Implicit Zero-Point Vibration Energy and Thermal Corrections in Rapid Estimation of Enthalpies of Formation from Hartree−Fock Total Energy and Partial Charges

Adrienn Ruzsinszky,*,[†] Christian Van Alsenoy,[‡] and Gábor I. Csonka*,[†]

Department of Inorganic Chemistry, Budapest University of Technology and Economics, H-1521 Budapest, Hungary, and Department of Chemistry, University of Antwerp UIA, Universiteitsplein 1, B-2610 Antwerpen, Belgium

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The rapid estimation of basis set error and correlation energy from partial charges (REBECEP) method is improved in a way that makes superfluous the explicit zero-point energy and thermal correction calculations. This saves considerable computational effort and increases the computational efficiency of the method. The new REBECZTEP (zero-point energy and thermal correction included) parameters provide an energy that can be used to calculate an enthalpy of formation using atomic enthalpies and energies without any further correction. An intermediate level where only the zero-point energy is included in the parameters, REBECZEP parameters, is also studied. The performance of the new parameter set that corrects the HF−SCF energy using atomic partial charges was studied for the 6-31G(d) and 6-311+G(2d,p) basis sets, for Mulliken, natural population, and stockholder charges. A total of 117 closed-shell neutral molecules with correctly measured experimental enthalpies of formation from the G2/97 and G3/99 database composed of H, C, N, O, and F atoms were selected for the test. The best REBECZTEP results were obtained using the HF/6-311+G(2d,p) natural population analysis charges. The average absolute deviation from the experimental enthalpies of formation for 115 molecules is 1.48 kcal/mol. This deviation was decreased to 1.22 kcal/mol on a reduced set of 110 molecules. This compares favorably to our previous best REBECEP results on the same test set of 117 molecules (average absolute deviation: 1.65 kcal/mol). These results also compare favorably to Gaussian-3 and B3LYP/6-311+G(3df,2p) enthalpies of formation (for 51 large molecules the corresponding average absolute deviations are 0.94 and 7.09 kcal/mol, respectively). The considerably faster REBECZTEP method performs considerably better for the 117 molecules with a moderate 6-31G(d) basis set than the B3LYP method with large 6-311+G(3df,2p) basis set.

Introduction

In a series of papers,[1−4] we developed a method that is suitable for rapid estimation of basis set error and correlation energy from partial charges (REBECEP). In these papers, we investigate REBECEP results obtained with Mulliken, natural population analysis (NPA),[5] and stockholder[6] atomic charges. For the development and test of the performance of the method, we selected 117 molecules of G2/97[7,8] and G3/99[9] molecular geometry databases. These closed-shell neutral molecules are composed of H, C, N, O, and F atoms. The performance of the method was compared to the performance of the Gaussian-3[10] (G3) and the B3LYP/6-311+G(3df,2p) methods on the same molecules.

In our latest study,[11] we improved the applicability (made the calculations faster) and increased the precision of the REBECEP method in several ways. We suggested using a total energy derived from experimental enthalpies of formation instead of G3 energies in our fitting procedure. This increases the precision because the error of the G3 method is eliminated. We also suggested the use of B3LYP/6-31G(d) equilibrium geometries instead of MP2/6-31G(d) geometries. This provides a considerable speed up, and the equilibrium geometries are usually closer to the experimental results.

We compared the various REBECEP enthalpies of formation to the experimental enthalpies of formation of 117 molecules. The performance of the REBECEP method combined with the 6-31G(d) basis set decreases in the following order: NPA,[5] stockholder,[6] and Mulliken. To obtain stockholder charges, we used the methodology described in ref 12. The conclusion is different for the 6-311+G(2d,p) basis set: using this basis set stockholder charges produced slightly better results. The root-mean-square (rms) and the average absolute (a.a.) deviations of ΔH_f^0 (M, REBECEP, expt., 6-31G(d), NPA) and experimental results for 117 molecules are 2.16 and 1.65 kcal/mol, respectively. Leaving out the three most problematic molecules, the azulene, the butanedinitrile, and the carbonic difluoride, the rms and the a.a. deviations decreased to 1.90 and 1.50 kcal/mol, respectively. These results are close to our goal to predict the molecular enthalpies of formation within the chemical accuracy (1−2 kcal/mol).

To improve the applicability of the REBECEP method in the current paper, we focus on the possible elimination of the most time-consuming step of the procedure the HF/6-31G(d) frequency calculation that is required for zero-point vibration energy (ZPE) and thermal correction calculations. This modification of the method requires the use a total energy corrected by ZPE and thermal corrections instead of total energy derived from experimental enthalpies in our fitting procedure. We shall study how this speeds up the method and influences the

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* To whom correspondence should be addressed.

