CHEMICAL PHYSICS LETTERS

Linear regression correction to first principle theoretical calculations – Improved descriptors and enlarged training set

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Abstract

The linear regression correction previously developed to reduce quantum chemical calculation errors [X.M. Duan, G.L. Song, Z.H. Li, X.J. Wang, G.H. Chen, K.N. Fan, J. Chem. Phys. 121 (2004) 7086] has been further improved by using new descriptors obtained from natural bond orbital analysis and an enlarged training set of 350 organic, inorganic molecules and radicals. The new scheme is better suited for correcting reaction barriers. Upon linear regression correction, the mean absolute deviation for the new set decreases from 284.1, 8.2, 12.4 kcal/mol to 7.3, 3.3, 2.7 kcal/mol for the HF/6-31G(d), B3LYP/6-31G(d), and B3LYP/6-311G(2d,d,p) methods, respectively, and the mean absolute deviation of 12 barrier heights for six hydrogen transfer reactions is reduced from 5.3 to 2.9 kcal/mol for the B3LYP/6-311G(2d,d,p) method.
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1. Introduction

A great success of computational chemistry in the last two decades is the successful prediction of the thermochemical properties of small- and medium-sized molecules. The calculated properties are often comparable to experimental measurements, and occasionally even better than the experimental counterparts. To achieve such accuracy electron correlation effects must be explicitly considered in the quantum chemical calculations [1–4]. After decades of efforts, a variety of methods suitable for tackling the correlation problem, including the configuration interaction (CI) [5], the coupled-cluster (CC) procedures [6] and the Gaussian 2 (G2) [7–9], Gaussian 3 (G3) [10,11] algorithms, have been devel-

oped. Taking G3 method as an example, its mean absolute deviation (MAD) on the heats of formation of 222 molecules is only 1.05 kcal/mol [12]. However, these procedures are most computational resource consuming and are still inapplicable to complex systems. Thus, a balance has to be found between accuracy and efficiency.

Density-functional theory (DFT), especially those hybrid methods, such as B3LYP [13–16], surely offers promising alternatives. However, all DFT calculations employ approximated exchange-correlation (XC) functionals, and there is no systematic way to improve these functionals. Moreover, the errors of DFT calculations are accumulated with the size of the molecule [17]. Recently, Chen et al. and we proposed two semi-empirical procedures, the neural-network (NEURON) scheme of Chen et al. [18] and our linear regression correction (LRC) approach [19] to improve the results of quantum chemical methods. For the B3LYP method, the

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root-mean-square (RMS) deviations of the calculated heats of formation for 180 organic molecules were decreased from more than 10 kcal/mol to about 3 kcal/mol upon DFT-NEURON and DFT-LRC corrections. Upon HF-LRC correction, the RMS deviations of the calculated heats of formation were decreased dramatically from more than 350 kcal/mol to just 6 kcal/mol. These procedures have also been successfully applied to predicting electron affinities (EA), ionization potentials (IP) and absorption energies [20].

Although very successful, these procedures are unsuitable for calculating potential energy profiles of chemical reactions, since the physical descriptors employed are the numbers of bonding electrons, lone pair electrons, core electrons, or atoms, which will either cancel or result in non-continuous potential energy surface. It is well known that a chemical reaction can be described as a rearrangement of the chemical bonding pattern between atoms. To characterize a chemical reaction at the electronic level along a chosen reaction coordinate, one must therefore describe the continuous electronic redistribution from the reactant-like to product-like bonding pattern. For this purpose, we use natural bond orbital (NBO) population analysis [21–25] to obtain the physical descriptors in the present procedure.

Another limitation of our previous LRC method is that the training set contains only closed-shell organic molecules, which limits the application range of the method. Thus, in the present Letter, the training set is enlarged to include 222 heats of formation in the G3/99 test set [12], and also those used in our previous work (with duplicated ones deleted). The new training set contains 350 heats of formation of small- and medium-sized organic, inorganic molecules, and radicals.

