0.7$ ). These are the best performers yielding the exact QCISD result with this PS. But now R3 cannot be grouped here.

(b) Reactions R3, R4, and R6 yield best results with PSs 1 and 2 ( $a_0 = 0.1$  and Becke original PS). R3 is the worst performer as compared to QCISD in energy differences calculations. As discussed before, the use of a larger basis set in this case leads to a significant improvement.<sup>21</sup>

(c) Reactions R5, R7, and R11 yield best results with PSs 6 and 7 ( $0.5 < a_0 < 0.6$ ).

(d) Reactions R8, R9, and R10 yield best results with PSs 3 and 4 ( $0.2 < a_0 < 0.3$ ).

Besides R3 and R9 that are the worst performers (with the best PS, the B3LYP result is off by 4 kcal mol<sup>-1</sup> with respect to QCISD), all other reactions at their best PS yield B3LYP

results that are off from QCISD by only a few tenths of a kcal mol<sup>-1</sup> on average and some yield the exact QCISD result such as R1, R2, R6, and R7.

As previously done for the energy barriers, we have studied the effect of changing the basis set on the calculation of the energy difference for R3 using the 6-311++G(3df,3pd) basis set (see Table 3). Energy differences obtained with the QCISD and B3LYP methods using this larger basis set are closer to the experimental result<sup>21</sup> and about 6 kcal mol<sup>-1</sup> more negative than those calculated with the 6-31G\* basis set. With the larger basis set, we have also found that the exothermicity of the reaction decreases as  $a_0$  increases. Therefore, qualitatively, the conclusions are the same for the two basis sets.

In summary, there is not a clear rule on the effect of  $a_0$  in the reaction energies, although in most cases, the exothermicity of the reaction is increased with increase in the  $a_0$  parameter. As compared to QCISD values, the original B3LYP parametrization yields, in general, satisfactory results.

### Geometrical parameters

One may expect that the PSs that perform better for reaction energies may also yield the best *geometrical parameters*. For the reactions studied we found the results displayed in Tables 4–6. In general, the HF bond lengths are underestimated as compared to the QCISD bond distances, while the B3LYP bond lengths are somewhat corrected, but still underestimated. This is not unexpected given that bond lengths calculated using pure GGA functionals tend to be slightly longer than those obtained by high-level *ab initio* calculations.<sup>20</sup> It is found that when  $a_0$  increases the B3LYP bond lengths get closer to the HF ones, as the HF contribution is increased. In general, both methods give equivalent distances when  $0.5 < a_0 < 0.7$ .

In Table 4, we show the standard deviation (STD) of the geometrical parameters indicated in Fig. 1, for all *reactants* of each reaction, computed with the B3LYP hybrid functional with 10 different PSs taking the QCISD results as the reference. In Table 4, it is seen that in general (the only exception is R10), for all reactions the smaller STD values are attained for PSs between 2 and 4 ( $0.1 < a_0 < 0.3$ ) and Becke's original PS.

In Table 5, we show the STD of the geometrical parameters indicated in Fig. 1, for all *transition states* of each reaction, computed with the B3LYP hybrid functional with 10 different

**Table 4** Calculation of the STD for the reactants of each reaction at the B3LYP/6-31G\* level of calculation, considering the different parameter sets, and at the HF/6-31G\* level<sup>a</sup>

Parameter set	Reaction										
	1	2	3	4	5	6	7	8	9	10 <sup>b</sup>	11
1	0.006	0.003	0.008	0.010	0.008	0.007	0.015	0.027	0.005	0.107	0.010
2	0.004	0.004	0.013	0.013	0.006	0.002	0.029	0.062	0.012	# <sup>c</sup>	0.009
3	0.005	0.003	0.012	0.010	0.008	0.007	0.013	0.034	0.005	0.103	0.010
4	0.010	0.007	0.029	0.018	0.017	0.014	0.008	0.011	0.019	0.068	0.017
5	0.015	0.011	0.045	0.028	0.025	0.020	0.018	0.017	0.032	0.049	0.025
6	0.020	0.015	0.061	0.039	0.034	0.027	0.029	0.035	0.045	0.040	0.034
7	0.024	0.019	0.077	0.049	0.043	0.033	0.040	0.052	0.057	0.036	0.042
8	0.029	0.023	0.092	0.058	0.051	0.038	0.050	0.067	0.069	0.037	0.050
9	0.033	0.027	0.106	0.068	0.059	0.044	0.059	0.081	0.080	0.039	0.057
10	0.037	0.031	0.120	0.077	0.067	0.049	0.069	0.094	0.091	0.044	0.065
HF	0.024	0.015	0.078	0.045	0.036	0.036	0.051	0.077	0.062	0.023	0.036

<sup>a</sup> For the calculation of the standard deviation values we have used the distances (in Å) and angles and dihedrals (in radians) of Fig. 1, except for reaction R11.<sup>85</sup> STD values have been calculated as:  $\left(\frac{\sum_{i=1}^N (d_i^{\text{B3LYP}} - d_i^{\text{QCISD}})^2}{N}\right)^{\frac{1}{2}}$ ,  $N$  being the number of geometrical parameters considered for each species. <sup>b</sup> For this reaction, diffuse functions were used (6-31+G\*). <sup>c</sup> For this set of parameters it was not possible to locate the minimum of reactants and calculate the corresponding RMS value.

