

# SVECV-f12: a composite scheme for an accurate and cost effective evaluation of reaction barriers. I. Benchmarking using the HTBH38/08 and NHTBH38/08 barrier heights databases.

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**Abstract:** A simple version of a composite scheme is described, based on a combination of density functional geometry and frequencies evaluation, valence energies obtained using the CCSD(T)-f12 method extrapolated to the complete basis set limit, and core-valence correlation corrections employing the MP2 method. The procedure was applied to the 38 reactions in Truhlar's HTBH38/08 and NHTBH38/08 databases. Mean unsigned deviation (MUD) for the complete set of 68 independent barriers is 0.43 kcal mol<sup>-1</sup>, compared to 1.37 kcal/mol for G4 and 1.69 kcal/mol for the dispersion-corrected M06-2X method. Its accuracy is also better than that of other calculations using composite methods of similar cost. The MUD of the new scheme on the barriers in the DBH24/08 subset (12 out of the 38 reactions in both other sets) is 0.31 kcal mol<sup>-1</sup>, better than that obtained at the expensive CCSD(T,full)/aug-cc-pCV(T+d)Z level (0.46 kcal mol<sup>-1</sup>) and comparable to the most exact (and costly) Wn calculations (MUD=0.14 kcal mol<sup>-1</sup>). The maximum unsigned deviation (MaxUD) of the new method for all the reactions studied is 1.71 kcal/mol. G4 and M06-2X, on the other side, exhibit MaxUDs of 6.7 and 8.4 kcal/mol respectively.

**Keywords:** Transition states; reaction barriers; chemical reactivity; CCSD(T); explicit correlation.

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## 1. Introduction

Accurate prediction of barrier heights for chemical reactions is a necessary, albeit not sufficient, prerequisite for the accurate calculation of reaction rates, as well as branching ratios for the products. While the prediction of the thermochemistry of chemical reactions in gas phase has reached the so-called chemical accuracy ( $\pm 1$  kcal/mol) for molecules of up to a dozen non-hydrogen atoms, such precision is not yet possible concerning barrier heights (see, for instance, Vereecken *et al.* [1] for a general discussion). Since the barriers depend on the precise evaluation of both stable species (reactants and products) and transition states, normally very resource intensive methods are required to achieve high precision. CCSD(T) calculations [2-4] or beyond (including non-perturbative triple and quadruple excitations) are being presently employed in combination with very extensive basis sets (from quadruple up to sextuple zeta) extrapolated to the CBS limit, to obtain sub-kJ/mol precision [5]. But, of course, at a terrible computer cost.

Simplified procedures, usually known as composite methods [1], have been devised to reduce the computer cost to manageable levels, allowing the treatment of molecules with more than the barest minimum number of atoms. Well known procedures in this area are the complete basis set methods developed by Petersson and coworkers [6-10] (of which the most popular is CBS-QB3 [9,10]), Gn methods developed by Pople and collaborators [11-19] (which latest version are G4 and G4MP2 [14,18]), Weizmann-n (Wn) methods of Martin and coworkers [19-23] (the most accurate and expensive of which is W4 [23]) and the correlation consistent composite approach (ccCA) method of Wilson *et al.* [24-29]. Other less well-known or purpose specific composite procedures, like the HL [30], HEAT [31,32], and focal point analysis [33,34] methods, have also been proposed and used less frequently in the literature. Wn, HEAT and focal point analysis are methods used normally for benchmarking, due to their high accuracy (maximum errors of less than 1 kJ/mol) and commensurate high demand of computer resources.

All composite methods have some characteristics in common. Normally, a density functional method (DFT) like B3LYP for instance, and/or MP2 perturbative theory are employed with relatively small basis sets to obtain geometries, frequencies and vibrational components of the thermodynamic functions. Single-point calculations are run then on the optimum geometries obtained, with progressively larger basis sets and post-Hartree-Fock methods to include the correlation energy of the valence shell (at the MP4, QCISD(T) or CCSD(T) levels). Finally, core-valence correlation energy may be included using especial basis sets with tight core functions (normally using some perturbative method of calculation) and, in some cases, empirical corrections are included as well.

As it is the case in other areas of computational chemistry, a compromise must be adopted between the accuracy desired and the resources available. Methods like CBS-QB3 are very fast and quite accurate on average for the study of thermochemistry, but they do not reach chemical accuracy (defined usually to mean  $\pm 1$  kcal mol<sup>-1</sup> or  $\sim \pm 4$  kJ mol<sup>-1</sup>) and in some cases the errors are quite large. G4 is much more accurate and costly, but still oftentimes fail (as an example, consider the barrier for the reaction  ${}^{\bullet}\text{CH}_3 + \text{FCl} \rightarrow \text{CH}_3\text{F} + \text{Cl}^{\bullet}$  for which the G4 error, with respect to the best calculation, is more than 6 kcal/mol). Other methods, like Wn, are normally very expensive and only applicable to small molecules. Thus, the development of new schemes which show a good cost/accuracy ratio is still an active area of research.