[†] Budapest University of Technology and Economics.

[‡] University of Antwerp UIA.

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precision of the predicted enthalpies of formation. For comparison reasons, we use the same database of charges, geometries, and energies of 117 closed shell molecules[13] for this study that was used in our previous REBECEP study.[11]

REBECZTEP Method

We briefly summarize the most important equations of the method. For a given molecule M, the so-called REBECEP enthalpy of formation, ΔH_f^0(M, REBECEP, expt., basis set, charge def.), can be obtained as follows:

$$\Delta H_f^0(\text{M, REBECEP, expt., basis set, charge def.}) = E_T(\text{M, REBECEP, expt., basis set, charge def.}) + E_{ZP}(\text{M, G3}) + E_{\text{therm}}(\text{M, G3}) + \sum_{A=1}^{M} [\Delta H_f^0(\text{A, expt.}) - E_T(\text{A, G3}) - E_{\text{therm}}(\text{A, expt.})] \quad (1)$$

where E_T(M, REBECEP, expt., basis set, charge def.) is the REBECEP total energy calculated from the parameter set fitted to experimental, expt., results and HF−SCF partial charges using a specific basis set, E_{ZP}(M, G3) is zero-point vibration energy of the molecule M (scaled HF/6-31G(d) ZPE),[14] E_{therm}(M, G3) is the difference between the enthalpy of the molecule at $T = 298.15$ and 0 K (calculated from the molecular heat capacity). The atomic contributions of the constituent atoms of molecule M are summed: ΔH_f^0(A, expt.)'s are the experimental standard enthalpies of formation, E_T(A, G3)'s are the G3 total energies, and E_{therm}(A, expt.)'s are the differences between the enthalpies at $T = 298.15$ and 0 K (calculated from the elemental heat capacities) of the atoms. The actual values of E_{ZP}(M, G3), E_{therm}(M, G3), and E_T(A, G3) are method dependent, and we use G3 values.

The E_T(M, REBECEP, expt., basis set, charge def.) total energy can be obtained as a sum of an E_T(HF−SCF/basis set) and the REBECEP energy correction:

$$E_T(\text{M, REBECEP, expt., basis set, charge def.}) = E_T(\text{HF-SCF/basis set}) + E_{\text{corr}}(\text{REBECEP, expt., basis set, charge def.}) \quad (2)$$

Because E_T(HF−SCF/basis set) contains basis set error, thus, the REBECEP energy correction is basis set dependent. In the ideal case, the E_T(M, REBECEP, expt., basis set, charge def.) is basis set independent; however, a small basis set dependence can be observed in practice.[11] The basis set dependence of the E_T(M, REBECEP, expt., basis set, charge def.) is considerably smaller than the basis set dependence of its components.[11] The energy correction is the sum of the atomic corrections:

$$E_{\text{corr}}(\text{REBECEP, expt., basis set, charge def.}) \equiv \sum_{A \in M} E_{\text{corr}}(Z_A, N_A, \text{expt., basis set, charge def.}) \quad (3)$$

where Z_A is the nuclear charge of atom A and N_A is the "electron content" on atom A, noninteger, it is equal to Z_A − partial charge. The E_{corr}(Z_A, N_A, expt., basis set, charge def.) atomic energy terms of eq 4 are interpolated:

$$E_{\text{corr}}(Z_A, N_A, \text{expt., basis set, charge def.}) = (N_A - \text{N1})\, E_{\text{par}}(Z_A, \text{N2, expt., basis set, charge def.}) + (\text{N2} - N_A)\, E_{\text{par}}(Z_A, \text{N1, expt., basis set, charge def.}) \quad (4)$$

where N1 and N2 are integer numbers of electrons, with $\text{N1} \le N_A \le \text{N2} = \text{N1} + 1$. E_{par}(Z_A, N2, expt., basis set, charge def.) and E_{par}(Z_A, N1, expt., basis set, charge def.) in eq 4 are the so-called REBECEP atomic parameters that transform the partial charge into energy correction. For hydrogen atoms, we suggest to use a single parameter, E_{corr}(1, N_A, expt., basis set, charge def.) = $N_A E_{\text{par}}$(1, 2, expt., basis set, charge def.)/2.

These REBECEP atomic parameters can be obtained from the fitting procedure that finds the minimum of root-mean-square deviation between calculated and experimental enthalpies of formation.