2. The linear regression correction method

In the LRC, the energy of a molecule $M(A_{n_A}, B_{n_B}, \cdots)$ is calculated by [19]

$$E_0^{LRC}(M) = E_e^{calc} + \sum_i a_i x_i + c \cdot ZPE \quad (1)$$

and that of atom A by

$$E_e^{LRC}(A) = E_e^{calc} + \sum_i b_i x_i, \quad (2)$$

where E_e^{calc} is the calculated electronic energy by a method without any correction; E_0^{LRC} is the energy at 0 K after linear regression correction; $\{x_i\}$ are physical descriptors; $\{a_i\}$ and $\{b_i\}$ are coefficients of the descriptors for the molecule and the atoms, respectively; c is the scaling factor for zero-point vibrational energy (ZPE). The physical descriptors previously used, the numbers of the electrons (all integers) in different bonding environment are now replaced with those calculated from

the NBO population analysis, which are the total electron populations of different types of NBOs: two-center bonds (BD), one-center core pair (CR), one-center valence lone pair (LP), one-center Rydberg (RY*), two-center anti-bond (BD*), and valence non-Lewis lone pair (LP*). The core electrons are further divided into several subsets according to the shell in the corresponding atoms. There are three shells for the core electrons in the molecules studied here. We define CR1, CR2, and CR3 as the first, the second and the third layer below the valence shell. The number of the unpaired electrons (an integer) of atom in its ground state is also included as a descriptor.

In an atomization energy scheme, the heat of formation of a molecule $M(A_{n_A}, B_{n_B}, \ldots)$ at 298.15 K after linear regression correction is calculated by

$$\Delta H_f^{298\ K} = \left[\sum_i a_i x_i - \sum_i b_i x_i + c \cdot ZPE + \Delta E_e^{calc} \right] \\ + \Delta H_f^{calc}(M) + \sum_A n_A \Delta H_{f,0\ K}^{exp}(A_{(g)}) \\ - \sum_A n_{A,S} \Delta H_{298\ K}^{exp}(A_{(S)}), \quad (3)$$

where $n_{A,S}$ is the molar ratio of the element A in the molecule (M) to that in its stable state of aggregation at 298.15 K, i.e. its standard state, with the subscript 'S' representing standard state; ΔE_e^{calc} is the atomization energy of M at 0 K without ZPE correction; $\Delta H_f^{calc}(M)$ is the calculated enthalpy change of M from 0 to 298.15 K; $\Delta H_{f,0\ K}^{exp}(A_{(g)})$ is the experimental heat of formation of atom A in gaseous state at 0 K; $\Delta H_{298\ K}^{exp}(A_{(S)})$ is the experimental enthalpy change of element A in its standard state from 0 to 298.15 K. Eq. (3) effectively corrects the unbalanced electron correlation energies in atoms and in molecule unaccounted by a theoretical method [19].

In order to determine the relative importance of a physical descriptor, its partial correlation coefficient, V_j is calculated

$$V_j = \sqrt{1 - q/Q_j}, \quad (4)$$

in which q is the square sum of deviations and Q_j is the square sum of deviations leaving out one descriptor x_j. The closer V_j is to 1, the more remarkable is the influence of x_j.

3. Computational methods

The enlarged training set contains 350 heats of formation: 222 are from G3/99 test set [12], and the remaining are from the training set employed in our previous works [18,19]. Geometry optimization and vibrational frequency analyses are carried out at the HF/6-31G(d),

B3LYP/6-31G(d) and B3LYP/6-311G(2d,d,p) levels of theories. The more balanced 6-311G(2d,d,p) basis set as employed in the modified complete basis set model (CBS-QB3) [26] is used in the present Letter, which includes two sets of d polarization functions on elements beyond the first row, one set of d polarization function on the first row elements, and one set of p polarization function on hydrogen as well. The scaling factors for ZPEs are 0.9135, 0.9806 and 0.9900, and those for calculating $\Delta H^{calc}_{298\ K}(M)$ are 0.8905, 0.9989 and 0.9900, for the HF/6-31G(d), B3LYP/6-31G(d) and B3LYP/6-311G(2d,d,p) methods, respectively [27,26]. The NBO analysis is performed with NBO 3.1 [28] as implemented in the GAUSSIAN 03 package of programs [29]. Attentions must be paid in the NBO calculations for radicals and strongly delocalized molecules. For example, for radicals NO, ClO, CN, HCO, CH_3CO and H_2COH the SCHOOSE keyword is needed to specify the correct bonding pattern, and for benzene and substituted benzene molecules the RESONANCE keyword should be used. All the calculations have been done with the GAUSSIAN 03 suite of programs [29].