Obviously, a new method may perform marvelously well for a given reaction and fail miserably for an unrelated one. Thus, it has been customary to assess the goodness of a new method according to the closeness to experiment or to very accurate calculation in some set(s) of chosen reactions. In the case of barrier heights, there exist two databases maintained by Don Truhlar and his group, HTBH38, containing 19 hydrogen transfer reactions with values for the forward and reverse classical barrier heights (excluding ZPE) [35], and NHTBH38 containing also 19 reactions, this time including "heavy"-atom transfer, bimolecular nucleophilic substitution (SN2), association, and unimolecular reactions [36]. Two versions of these databases are available. In the 2004 version [35,36], most of the barrier heights were derived from W1, some from the next computational level, W2h, or from accurate literature values. The 2008 version of the databases, which are those we used in this paper, contain also values calculated at

the CCSDTQ5/CBS level via the W4 method by Karton *et al.* [37]. Zheng, Zhao and Truhlar [38] specifically developed a subset of those databases, consisting of a representative group of 12 reactions which they called DBH24/08 and used it to assess 348 model chemistries. They arrived to the conclusion that the best performance among those model chemistries was achieved by the CCSD(T)(full)/aug-cc-pCV(T+d)Z method with a mean unsigned error of 0.46 kcal/mol ( $\sim 2$  kJ mol<sup>-1</sup>). We preferred to use the whole set of 38 reactions in this paper, to obtain a better sampling, but we give also the metrics for the reduced subset as a subproduct. The results obtained are compared to those published using other methods in the literature, to assess the behavior of our new simple scheme.

## 2. Computational details

The reactions in the HTBH38/04, NHTBH38/04 and modified data in the DBH24/08 databases were used as benchmark targets for the new composite method proposed. Individual barrier heights for the reactions were obtained from the repository at the University of Minnesota database web site [39]. Results at the G4 level for the 04 version of the databases were taken from the paper by Curtiss, Redfern and Raghavachari [40]. These calculations were also checked against the 08 databases, and the G4 values recalculated increasing the threshold for geometry optimizations and the density of the grid for calculation of the integrals in the B3LYP portion of the G4 scheme. Some small differences were noticed between the two sets of calculations. Results at the ccCA level of calculation were taken from the paper by Grimes *et al.* [29], while the most recent results by Karton at the W3lite-F12 level were also considered [5,37].

The new composite method proposed, which we have nicknamed SVECV-f12 (a Simple Version of an Extrapolated, Core-Valence correlation corrected, CCSD(T)-f12 method), consists of three steps

- (a) Geometry optimization and frequency calculation are performed using a DFT method. We have chosen M06-2X [41] because of its good accuracy, but with the caveat that it may give wrong results if transition states have a heavy multireference character. Although the M06 methods and related include dispersion implicitly through the determination of the empirical parameters, we included it explicitly using Grimme's original D3 method [42]. Dunning's aug-cc-pVTZ basis set was adopted as a compromise between accuracy and speed of calculation [43]. Zero-point energy, as well as thermal and vibrational contributions to the final energies, are taken from these calculations.
- (b) A single-point energy calculation using the DFT geometries is then performed at the CCSD(T)-f12 level [44,45], using both the pVDZ-f12 and pVTZ-f12 basis set [46]. Extrapolation to the CBS limit is performed using Martin's two-point extrapolation formula [47]:

$$E = E(CBS) + \frac{A}{(n+\frac{1}{2})^4}, n=2, 3$$

- (c) Finally, the core-valence correlation energy is calculated at the MP2 level, as

$$\Delta E_{corr}^{CV} = E_{cc-pCVTZ}^{MP2}(full) - E_{cc-pCVTZ}^{MP2}(valence)$$

All geometry optimizations were performed using very tight thresholds and the finest available grids for evaluation of integrals. Transition state optimizations were started performing an analytical evaluation of the hessian at the DFT level employed. If necessary because of convergence problems, analytical evaluation of the hessian was repeated at each step in the geometry optimization procedure. DFT and MP2 calculations were

performed with Gaussian 09, Revision D.01 [48], while CCSD(T)-f12 calculations were performed using Molpro version 2019.2 [49,50]. Basis sets for the calculations were either the ones included in the codes employed or, when necessary, obtained from the Basis Set Exchange [43].

A few words are perhaps necessary as to the choice of the different components. It is known that the B3LYP DFT method used in G4 produces bad geometries in some cases. Curtiss *et al.* [40] attributed these failures in the group of reactions contained in the datasets to the bad description of transition states for fluorine-containing systems. We chose then a better method in this respect, M06-2X [41], which has a smaller error [38] in the determination of geometries. We included explicit empirical dispersion corrections [42] to describe better the non-covalent attractive forces present in some of the transition states in the databases. DFT methods exhibit a better convergence behavior than molecular orbital procedures with respect to basis sets. Therefore, no larger set than a valence triple-zeta (enlarged by diffuse functions) is deemed necessary to achieve good convergence. Zheng, Zhao and Truhlar [38] even recommend a smaller basis set, cc-pVTZ+, as being more efficient with the same degree of accuracy.

For the calculation of the main component of the energies we chose the explicitly correlated CCSD(T)-f12 method, which of course is more expensive than CCSD(T). However, we have noticed in previous calculations that the convergence properties of CCSD(T)-f12 with the increase of the basis set are much better than for CCSD(T). Thus, only DZ and TZ basis sets are needed for obtaining a good extrapolated energy and the less demanding basis sets compensate for the more expensive calculation method. Finally, we have already observed that there is not much gaining in using a CCSD(T) method for the calculation of the core-valence correlation correction, and we chose MP2 as the simplest and sufficient method. A triple-zeta basis set augmented with tight core functions was chosen for these calculations. Notice that CCSD(T)-f12 calculations for open-shell molecules are based on ROHF calculations.