PSs taking the QCISD results as the reference. In Table 5, it is seen that in general (the only exceptions are R4 and R10 that were also the reactions yielding the best energy barriers with  $a_0 = 0.9$ ), for all reactions the smaller STD values are obtained for PSs between 3 and 4 ( $0.2 < a_0 < 0.3$ ) and Becke's original PS.

In Table 6, we show the STD of the geometrical parameters indicated in Fig. 1, for all *products* of each reaction, computed with the B3LYP hybrid functional with 10 different PSs taking the QCISD results as the reference. In Table 6, it is seen that for all reactions the smaller STD are attained for PSs between 2 and 4 ( $0.1 < a_0 < 0.3$ ) and Becke's original PS.

Remarkably, for equilibrium species (reactants and products) the best PS is Becke's original set of parameters or a similar PS, while for transition states, it seems that an  $a_0$  value slightly larger than the original  $a_0$  parameter is the most convenient for geometry optimizations.

To sum up, for most of the reactions studied in this work, the original Becke's PS yields adequate results for geometry optimizations of reactants, transition states, and products, as well as for the calculation of reaction energies. On the other hand, energy barriers are usually improved by using  $a_0$  values larger than 0.2. The reason that adding exact exchange to hybrid functionals leads to better energy barriers is probably because of the cancellation of errors when mixing DFT that provides underestimated energy barriers with HF that overestimates energy barriers. Based on these results we may recommend a computational strategy that carries out geometry optimizations with the original Becke's PS followed by single point energy calculations with an  $a_0$  value of about 0.5, as in the BH&HLYP functional to get energy barriers. However, although this recipe can be practical for most cases, it cannot be generalized for all reactions.

**Table 5** Calculation of the STD for the transition state of each reaction at the B3LYP/6-31G\* level of calculation, considering the different parameter sets, and at the HF/6-31G\* level<sup>a</sup>

Parameter set	Reaction										
	1	2	3	4	5	6	7	8	9	10 <sup>b</sup>	11
1	0.008	0.006	0.029	0.066	0.025	0.011	0.029	0.018	0.015	0.102	0.016
2	0.011	0.006	0.042	0.070	0.032	0.017	0.044	0.041	0.014	# <sup>c</sup>	0.016
3	0.008	0.005	0.015	0.055	0.023	0.010	0.026	0.024	0.011	0.109	0.013
4	0.012	0.009	0.028	0.044	0.017	0.023	0.018	0.014	0.011	0.076	0.012
5	0.017	0.014	0.045	0.036	0.014	0.037	0.026	0.021	0.012	0.057	0.012
6	0.024	0.019	0.057	0.031	0.017	0.051	0.039	0.034	0.016	0.045	0.013
7	0.029	0.023	0.068	0.028	0.022	0.063	0.053	0.047	0.021	0.038	0.016
8	0.035	0.028	0.078	0.028	0.028	0.076	0.065	0.059	0.026	0.034	0.018
9	0.040	0.032	0.086	0.030	0.034	0.087	0.077	0.070	0.031	0.034	0.021
10	0.045	0.036	0.093	0.032	0.041	0.097	0.089	0.080	0.036	0.035	0.024
HF	0.036	0.021	0.081	0.024	0.029	0.090	0.063	0.063	0.023	0.048	0.016

<sup>a</sup> For the calculation of the standard deviation values we have used the distances (in Å) and angles and dihedrals (in radians) of Fig. 1, except for reaction R11.<sup>85</sup> STD values have been calculated as:  $\left(\frac{\sum_{i=1}^N (d_i^{\text{B3LYP}} - d_i^{\text{QCISD}})^2}{N}\right)^{\frac{1}{2}}$ ,  $N$  being the number of geometrical parameters considered for each species. <sup>b</sup> For this reaction, diffuse functions were used (6-31+G\*). <sup>c</sup> For this set of parameters it was not possible to locate the transition state and calculate the corresponding RMS value.