4. Results and discussion

4.1. Linear regression correction of the heats of formation

Theoretical results compared to their experimental counterparts are illustrated in Fig. 1. Raw calculated ΔH^{θ}_fs by the HF method have huge errors and the errors increased with the molecule size [19]. The maximal deviation of HF/6-31G(d) reaches to 883.3 kcal/mol for $C_{10}H_{18}O_4$. The MAD is 284.1 kcal/mol for the HF/6-31G(d) method. In comparison, B3LYP/6-31G(d) and B3LYP/6-311+G(2d,d,p) perform much better than the HF method, since DFT methods have already involved some electron correlation correction, but HF methods have not. From Fig. 1b and c, we can see that most raw calculated ΔH^{θ}_fs from DFT methods are larger than experimental values. Some results even have large errors. For example, the raw calculated ΔH^{θ}_fs of Cl_2 O_2S, SO_3, PCl_5, $C_2H_6O_2S$, and $POCl_3$ molecules are about 40 kcal/mol above experimental values for the B3LYP/6-31G(d) method. For the B3LYP/6-311G (2d,d,p) method, the errors of the calculated ΔH^{θ}_fs of SF_6 and PF_5 molecules even come to 60.3 and 50.1 kcal/mol, respectively. Compared to the experimental measurements, the MAD is 8.2 kcal/mol for the B3LYP/6-31G(d) method, and 12.4 kcal/mol for the B3LYP/6-311G(2d,d,p) method.

It is obvious that there are systematic deviations between the calculated and experimental ΔH^{θ}_f values. To reduce such deviations, Eq. (3) employing the nine descriptors as previously described is used to correct the heats of formation. Fifty molecules out of 350 mol-

ecules are set aside randomly as testing set, and the rest are training set. The 300 training molecules are randomly divided into six subsets of equal size. Five of them are used to train the linear regression approach, and the sixth to validate its predictions. This procedure is repeated six times in rotation. The MAD and the RMS deviations are listed in Table 1. The linear regression coefficients obtained for the descriptors are listed in Table 2.

Upon linear regression correction the deviations are all substantially decreased. For the HF/6-31G(d) method, the MAD is reduced from 284.1 to 7.3 kcal/mol, by more than 30 times. For the B3LYP/6-31G(d) method, the MAD is reduced from 8.2 to 3.3 kcal/mol, and for the B3LYP/6-311G(2d,d,p) method, it is reduced from 12.4 to 2.7 kcal/mol. For the DFT methods, the deviation using the smaller 6-31G(d) basis set is comparable to the larger 6-311G(2d,d,p) basis set upon linear regression correction. This implies that the truncation error in the basis set can be greatly corrected by the LRC approach. Thus, the smaller 6-31G(d) basis set can be used in our scheme to save mounts of computer time for large molecules. A comparison between the linear regression corrected ΔH^{θ}_fs and the experimental values are illustrated in Fig. 1d–f. The figures clearly show that the corrected results are much closer to their experimental counterparts for both the training and testing sets. The surprising effects of the correction indicate that quantum chemical calculation results can be greatly improved by linear regression correction approach. Moreover, while uncorrected calculations yield worse results for large molecules compared to small ones, our LRC approach does not discriminate against large molecules [19]. The deviations of large molecules are of the same magnitude as those of small molecules. The histograms for the deviations (from the experiments) as shown in Fig. 2 further demonstrate that our LRC approach greatly decreases the large systematic calculation errors of the DFT methods.