### 3. Results and discussion

Geometries and energies for all the species involved in this work are given in the Supplementary Information section. Only the values of the barriers and the errors with respect to the more exact calculations are considered in the following.

Table 1 shows the reactions in the HTBH38/08 database, listing the best calculated values for the direct and reverse reactions, as well as the errors of the M06-2X-GD3/aug-cc-pVTZ, G4 and SVECV-f12 calculations performed in this paper. Table 2 shows the same for the NHTBH38/08 database. Two metrics have been included in both tables, the mean unsigned deviation (MUD), the usual metric in this field, and the root mean square deviation (RMSD), which we believe is more significant statistically. Repeated values, corresponding to equal forward and reverse barriers for symmetric reactions, have been excluded from the evaluation of MUD and RMSD, resulting in 68 different barriers in total, divided in 36 for HTBH38/08, 32 for NHTBH38/04 and 22 for DBH24/08 (included already in the former). Very small difference in MUD and RMSD are noticed if the repeated values are not excluded. The selected barrier heights from the previous two sets that are included in the DBH24/08 subset, are specified in the footnotes to the tables. Collective metrics for the three data sets, along with values taken from the literature, are shown in Table 3. The correlation between individual values obtained with the new method and “best” ones is shown in Fig. 1.

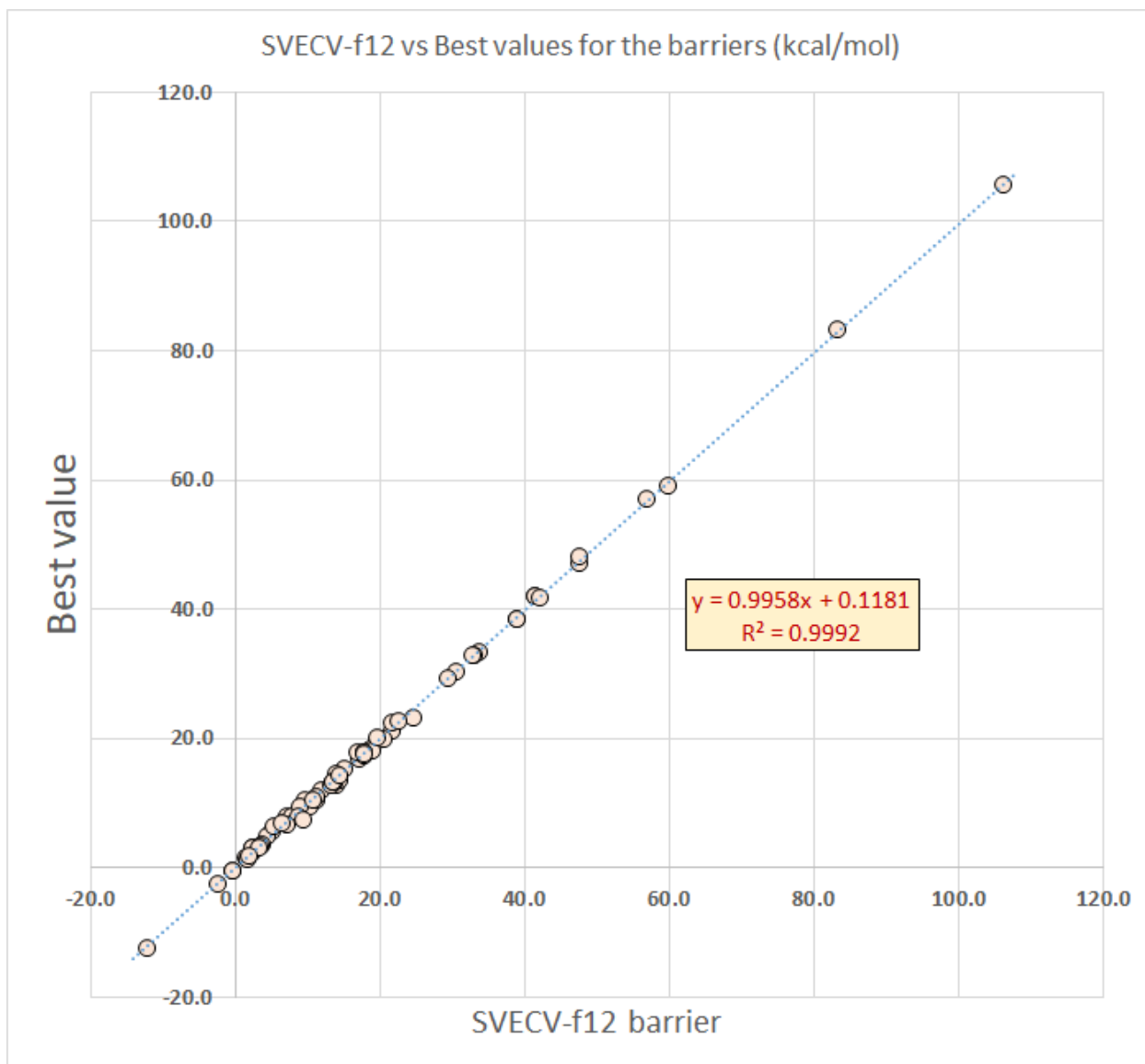


Figure 1. Linear correlation between SVECV-f12 calculated barriers and best known values (in kcal/mol). The linear equation and correlation coefficient are depicted on the graph.

Table 1. Theoretical values obtained in this paper at the G4, M06-2X/aug-cc-pVTZ + GD3 and SVECV-f12 levels, for the reactions in the HTBH38/08 dataset, together with best values taken from [39]. MUD = mean unsigned deviation, RMSD = root mean square deviation. All values in Kcal/mol.