An energy that includes the so-called "experimental" total energy plus zero-point vibrational energy and thermal corrections, E_{TZT}(M, G3, expt.), can be obtained from the experimental enthalpy of formation:

$$E_{TZT}(\text{M, G3, expt.}) = E_T(\text{M, G3, expt.}) + E_{ZP}(\text{M, G3}) + E_{\text{therm}}(\text{M, G3}) - \sum_{A=1}^{M} E_{\text{therm}}(A, \text{G3}) = \Delta H_f^0(\text{M, expt.}) - \sum_{A=1}^{M} [\Delta H_f^0(A, \text{expt.}) - E_T(A, \text{G3})] \quad (5)$$

where ΔH_f^0(M, expt.) is the experimental enthalpy of formation. Using this energy in the fitting procedure provides considerable computational advantages over the method used in our previous paper. This procedure makes redundant the very time-consuming frequency calculations. Using such fitted correction parameters, one can obtain the ZPE and thermal energy corrected REBECZTEP energy in a single step:

$$E_{TZT}(\text{M, REBECZTEP, expt., basis set, charge def.}) = E_T(\text{HF-SCF/basis set}) + E_{\text{corr}}(\text{REBECZTEP, expt., basis set, charge def.}) \quad (6)$$

This energy is used in the following way:

$$\Delta H_f^0(\text{M, REBECZTEP, expt., basis set, charge def.}) = E_{TZT}(\text{M, REBECZTEP, expt., basis set, charge def.}) + \sum_{A=1}^{M} [\Delta H_f^0(A, \text{expt.}) - E_T(A, \text{G3})] \quad (7)$$

In the fitting procedure we minimize $Y = \sum_{(i=1,L)} [E_{TZT}(\text{M, G3, expt.})_i - E_{TZT}(\text{M, REBECZTEP, expt., basis set, charge def.})_i]^2$ for a selected set of L molecules. The details of the fitting procedure are described elsewhere.[2,3] We note that a similar procedure can be used just for the inclusion of the ZPE correction into the atomic correlation energy parameters. The E_{TZ}(M, REBECZEP, expt., basis set, charge def.) energy obtained this way requires the usual thermal corrections in eq 1 in order to obtain the calculated ΔH_f^0 values.

Results and Discussion

In Table 1, we show the fitted atomic parameters to be used in eq 4 for closed shell molecules in the vicinity of their equilibrium geometry. We present 12 parameter sets for two basis sets and three partial charge calculation methods. The REBECZEP atomic parameters were fitted using the total energy plus the zero-point energy (cf. E_{corr}(ZPE) in Table 2), and the REBECZTEP atomic parameters were fitted using the total energy plus the zero-point energy and thermal correction (cf. E_{corr}(therm) in Table 2). The parameters in Table 1 transform

TABLE 1: Fitted Atomic Correction Parameters, E_{corr}(N1, Z_A), in Hartree for eq 4 to Obtain E_{corr}(REBECZEP or REBECZTEP) from HF−SCF/6-31G(d) or 6-311+G(2d,p) Energies and NPA, Stockholder, and Mulliken Charges

atomic number		basis: 6-31G(d)						basis: 6-311+G(2d,p)					
		REBECZEP[a]			REBECZTEP[b]			REBECZEP[a]			REBECZTEP[b]		
Z_A	N1	NPA	Stockh.	Mulliken	NPA	Stockh.	Mulliken	NPA	Stockh.	Mulliken	NPA	Stockh.	Mulliken
1	2	−0.0085	−0.0204	−0.0119	−0.0116	−0.0228	−0.0152	−0.0151	−0.0188	−0.0157	−0.0181	−0.0213	−0.0187
6	4	−0.1207		−0.1085	−0.1215		−0.1125	−0.1595		−0.1628	−0.1606		−0.1660
6	5	−0.1674	−0.1243	−0.1625	−0.1672	−0.1228	−0.1637	−0.1762	−0.1591	−0.1785	−0.1763	−0.1576	−0.1795
6	6	−0.2149	−0.2133	−0.2134	−0.2150	−0.2136	−0.2137	−0.2060	−0.2055	−0.2062	−0.2061	−0.2057	−0.2062
6	7	−0.2501	−0.2982	−0.2549	−0.2495	−0.2903	−0.2527	−0.2272	−0.2444	−0.2325	−0.2263	−0.2359	−0.2306
6	8									−0.2667			−0.2623
7	6	−0.2672	−0.2771	−0.2642	−0.2697	−0.2761	−0.2689	−0.2672	−0.2996	−0.2855	−0.2703	−0.2985	−0.2911
7	7	−0.2770	−0.2804	−0.2792	−0.2766	−0.2816	−0.2781	−0.2620	−0.2656	−0.2610	−0.2614	−0.2669	−0.2608
7	8	−0.3079	−0.3131	−0.3083	−0.3092	−0.3098	−0.3091	−0.2764	−0.2562	−0.2768	−0.2777	−0.2519	−0.2775
7	9	−0.3842			−0.3725			−0.3554			−0.3034		
8	8	−0.3360	−0.3340	−0.3335	−0.3358	−0.3345	−0.3329	−0.3120	−0.3098	−0.3133	−0.3117	−0.3103	−0.3136
8	9	−0.3643	−0.3770	−0.3643	−0.3649	−0.3768	−0.3644	−0.3210	−0.3103	−0.3114	−0.3214	−0.3100	−0.3109
9	9	−0.3650	−0.3683	−0.3680	−0.3651	−0.3693	−0.3670	−0.3369	−0.3365	−0.3385	−0.3368	−0.3374	−0.3387
9	10	−0.4093	−0.4211	−0.4077	−0.4102	−0.4185	−0.4094	−0.3485	−0.3341	−0.3438	−0.3495	−0.3314	−0.3434