Table 3 lists the partial correlation coefficients of all descriptors. Examination of the data indicates that bonding electrons are very important for electron correlation correction for the three methods. The large partial correlation values of the inner-layer electrons indicate that the changes of electron correlation from atoms to molecules are large and non-negligible. Generally, the closer the electrons to the nucleus, the less important are their contributions in chemical reactions. The large partial correlation values of RY* imply that the contribution of Rydberg orbitals are also important. In the NBO analysis, the NBOs are partitioned into high- and low-occupancy orbital types. The high-occupancy orbitals (BD, CR, LP) play the primary role in determining the properties of molecules. The low-occupancy orbitals (BD*, LP* and RY*) are consisting of the remaining (formally unoccupied) orbitals. In the molec-
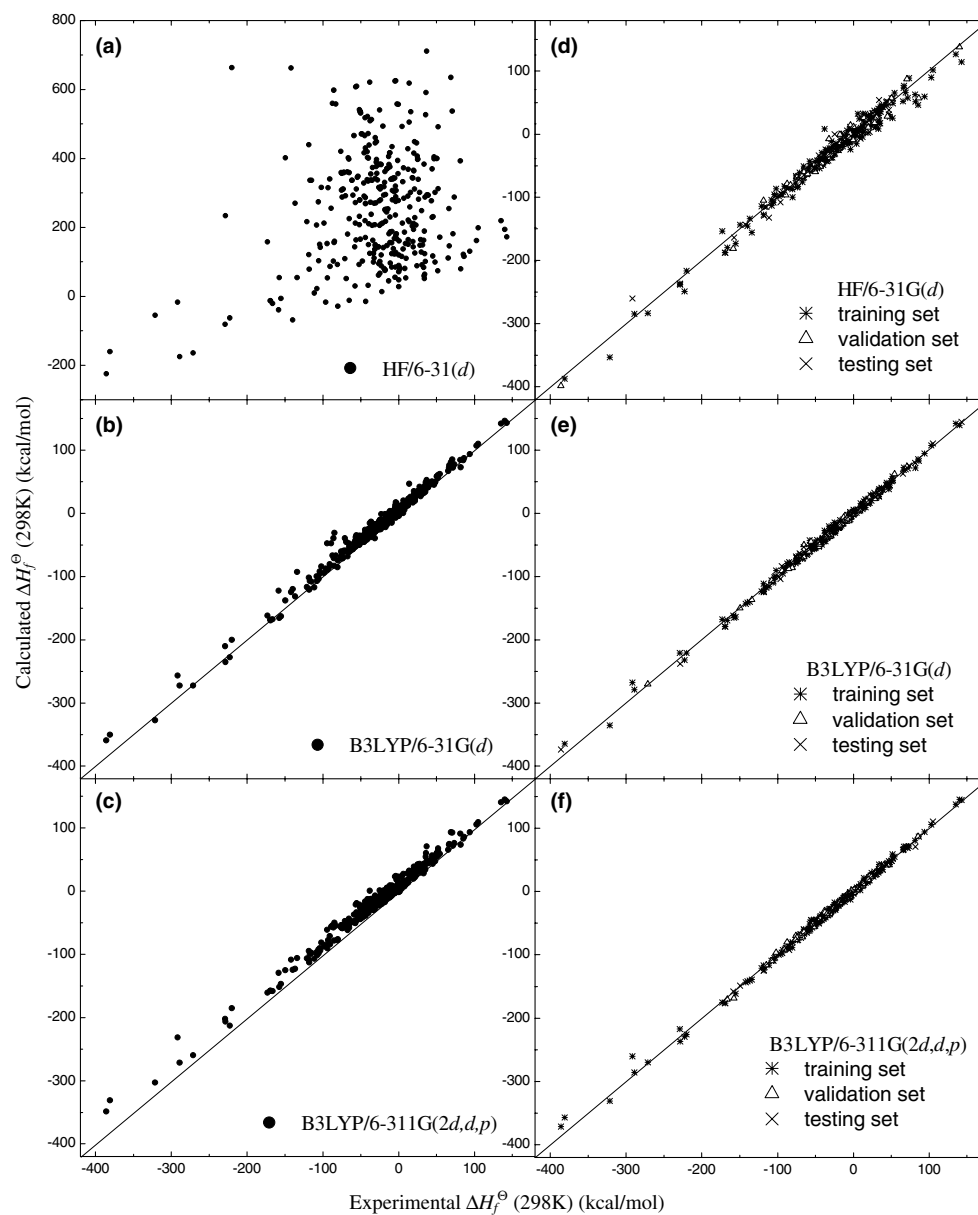
Fig. 1. Experimental vs. calculated ΔH_f^{θ} for all 350 molecules: (a)–(c) raw calculated results; (d)–(f) linear regression corrected results.