	Reaction <sup>f,g</sup>	Barrier <sup>a</sup>	G4 <sup>b</sup>	M062X <sup>b,c</sup>	SVECV-f12 <sup>b</sup>	Best <sup>d</sup>
1	H• + HCl → H <sub>2</sub> + Cl•	V <sub>f</sub> <sup>‡</sup>	3.13	4.80	4.90	5.70
2		V <sub>r</sub> <sup>‡</sup>	7.10	7.54	6.95	7.86
3	•OH + H <sub>2</sub> → H <sub>2</sub> O + H•	V <sub>f</sub> <sup>‡</sup>	6.91	4.97	4.20	4.90
4		V <sub>r</sub> <sup>‡</sup>	21.92	21.05	21.60	21.20
5	•CH <sub>3</sub> + H <sub>2</sub> → CH <sub>4</sub> + H•	V <sub>f</sub> <sup>‡</sup>	13.02	5.60	11.83	12.10
6		V <sub>r</sub> <sup>‡</sup>	15.28	15.54	14.91	15.30
7	•OH + CH <sub>4</sub> → •CH <sub>3</sub> + H <sub>2</sub> O	V <sub>f</sub> <sup>‡</sup>	7.09	5.42	5.16	6.50
8		V <sub>r</sub> <sup>‡</sup>	19.84	11.56	19.49	19.60
9	H• + H <sub>2</sub> → H <sub>2</sub> + H•	V <sub>f</sub> <sup>‡</sup>	10.47	11.56	9.67	9.60
10		V <sub>r</sub> <sup>‡</sup>	10.47	11.56	9.67	9.60
11	•OH + NH <sub>3</sub> → H <sub>2</sub> O + •NH <sub>2</sub>	V <sub>f</sub> <sup>‡</sup>	4.60	2.63	2.41	3.0
12		V <sub>r</sub> <sup>‡</sup>	14.77	12.21	13.84	12.70
13	HCl + •CH <sub>3</sub> → Cl• + CH <sub>4</sub>	V <sub>f</sub> <sup>‡</sup>	1.08	-6.22	1.43	1.70
14		V <sub>r</sub> <sup>‡</sup>	7.32	6.46	6.55	7.06
15	•OH + C <sub>2</sub> H <sub>6</sub> → H <sub>2</sub> O + •C <sub>2</sub> H <sub>5</sub>	V <sub>f</sub> <sup>‡</sup>	4.20	3.04	2.48	3.20
16		V <sub>r</sub> <sup>‡</sup>	20.73	19.62	20.36	19.90
17	F• + H <sub>2</sub> → HF + H•	V <sub>f</sub> <sup>‡</sup>	1.72	0.48	1.54	1.42
18		V <sub>r</sub> <sup>‡</sup>	33.09	31.87	33.65	33.40
19 <sup>e</sup>	O + CH <sub>4</sub> → •OH + •CH <sub>3</sub>	V <sub>f</sub> <sup>‡</sup>	9.09	0.04	7.63	7.90
20		V <sub>r</sub> <sup>‡</sup>	14.09	11.74	14.21	13.47
21	H• + PH <sub>3</sub> → •PH <sub>2</sub> + H <sub>2</sub>	V <sub>f</sub> <sup>‡</sup>	1.54	3.56	2.81	3.10
22		V <sub>r</sub> <sup>‡</sup>	24.33	25.99	24.55	23.20
23 <sup>e</sup>	H• + HO• → H <sub>2</sub> + O	V <sub>f</sub> <sup>‡</sup>	10.75	9.69	9.61	10.50
24		V <sub>r</sub> <sup>‡</sup>	13.48	11.45	13.12	12.87
25	H• + H <sub>2</sub> S → H <sub>2</sub> + HS•	V <sub>f</sub> <sup>‡</sup>	2.50	4.33	3.67	3.50
26		V <sub>r</sub> <sup>‡</sup>	17.26	18.47	16.98	16.76
27 <sup>e</sup>	O + HCl → •OH + Cl•	V <sub>f</sub> <sup>‡</sup>	8.75	7.08	10.32	9.57
28		V <sub>r</sub> <sup>‡</sup>	9.99	8.07	8.85	9.36
29 <sup>e</sup>	•NH <sub>2</sub> + •CH <sub>3</sub> → CH <sub>4</sub> + NH	V <sub>f</sub> <sup>‡</sup>	9.43	0.37	8.65	8.0
30		V <sub>r</sub> <sup>‡</sup>	23.00	20.85	21.69	22.40
31 <sup>e</sup>	•NH <sub>2</sub> + C <sub>2</sub> H <sub>5</sub> → NH + C <sub>2</sub> H <sub>5</sub>	V <sub>f</sub> <sup>‡</sup>	9.86	7.59	9.21	7.50
32		V <sub>r</sub> <sup>‡</sup>	19.64	17.63	18.70	18.30
33	•NH <sub>2</sub> + C <sub>2</sub> H <sub>6</sub> → NH <sub>3</sub> + •C <sub>2</sub> H <sub>5</sub>	V <sub>f</sub> <sup>‡</sup>	11.55	10.23	11.20	10.40
34		V <sub>r</sub> <sup>‡</sup>	17.90	17.23	17.65	17.40
35	•NH <sub>2</sub> + CH <sub>4</sub> → NH <sub>3</sub> + •CH <sub>3</sub>	V <sub>f</sub> <sup>‡</sup>	14.56	12.80	13.88	14.50
36		V <sub>r</sub> <sup>‡</sup>	17.13	9.36	16.78	17.80
37	s-trans cis-C <sub>5</sub> H <sub>8</sub> → s-trans cis-C <sub>5</sub> H <sub>8</sub>	V <sub>f</sub> <sup>‡</sup>	40.00	38.42	38.78	38.40
38		V <sub>r</sub> <sup>‡</sup>	40.00	38.42	38.78	38.40
	MUD <sup>g</sup>		0.95	1.98	0.57	
	RMSD <sup>g</sup>		1.13	3.34	0.70	