[a] Only ZPE correction is applied in eq 5. [b] Corresponds to eq 5.

the atomic charges into atomic energy corrections according to eq 4, and these atomic corrections are summed according to eq 3. Equation 6 and 7 and yield the desired enthalpy of formation. We note that eq 7 is valid for the REBECZTEP parameter set; to obtain enthalpy of formation from the REBECZEP parameter set, one should add the thermal corrections shown in eq 1

$$[E_{\text{therm}}(\text{M, G3}) - \sum_{A=1}^{M} E_{\text{therm}}(A, \text{expt.})]$$

The main question is now how the inclusion of the zero-point energy and the thermal correction into the atomic parameter set will influence the quality of the results?

In another recent study, to be published elsewhere, the rapid estimation of the explicit G3 ZPE from HF/6-31G(d) partial charges is analyzed. The results show that a.a. deviation between the approximated and G3 ZPE is about 0.9−1.0 kcal/mol.[15] This shows that the ZPE in itself can be approximated by atomic contributions. However, if this error would be added to the REBECEP error that would considerably decrease the value of such method.

For comparison reasons, the same 117 test molecules were taken from the G3/99 thermochemistry database as in our previous study.[11] The program used to obtain the fitted parameters is available from the authors via e-mail or regular mail.

Analysis of the atomic parameters in Table 1 shows that the difference between the atomic parameters obtained with the large and small basis sets are increasing with the electronegativity of the atom. This effect is the largest for stockholder partial charges (cf. parameters for F in Table 1). Similar observation can be made for the REBECEP parameters published previously.[11] In our previous paper, we identified the molecules with largest deviations from the experimental results using the REBECEP, NPA, and 6-31G(d) parameter set: the butanedinitrile (92) and azulene (117) (deviations: +5.1 and −8.1 kcal/mol, respectively). These two molecules show +6.0 and −8.0 kcal/mol deviations, respectively, if the REBECZEP or REBECZTEP parameter set is used together with NPA charges and the 6-31G(d) basis set (Table 3). These small differences suggest that REBECEP, REBECZEP, and REBECZTEP parametrizations provide similar results. For a more general comparison, we show the rms and a.a. deviations between the experimental and calculated enthalpies of formation in Table 4. Comparison of these results with our previous results for REBECEP data yields the following: The inclusion of the ZPE into the parametrizations provide worsening for the combination of NPA charges with 6-31G(d) basis set (e.g., the a.a. deviation increases from 1.65[11] to 2.04 kcal/mol). It is worth noting that inclusion of the thermal corrections in the current very simple form improves these results (a.a. deviation is decreased to 1.85 kcal/mol, cf. Table 4). The stockhholder charges provide better REBECZEP or REBECZTEP results than REBECEP results. For example, the stockholder-6-31G(d) REBECZTEP a.a. deviation (1.67 kcal/mol in Table 4) is smaller than the corresponding REBECEP deviation (1.79 kcal/mol).[11] The combination of Mulliken charges with the 6-31G(d) basis set provide a.a. deviation of 1.93, 1.95, and 1.88 kcal/mol for REBECEP, REBECZEP, and REBECZTEP parametrizations, respectively. This shows that the latter two approximations do not influence the quality of the results obtained with Mulliken population analysis.