Table 1
The MAD and RMS deviations (kcal/mol) before and after linear regression correction

	HF	B3LYP	
	6-31G(d)	6-31G(d)	6-311G(2d,d,p)
B-MAD[a]	284.1	8.2	12.4
A-MAD[b]	7.3	3.3	2.7
B-RMS[a]	327.1	11.2	15.2
A-RMS[b]	10.2	4.5	4.0

[a] Before correction.
[b] After correction.

ular environment, their occupancies are not necessarily
zero. These extra-valence shell orbitals play the second-
ary role in describing the electron density associated

Table 2
Optimized coefficients (kcal/mol) of the descriptors employed in Eq. (3)

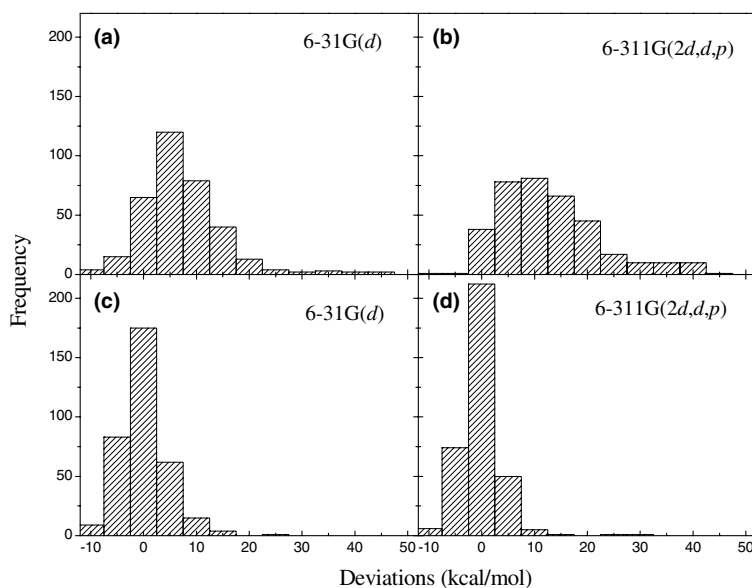|	HF	B3LYP	
	6-31G(d)	6-31G(d)	6-311G(2d,d,p)
BD(a_1)	1.173	−0.2598	−1.964
LP(a_2)	−0.9471	0.1790	−0.6625
CR1(a_3)	−4.400	0.8702	0.9719
CR2(a_4)	19.56	−5.088	−3.139
CR3(a_5)	−32.29	15.58	6.732
RY*(a_6)	−268.3	−158.0	−106.8
BD*(a_7)	−21.74	0.9951	2.306
LP*(a_8)	11.87	1.361	3.095
Unpaired(b_1)	16.18	0.04581	−2.050

Fig. 2. Histograms for the deviations of the B3LYP methods before correction (a, b) and after correction (c, d).