**Table 6** Calculation of the STD for the products of each reaction at the B3LYP/6-31G\* level of calculation, considering the different parameter sets, at the HF/6-31G\* level<sup>a</sup>

Parameter set	Reaction										
	1	2	3	4	5	6	7	8	9	10 <sup>b</sup>	11
1	0.007	0.005	0.004	0.015	0.163	0.010	0.008	0.024	0.006	0.007	0.018
2	0.009	0.005	0.012	0.020	0.163	0.003	0.019	0.041	0.007	0.020	0.193
3	0.007	0.005	0.005	0.014	0.163	0.010	0.008	0.025	0.005	0.023	0.186
4	0.009	0.008	0.010	0.012	0.163	0.017	0.009	0.017	0.008	0.026	0.184
5	0.013	0.012	0.017	0.012	0.164	0.023	0.019	0.021	0.012	0.028	0.185
6	0.017	0.016	0.024	0.016	0.164	0.029	0.029	0.029	0.016	0.030	0.192
7	0.021	0.020	0.031	0.020	0.164	0.035	0.038	0.039	0.020	0.032	0.199
8	0.026	0.024	0.038	0.024	0.165	0.041	0.047	0.048	0.025	0.034	0.208
9	0.030	0.028	0.045	0.028	0.166	0.047	0.055	0.057	0.029	0.036	0.219
10	0.034	0.031	0.051	0.032	0.167	0.052	0.062	0.065	0.033	0.038	0.234
HF	0.020	0.017	0.037	0.017	0.164	0.039	0.045	0.054	0.018	0.084	0.167

<sup>a</sup> For the calculation of the standard deviation values we have used the distances (in Å) and angles and dihedrals (in radians) of Fig. 1, except for

reaction R11.<sup>85</sup> STD values have been calculated as:  $\left(\frac{\sum_{i=1}^N (d_i^{\text{B3LYP}} - d_i^{\text{QCISD}})^2}{N}\right)^{\frac{1}{2}}$ ,  $N$  being the number of geometrical parameters considered for each species. <sup>b</sup> For this reaction, diffuse functions were used (6-31+G\*).

## 4. Conclusions

In this paper we present a systematic study on the effect of the  $a_0$  parameter on the transition state geometries, energy barriers, and energy differences between reactants and products for eleven prototypical chemical reactions. The results have been compared with HF and QCISD values to discuss the effect of changing the  $a_0$  parameter on these properties. We are especially interested in the evaluation of activation barriers. We chose the QCISD method as reference since it is a well accepted high level post-HF calculation scheme. As suggested previously,<sup>38,39</sup> we have varied the values of  $a_0$  by 0.100 increments in the interval  $0.100 \leq a_0 \leq 0.900$  keeping the relations  $a_0 = 1 - a_x$  and  $a_c = a_x$ . For small molecules in their equilibrium structures, it has been reported<sup>39</sup> that the optimum  $a_0$  parameter tends to attain values between 0.1 and 0.3. Larger values of this parameter were also tested in this study since non-equilibrium systems (TSs) are involved.

The main conclusion of this work is that commonly B3LYP calculations underestimate energy barriers and that an increase in the  $a_0$  values corrects this trend. We also conclude that the hybrid DFT B3LYP functional yields geometrical parameters and thermochemistry features much better than those obtained by HF, often reaching almost the QCISD level of quality at a fraction of the computational cost.

We have shown that, there does not seem to exist a universal set of parameters for use in the B3LYP calculations that performs equally well for all reactions studied in this work. Different classes of chemical reactions require different sets of parameters. It is not the objective of this work to reparameterize the B3LYP functional, however we have found that for most reactions, geometry optimizations with the original Becke's PS followed by single point energy calculations with an  $a_0$  value of about 0.5 seems to be a reasonable strategy to obtain quite accurate energy barriers.

Regarding the standard deviation of the geometrical parameters given in Fig. 1, for all reactants, TSs, and products of each reaction, computed with the B3LYP hybrid functional with the 10 different PSs with respect to the QCISD, it is found that the smaller STD values are attained in the average for PSs between 2 and 4 ( $0.1 < a_0 < 0.3$ ). Becke's original PS performs very well for predicting geometries except for transition states where, in most reactions, there are PS combinations with an  $a_0$  value slightly larger than 0.2 that outperform it.

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- 44 To do this, one must define the Gaussian route as #B3LYP IOP(5/45=P<sub>1</sub>P<sub>2</sub>) IOP(5/46=P<sub>3</sub>P<sub>4</sub>) IOP(5/47=P<sub>5</sub>P<sub>6</sub>). The  $E_{B3LYP}$  energy is therefore given by  $E_{B3LYP}/p_2 E_x^{HF} + p_1(p_4 E_x^{LDA} + p_3 E_x^{B88}) + p_6 E_C^{VWN} + p_5(E_C^{LYP} - E_C^{VWN})$ , where  $p_i = P_i/1000$ , for  $i = 1$  to 6. Then relations to Becke's parameters are given by  $a_0 = p_2$  or  $1 - p_1 p_4$ ,  $a_x = p_1 p_3$  and  $a_c = p_5$ . The  $p_1$  and  $p_6$  have been set equal to 1 in this work. The values  $P_1 = 1000$ ,  $P_2 = 0200$ ,  $P_3 = 0720$ ,  $P_4 = 0800$ ,  $P_5 = 0810$  and  $P_6 = 1000$  reproduce the original B3LYP results.
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