<sup>a</sup> V<sub>f</sub><sup>‡</sup> and V<sub>r</sub><sup>‡</sup> are the barrier heights for the forward and reverse reactions respectively, in kcal/mol, excluding zero point energy. <sup>b</sup> This work. <sup>c</sup> M06-2X/aug-cc-pVTZ calculations including Grimme's D3 empirical dispersion energy. <sup>d</sup> From ref. [38] and references therein, as collected in Don Truhlar's web site (<https://comp.chem.umn.edu/db/dbs/htbh38.html>). <sup>e</sup> The O atom and NH species were calculated in the triplet ground state.

<sup>f</sup> Barrier heights 7, 8, 23, 24, 25 and 26 are also considered in the DBH24/08 dataset. <sup>g</sup> Duplicated values 10 and 38 (symmetrical reactions) were excluded from the calculation of MUD and RMSD.

Table 2. Theoretical values obtained in this paper at the G4, M06-2X/aug-cc-pVTZ + GD3 and SVECV-f12 levels for the reactions in the NHTBH38/08 dataset, together with best values taken from ref. [39]. MUD = mean unsigned deviation, RMSD = root mean square deviation. All values in Kcal/mol.

Reaction <sup>f,g</sup>	Barrier <sup>a</sup>	G4 <sup>b</sup>	M062X <sup>b,c</sup>	SVECV-f12 <sup>b</sup>	Best <sup>d</sup>	
1	$\text{H}^\bullet + \text{N}_2\text{O} \rightarrow \bullet\text{OH} + \text{N}_2$	$V_f^\ddagger$	17.19	17.22	18.86	18.14
2		$V_r^\ddagger$	82.04	82.28	83.06	83.22
3	$\text{H}^\bullet + \text{FH} \rightarrow \text{HF} + \text{H}^\bullet$	$V_f^\ddagger$	41.47	37.78	41.47	42.18
4		$V_r^\ddagger$	41.47	37.78	41.47	42.18
5	$\text{H}^\bullet + \text{ClH} \rightarrow \text{HCl} + \text{H}^\bullet$	$V_f^\ddagger$	18.41	18.55	17.73	18.00
6		$V_r^\ddagger$	18.41	18.55	17.73	18.00
7	$\text{H}^\bullet + \text{FCH}_3 \rightarrow \text{HF} + \bullet\text{CH}_3$	$V_f^\ddagger$	29.19	29.76	30.50	30.40
8		$V_r^\ddagger$	56.36	53.41	56.92	57.00
9	$\text{H}^\bullet + \text{F}_2 \rightarrow \text{HF} + \text{F}^\bullet$	$V_f^\ddagger$	1.46	3.27	2.16	2.27
10		$V_r^\ddagger$	102.3	109.0	106.1	105.8
11	$\bullet\text{CH}_3 + \text{FCl} \rightarrow \text{CH}_3\text{F} + \text{Cl}^\bullet$	$V_f^\ddagger$	0.06	4.53	6.99	6.75
12		$V_r^\ddagger$	52.63	59.24	59.78	59.16
13	$\text{F}^\bullet + \text{CH}_3\text{F} \rightarrow \text{FCH}_3 + \text{F}^\bullet$	$V_f^\ddagger$	-0.03	0.01	-0.40	-0.34
14		$V_r^\ddagger$	-0.03	0.01	-0.40	-0.34
15	$\text{F}^\bullet \cdots \text{CH}_3\text{F} \rightarrow \text{FCH}_3 \cdots \text{F}^\bullet$	$V_f^\ddagger$	11.44	14.99	13.53	13.38
16		$V_r^\ddagger$	11.44	14.99	13.53	13.38
17	$\text{Cl}^\bullet + \text{CH}_3\text{Cl} \rightarrow \text{ClCH}_3 + \text{Cl}^\bullet$	$V_f^\ddagger$	3.47	1.86	2.28	3.10
18		$V_r^\ddagger$	3.47	1.86	2.28	3.10
19	$\text{Cl}^\bullet \cdots \text{CH}_3\text{Cl} \rightarrow \text{ClCH}_3 \cdots \text{Cl}^\bullet$	$V_f^\ddagger$	13.59	13.28	13.29	13.41
20		$V_r^\ddagger$	13.59	13.28	13.29	13.41
21	$\text{F}^\bullet + \text{CH}_3\text{Cl} \rightarrow \text{FCH}_3 + \text{Cl}^\bullet$	$V_f^\ddagger$	-8.74	-13.57	-12.31	-12.54
22		$V_r^\ddagger$	20.86	22.22	19.52	20.11
23	$\text{F}^\bullet \cdots \text{CH}_3\text{Cl} \rightarrow \text{FCH}_3 \cdots \text{Cl}^\bullet$	$V_f^\ddagger$	-2.76	3.55	3.46	3.44
24		$V_r^\ddagger$	30.12	32.30	29.34	29.42
25	$\text{OH}^\bullet + \text{CH}_3\text{F} \rightarrow \text{HOCH}_3 + \text{F}^\bullet$	$V_f^\ddagger$	-2.94	-2.51	-2.59	-2.44
26		$V_r^\ddagger$	18.14	18.18	17.67	17.66
27	$\text{OH}^\bullet \cdots \text{CH}_3\text{F} \rightarrow \text{HOCH}_3 \cdots \text{F}^\bullet$	$V_f^\ddagger$	43.41	50.73	47.59	47.20
28		$V_r^\ddagger$	7.11	12.23	11.10	10.96
29	$\text{H}^\bullet + \text{N}_2 \rightarrow \text{HN}_2^\bullet$	$V_f^\ddagger$	13.85	13.68	14.29	14.36
30		$V_r^\ddagger$	9.50	11.22	10.78	10.61
31	$\text{H}^\bullet + \text{CO} \rightarrow \text{HCO}^\bullet$	$V_f^\ddagger$	1.52	3.67	3.10	3.17
32		$V_r^\ddagger$	20.73	23.10	22.60	22.68
33	$\text{H}^\bullet + \text{C}_2\text{H}_4 \rightarrow \bullet\text{C}_2\text{H}_5$	$V_f^\ddagger$	-0.41	2.71	1.90	1.72
34		$V_r^\ddagger$	39.64	43.63	42.08	41.75
35	$\text{CH}_3^\bullet + \text{C}_2\text{H}_4 \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2^\bullet$	$V_f^\ddagger$	6.13	5.94	6.25	6.85
36		$V_r^\ddagger$	32.27	34.05	32.99	32.97
37	$\text{HCN} \rightarrow \text{HNC}$	$V_f^\ddagger$	48.01	46.01	47.51	48.07
38		$V_r^\ddagger$	32.83	33.10	32.68	32.82
	MUD		1.71	1.25	0.31	
	RMSD		2.44	1.68	0.45	