Table 3
Partial correlation coefficients of the descriptors

	HF	B3LYP	
	6-31G(d)	6-31G(d)	6-311G(2d,d,p)
BD(a_1)	0.94	0.83	0.99
LP(a_2)	0.65	0.35	0.82
CR1(a_3)	0.99	0.95	0.96
CR2(a_4)	0.98	0.96	0.90
CR3(a_5)	0.80	0.88	0.61
RY*(a_6)	0.89	0.92	0.90
BD*(a_7)	0.73	0.13	0.33
LP*(a_8)	0.07	0.02	0.05
Unpaired(b_1)	0.99	0.18	0.99

Table 4
The MADs of linear regression correction for different descriptors (kcal/mol)

	HF	B3LYP	
	6-31G(d)	6-31G(d)	6-311G(2d,d,p)
I	12.0	4.4	2.8
II	8.6	3.9	3.2
III	13.4	3.3	3.0
IV	8.8	4.0	2.8
V	7.3	3.3	2.7

I: BD, LP, RY*, BD*, LP*, and unpaired electrons of atom as descriptors.
II: BD, LP, CR1, CR2, CR3, and unpaired electrons of atom as descriptors.
III: BD, LP, CR1, CR2, CR3, RY*, BD*, and LP* as descriptors.
IV: BD, LP, the sum of inner layer, RY*, BD*, LP*, and unpaired electrons of atom as descriptors.
V: BD, LP, CR1, CR2, CR3, RY*, BD*, LP*, and unpaired electrons of atom as descriptors.

with the atom. The unpaired electrons of atom have a large effect on the HF/6-31G(d) and B3LYP/6-311G(2d,d,p) calculation results. For both methods the partial correlation coefficient reaches to 0.99.

We have also tested the relative importance of a descriptor by leaving it out and re-training the rest. The results are listed in Table 4. It is the common sense that electron correlation energy of the inner-layer electrons may not change too much when forming chemical bonds. On the contrary, our results show that the correlation energy changes of the inner-layer electrons from atoms to molecule also have significant contribution to the overall correlation energy changes. Without inner-layer-electron descriptors, the MADs increase from 7.3 to 12.0 kcal/mol and from 3.3 to 4.4 kcal/mol for the HF/6-31G(d) and B3LYP/6-31G(d) methods, respectively. When taking the sum of three inner-layer electrons as one descriptor, the MADs reach to 8.8 and 4.0 kcal/mol, respectively. These indicate that electron correlation energy changes of different inner-layer elec-

trons are not the same and non-negligible when forming a bond. On the contrary, for the B3LYP/6-311G(2d,d,p) method, the MADs change little with the absence of the three inner-layer-electron descriptors, or including their sum. Unpaired electrons of the atoms also have remarkable contributions to the correction of correlation energy at the HF level. Without unpaired-electron descriptor, the MAD of the HF method increases by 6.1 kcal/mol. This reflects a large discrepancy in the correlation energy of the unpaired electrons before and after forming bonds at the HF level. On the contrary, for the two DFT methods, the effect of unpaired electrons is not so significant. However, without low-occupancy-orbital descriptors (RY*, BD*, and LP*), the MADs of the three methods all increase greatly,

Table 5
Classical barrier heights (kcal/mol) at the B3LYP/6-311G(2d,d,p) level[a]

Reactions	Best-estimate		Raw calculation		B3LYP-LRC	
	$V_f^{\neq}$	$V_r^{\neq}$	$V_f^{\neq}$	$V_r^{\neq}$	$V_f^{\neq}$	$V_r^{\neq}$
$OH + CH_4 \rightarrow CH_3 + H_2O$	6.7	19.6	2.6	10.7	6.2	15.1
$CH_3 + NH_2 \rightarrow CH_4 + NH$	8.0	22.4	3.7	17.5	5.1	18.4
$C_2H_5 + NH_2 \rightarrow C_2H_6 + NH$	7.5	18.3	5.3	14.4	6.7	15.3
$C_2H_6 + NH_2 \rightarrow C_2H_5 + NH_3$	10.4	17.4	7.9	13.1	9.2	14.4
$CH_4 + NH_2 \rightarrow CH_3 + NH_3$	14.5	17.8	10.3	10.9	11.8	12.9
s-trans, cis-C_5H_8 → s-trans, cis-C_5H_8	38.4	38.4	34.9	34.9	38.7	38.7

[a] $V_f^{\neq}$ for the forward direction and $V_r^{\neq}$ for the reverse direction.

which implying that the effects of low-occupancy orbitals cannot be ignored.