<sup>a</sup>  $V_f^\ddagger$  and  $V_r^\ddagger$  are the barrier heights for the forward and reverse reactions respectively, in kcal/mol, excluding zero point energy. <sup>b</sup> This work. <sup>c</sup> M06-2X/aug-cc-pVTZ calculations including Grimme's D3 empirical dispersion energy. <sup>d</sup> From ref. [38] and references therein as collected in Don Truhlar's web site (<https://comp.chem.umn.edu/db/dbs/htbh38.html>). <sup>e</sup> Barrier heights 1, 2, 5, 6, 11, 12, 19, 20, 23, 24, 25, 26, 29, 30, 33, 34, 37, and 38 are also considered in the DBH24/08 dataset. <sup>f</sup> Duplicated values 4, 6, 14, 16, 18 and 20 (symmetrical reactions) were excluded from the calculation of MUD and RMSD.

Table 3. Comparison of quality statistics for different methods applied to the reaction height datasets employed in this paper. Values in kcal/mol

Dataset <sup>a</sup>	Metric <sup>b</sup>	This work			Wilson <sup>c</sup>			Truhlar <sup>d</sup>			Curtiss <sup>g</sup>		Karton <sup>h</sup>
		G4	M06-2X	SVECV-f12	ccCA-S4	ccCA-P	G3B	CCSD(T)	M06-2X	G4	G4(B3LYP)	G4(QCISD)	W3lite-F12
DBH24/08 (22 barriers)	MUD	1.50	1.31	<b>0.31</b>				0.46 <sup>e</sup>	0.93	0.58			0.14
	RMSD	2.54	2.10	<b>0.45</b>									0.21
	MaxUD	6.69	8.04	<b>0.72</b>									
HTBH38/08 (36 barriers)	MUD	0.94	2.04	<b>0.58</b>	0.91	0.92	1.71				0.91	0.95	
	RMSD	1.13	3.34	<b>0.70</b>									
	MaxUD	2.57	8.44	<b>1.71</b>	2.88	2.95	5.04				2.39	2.79	
NHTBH38/08 (32 barriers)	MUD	1.85	1.31	<b>0.26</b>	0.98	0.99	2.28	0.96 <sup>f</sup>			1.81	0.47	
	RMSD	2.64	1.73	<b>0.35</b>									
	MaxUD	6.69	4.40	<b>0.82</b>	3.67	3.75	6.70				8.48	1.93	
All reactions (68 barriers)	MUD	1.37	1.69	<b>0.43</b>	0.94	0.95	1.98	1.10 <sup>f</sup>			1.36	0.71	
	RMSD	1.99	2.70	<b>0.56</b>									
	MaxUD	6.69	8.44	<b>1.71</b>									

<sup>a</sup> HTBH38 and NHTBH38 data sets consist each of 19 reactions with forward and reverse barriers, but since some of them are symmetrical, barriers in this case were counted only once; same with the DBH24 data set which is a subset of the combination of the other two; the number of barrier heights employed in each case is written under the name of the set. <sup>b</sup> MUD = mean unsigned deviation, RMSD = root mean square deviation, MaxUD = maximum unsigned deviation. <sup>c</sup> Ref. [29], geometries optimized at the B3LYP/6-31G(d) level for the G3B calculations and at the B3LYP/6-31G(2df,p) level for ccCA; ccCA-S4 and ccCA-P differ only in the form of the extrapolation formula used to obtain the CBS MP2 energy. <sup>d</sup> Refs. [38] and [36], geometries calculated at the QCISD/MG3 level. <sup>e</sup> CCSD(T)(full)/aug-cc-pCV(T+d)Z calculations. <sup>f</sup> QCISD(T)/MG3 calculations. <sup>g</sup> Ref. [40], G4(B3LYP) is the conventional procedure, G4(QCISD) a modified G4 method where geometries are calculated at the QCISD/MG3 level. <sup>h</sup> Ref. [5], MUD and RMSD quoted as 0.9 kJ mol<sup>-1</sup> and 0.6 kJ mol<sup>-1</sup> respectively.

The main results of this paper are summed up in Fig. 1 and Table 3. The correlation between the SVECV-f12 values and the best ones (mostly at the W1 and W2h level [35,36,39]), but those in the DBH24 data base updated using the W4 method [37-39]) is close to perfect on a range of energy barriers larger than 100 kcal/mol. Actually, an extra corrective step could be taken, using the linear equation to modify the raw SVECV-f12 values. In this way a reduction of the MUD from 0.42 to 0.41 kcal/mol (on the whole set, including repetitions) is obtained. Since the decrease is so small, we don't think it is necessary to include this *ad hoc* correction.

The numbers in Table 3 provide some more insight. The first observation is that the MUD of the present method is smaller than the best ones available in the literature using other composite schemes of similar cost. Even in the worst case, the HTBH38/08 dataset, the MUD is almost half of that obtained with the ccCA methods or G4. A very enlightening result is that obtained for the NHTBH38/08 dataset (which then carries over into the result for the combined sets). In this case, the MUD for the new method is about three times smaller than that of ccCA and five times smaller than that of conventional G3B or G4 (using B3LYP for geometry optimization). Substitution of the B3LYP geometries by the QCISD ones, as in the work by Curtiss *et al.* [40] reduces the factor of 5-6 to about 1.5, still with SVECV-f12 as the front runner. This demonstrates that most of the error in the G4 results stems from the B3LYP geometries. It seems to be a good time for this method to be abandoned altogether, since newer exchange-correlation potentials are more accurate. This is clear in our use of M06-2X as the underlying DFT method for the procedure (more about this will follow later). Concerning the DFT method itself, it is noticeable that the MUD is always larger than both the G4 and SVECV-f12 values. However, the geometries are sound, since the calculation of the rest of the energies on top of these geometries give excellent results.

As was to be expected, since Karton's W3lite-f12 method is very similar to the other Wn methods used to obtain the target results, the error in the barrier obtained with this method is about half that obtained with our SVECV-f12 method. Even if this method is dubbed as "lite", it still requires the use, for instance, of quadruple basis sets for the evaluation of the energy at the CCSD-f12 level and the use of the very costly CCSDT(Q) method to include the effect of higher excitations. The reduction in the MUD with respect to our procedure is still only 0.17 kcal/mol (or 0.7 kJ mol<sup>-1</sup>) which is most probably unimportant except for extremely accurate calculations.



A final observation concerns the point already mentioned in the Introduction about the spread of the calculated barriers. The results are shown graphically in Fig. 2, where our own data and the original G4 and modified G4 data of Curtiss et al are plotted. It is immediately obvious that the spread of the results at the M06-2X and G4 levels are too big. The effect of tightening the thresholds does produce an observable but small effect in the G4 results, which are more affected nonetheless by the change in the method for the geometry optimization [40]. The spread is then reduced to about one third of the original one. Nonetheless, neither the MUD nor the spread are so good as for the SVECV-f12 procedure. An interesting observation is that all methods cluster their outliers on the negative region, i.e. where the calculated height of the barrier is lower than the best theoretical value. This asymmetry is less marked in the case of the SVECV-f12 method, but even in this case the maximum positive deviation (1.71 kcal/mol) is larger than the maximum negative deviation (-1.34 kcal/mol). Notice that in this case the behavior is opposite to that of the G4 or M062X methods, the largest error is found as an overestimation of some barriers, not underestimation as in the other methods.



Figure 2. MUD, RMSD, maximum positive and negative deviations plotted for the methods used in this work and for the original G4 data in Curtiss et al. [40] paper. All values in kcal/mol.

A final concern is the presence of “difficult” cases, i.e. those where the methods misbehave to a larger extent than on average. For G4, we have already mentioned that this is caused mainly for bad geometries at the underlying B3LYP geometry optimization level. Curtiss *et al.* [40] describe this problem with respect to two reactions,

(9) and (11) in Table 2. For the first of these reactions,  $\text{H}^\bullet + \text{F}_2 \rightarrow \text{HF} + \text{F}^\bullet$ , the B3LYP structure exhibits an unrealistically long  $\text{H}\cdots\text{F}$  forming bond in the transition state, 4.412 Å, while the QCISD/MG3 optimization affords a much more reasonable distance of 1.615 Å in fair agreement with the M06-2X value we obtained of 1.721 Å (the F-F bond is 1.480 Å at the QCISD/MG3 level and 1.420 Å at the M06-2X level). The situation is even worse for reaction (11),  $^\bullet\text{CH}_3 + \text{FCl} \rightarrow \text{CH}_3\text{F} + \text{Cl}^\bullet$ , where not only the  $\text{F}\cdots\text{C}$  distance in the transition state is much longer in B3LYP than QCISD (3.101 Å vs. 2.064 Å) but also the geometry and bonding patterns are distorted. B3LYP TS is mostly described by a FH interaction, while the QCISD calculation shows a more reasonable structure with a three-fold symmetry axis and the F-C interaction. This is exactly the same structure predicted by M06-2X and even the distance of the bond being formed between F and C, 2.078 Å, is very well in agreement with the QCISD value.