Although the overall results of the LRC approach are quit satisfactory for all three methods, the deviations for non-hydrogen systems are still far beyond the mean absolute deviation. There are 53 non-hydrogen molecules in the total 350 molecules. The MADs for this type of molecules are 12.7, 5.8, and 5.3 kcal/mol for the HF/6-31G(d), B3LYP/6-31G(d), and B3LYP/6-311G(2d,d,p) methods, respectively. For the two DFT methods, the deviations of PF_5 and SF_6 are above 20 kcal/mol. For the HF method, the deviations for molecules containing fluorine element are especially large, such as for ClF_3, F_2O, SF_6 and C_2F_6. The large deviations may be aroused by the inaccurate geometries optimized at these levels of theories and other factors unconsidered in the present Letter, such as spin–orbital coupling and relativistic effects [10,12].

The current LRC approaches using NBO descriptors further decrease the calculation error of a quantum mechanical method compared with the original approaches using electron pairs. After retraining using the same descriptors as in our previous work [19], the MADs for the 350 molecules are 7.4, 3.8 and 3.2 kcal/mol for the HF/6-31G(d), B3LYP/6-31G(d) and B3LYP/6-311G(2d,d,p) methods, respectively. Compared to the results of NBO descriptors (7.3, 3.3 and 2.7 kcal/mol), the deviations are all still larger.

4.2. Testing of the reaction barrier heights

Reaction barrier heights can now be corrected using the current LRC approach. This is achieved by substituting the fitted coefficients back to Eqs. (1) and (2) to calculate energies of molecules and atoms and then use them to calculate reaction barriers. It should be noticed that our LRC approach is designed to obtain relatively accurate energy of a molecule relative to its composing atoms and the selected descriptors characterize molecules best, while only one descriptor (unpaired electrons of atom) is used for atoms. Consequently, the correction coefficients obtained from this approach are most suitable for molecular systems. There are eight chemical

reactions involving no atoms in the BH42/03 reaction database [30,31]. However, two reactions of them have negative reaction barriers due to the well-known self-interaction problem of the DFT methods. In the end we just choose the remaining six reactions as our testing sets. The results presented in Table 5 are obtained at the B3LYP/6-311G(2d,d,p) level. The raw calculated barrier heights are all lower than the given best estimates [30,31], which is typical for most DFT methods. After linear regression correction, there is an obvious increase for every barrier height. The corrected barrier heights are all closer to the best-estimated values. The MAD for the 12 barrier heights is reduced from 5.3 to 2.9 kcal/mol, almost to the same accuracy as that for the heats of formation. It should be clarified that barrier heights of reactions involving atoms can also be improved, but the improvement is not as remarkable as for those involving only molecules.

5. Conclusions

The training set of 180 heats of formation used in our previous work is expanded to 350 heats of formation including 222 heats of formation in the G3/99 test set (with duplicated molecules deleted). The new set includes 350 heats of formation of small- and medium-sized organic, inorganic molecules, and radicals. At the same time, new descriptors obtained by the NBO analysis are employed in this Letter. The descriptors are the electron populations of different types of NBOs: two-center bonds (BD), one-center core pair (CR), one-center valence lone pair (LP), one-center Rydberg (RY*), two-center anti-bond (BD*), and non-Lewis valence lone pair (LP*). The number of the unpaired electrons of atom in ground state is also included as the descriptor. After linear regression correction, the MADs of the calculated ΔH_f^0s for the 350 molecules are greatly reduced from 284.1 to 7.3 kcal/mol for the HF/6-31G(d) method. In the mean time, the calculated ΔH_f^0 of the DFT methods have also been improved. The MADs are reduced from 8.2 to 3.3 kcal/mol and from 12.4 to 2.7 kcal/mol for the B3LYP/6-31G(d) and B3LYP/6-311G(2d,d,p)

methods, respectively. The current approach is not only an improvement over the previous approach on calculating heats of formation, but also is suitable for the calculation of reaction barriers. The MAD for 12 barrier heights is reduced from 5.3 to 2.9 kcal/mol.

Acknowledgements

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