On the other side, Grimes *et al.* [29] described also those structures as problematic, as well as a third one, that corresponding to the ionic pair in reaction (23) which exhibits the same structural problem than the others, due to the drawbacks of B3LYP. However, they also describe four other reactions which are pairwise troublesome, two of them for the G3B method, the other two for the ccCA methods (see their Table IV, problematic reactions). We have reproduced their values, together with the best ones and our own, in Table 4.

Table 2. Problematic reactions for ccCA and G3B cited in Grime's *et al* work [29]. Values in Kcal/mol.

Reaction	Best <sup>a</sup>	ccCA-S4 <sup>b</sup>	ccCA-P <sup>b</sup>	G3B <sup>b</sup>	G4 <sup>c</sup>	M06-2X-G3 <sup>c</sup>	SVECV-f12 <sup>c</sup>
2 $\text{H}_2 + \text{Cl} \rightarrow \text{H} + \text{HCl}$	7.86	5.82	5.75	4.59	7.1	7.54	6.95
19 $\text{O} + \text{CH}_4 \rightarrow \text{OH} + \text{CH}_3$	13.7	14.37	14.36	8.66	14.09	11.74	14.21
27 $\text{F}\cdots\text{CH}_3\text{OH} \rightarrow \text{FCH}_3\cdots\text{OH}^\bullet$	47.2	43.53	43.45	43.67	43.41	50.73	47.59
31 $\text{H} + \text{CO} \rightarrow \text{HCO}$	3.17	5.82	5.92	9.87	1.52	3.67	3.10
MUD		2.26	2.32	4.64	1.65	1.58	0.47
RMSE		2.51	2.57	4.83	2.11	2.04	0.56

<sup>a</sup> Values from ref. [39]. <sup>b</sup> Ref. [29]. <sup>c</sup> This work.

We have added in this table the MUD and RMSE values for the four reactions, in order to make a comparison across methods. They show that the problematic cases are largely corrected when larger levels of theory are used. All methods employed in this paper show a MUD much smaller than those from ref. [29]. In particular, our new procedure gives a MUD which is about one third as large as the second best and well in agreement with the overall MUD for the whole set of reactions.

A final word must be said about the timing of the methods. Truhlar estimated the relative cost of each method as the single-processor CPU time for calculating an energy gradient of the molecule phosphinomethanol divided by the time for an MP2/6-31+G(d,p) energy gradient calculation with the same computer program on the same computer. In this paper we have preferred to obtain a relative estimate of the cost of our procedure, measuring the CPU time necessary for the SVECV-f12 complete calculation of all the molecules of a given reaction, calculating the ratio for the same process at the G4 level, and then averaging these ratios for the 38 reactions. The process is of course not exact, because in a heterogeneous cluster it will depend on the nodes being active for a given calculation, the load of the clusters and other considerations. At any rate, a rule of thumb says that the SVECV-f12 procedure will be on average about 5 times more costly than a G4 calculation. Even so, the calculations are much faster than CCSD(T)/CBS, especially if geometries are calculated at some CCSD(T) level, because CBS extrapolation for CCSD(T) requires at least a quadruple-zeta basis set. Needless to say, SVECV-f12 is much faster than Wn procedures. Therefore, both in terms of accuracy (much better than all 348 chemical models in Zheng's paper [38]) and speed (faster than

the best CCSD(T)/CBS and Wn methods) our method seems to be a good compromise for the accurate study of barrier heights of chemical reactions involving middle size species.

#### 4. Conclusions

A new composite scheme, SVRCV-f12, based on a combination of density functional geometry and frequencies evaluation, inclusion of explicit correlation using the CCSD(T)-f12 method extrapolated to the complete basis set limit, and core-valence correlation corrections employing the MP2 method has been conceived and tested on Truhlar's HTBH38/08, NHTBH38/08, and DBH24/08 databases of 68 forward and reverse reaction barriers corresponding to 38 different reactions. The results have been compared with G4 and M06-2X results and with data present in the literature employing other procedures.

The SVRCV-f12 calculated values correlate almost perfectly with the accurate and expensive W1 and W4 barriers for the studied reactions. A correlation coefficient  $R^2$  larger than 0.999 and an almost perfect straight line for barriers spanning a range larger than 100 kcal/mol were obtained. MUD values obtained for the datasets were in all cases smaller than those obtained with other composite methods of comparable cost (G3B, G4, ccCA) and better than those obtained with very expensive CCSD(T)/CBS calculations. In the case of the landmark DBH24/08 smaller database, a MUD of 0.31 kcal/mol (i.e. about 1.3kJ/mol) was obtained, to be compared to a 0.46 kcal/mol MUD value obtained at the CCSD(T,Full)/aug-cc-pCV(T+d)Z level, the best one obtained by Zheng *et al.* [38] after testing 348 different chemical models on the set. The MUD for the whole set of 68 barriers was 0.43 Kcal/mol (about 2kJ/mol) and all the values lied in the interval [-1.34,1.71] Kcal/mol.

We believe that the proposed composite scheme can rival very accurate and expensive procedures, and may be a useful tool for the calculation of rate coefficients. Further application of this procedure to larger and more complex transition states and reaction barriers is going to be published elsewhere.

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