The results in Table 4 also show that the REBECZTEP results calculated using the large 6-311+G(2d,p) basis set is superior to any previous results. Our previous REBECEP results[11] provided 1.86 and 2.35 kcal/mol a.a. and rms deviations for this larger basis set and NPA charges. Our current results show a considerable improvement for the combination of NPA charges with this larger basis set; the inclusion of the ZPE decreases the a.a. and rms deviations to 1.48 and 1.96 kcal/mol, respectively (cf. Table 4). The use of stockholder charges or the thermal corrections provide only very small changes in this respect. The use of Mulliken charges with this large basis set yields 1.82 kcal/mol a.a. deviation. We note that leaving out the five most problematic molecules (vide infra) yielded 1.22 and 1.52 kcal/mol a.a. and rms deviations, respectively, for 110 molecules (NPA and 6-311+G(2d,p) basis set). These are the best results we could obtain with the current method, and these results compare rather favorably to Gaussian-3 and B3LYP/6-311+G(3df,2p) enthalpies of formation. For larger molecules (57−117 in Table 3), the corresponding a.a. deviations are 0.94 and 7.09 kcal/mol, respectively.

After this general discussion, we identify the molecules which show the largest deviation from the experiment. The azulene was already mentioned. This molecule shows far the largest negative deviation from experiment (from −8.0 to −10 kcal/mol depending on the method). This behavior is general for the REBECEP type of method and shows that our model requires a different parameter set to capture the correlation

TABLE 2: Species, Number of Nuclei and Electrons, the HF−SCF, and Correction Energies (Hartree) for Experimental Quality Total Energy for 117 Selected Molecules Calculated with 6-31G(d) and 6-311+G(2d,p) Basis Sets

		no.		6-31G(d)			6-311+G(2d,p)		
no.	species	nuclei	elect	E(HF)	E_{corr}(ZPE)	E_{corr}(therm)	E(HF)	E_{corr}(ZPE)	E_{corr}(therm)
1	methane(CH_4)	5	10	−40.1949	−0.2621	−0.2652	−40.2101	−0.2470	−0.2500
2	ammonia(NH_3)	4	10	−56.1836	−0.3247	−0.3274	−56.2148	−0.2935	−0.2963
3	water(H_2O)	3	10	−76.0098	−0.3727	−0.3739	−76.0527	−0.3298	−0.3309
4	hydrogenfluoride(HF)	2	11	−100.0023	−0.3984	−0.3984	−100.0526	−0.3481	−0.3481
5	acetylene(C_2H_2)	4	14	−76.8168	−0.4600	−0.4602	−76.8436	−0.4333	−0.4335
6	ethylene($H_2C{=}CH_2$)	6	16	−78.0311	−0.4760	−0.4792	−78.0583	−0.4486	−0.4520
7	ethane($H_3C{-}CH_3$)	8	18	−79.2283	−0.4946	−0.5007	−79.2538	−0.4691	−0.4752
8	hydrogencyanide(HCN)	3	14	−92.8735	−0.5016	−0.5018	−92.9018	−0.4733	−0.4735
9	formaldehyde($H_2C{=}O$)	4	16	−113.8648	−0.5653	−0.5669	−113.9047	−0.5254	−0.5271
10	methanol($CH_3{-}OH$)	6	18	−115.0341	−0.5949	−0.5992	−115.0814	−0.5477	−0.5520
11	hydrazine($H_2N{-}NH_2$)	6	18	−111.1678	−0.6109	−0.6164	−111.2173	−0.5614	−0.5670
12	hydrogenperoxide(HO−OH)	4	18	−150.7613	−0.7047	−0.7071	−150.8250	−0.6411	−0.6435
13	carbon dioxide (CO_2)	3	22	−187.6310	−0.8673	−0.8675	−187.6923	−0.8059	−0.8062
14	carbon tetrafuoride (CF_4)	5	42	−435.6415	−1.6649	−1.6670	−435.7779	−1.5284	−1.5306
15	carbonic difluoride (COF_2)	4	32	−311.6116	−1.2757	−1.2768	−311.7115	−1.1758	−1.1770
16	dinitrogen monoxide (N_2O)	3	22	−183.6745	−0.9053	−0.9068	−183.7333	−0.8465	−0.8480
17	nitrogen trifluoride (NF_3)	4	34	−352.5318	−1.4009	−1.4032	−352.6473	−1.2855	−1.2877
18	ethene, tetrafluoro- ($F_2C{=}CF_2$)	6	48	−473.4123	−1.8891	−1.8904	−473.5679	−1.7333	−1.7347
19	acetonitrile, trifluoro- (CF_3CN)	6	46	−428.4764	−1.7926	−1.7941	−428.6057	−1.6630	−1.6647
20	propyne(C_3H_4)	7	22	−115.8630	−0.6927	−0.6954	−115.8996	−0.6561	−0.6588
21	allene(C_3H_4)	7	22	−115.8603	−0.6932	−0.6962	−115.8971	−0.6563	−0.6594
22	cyclopropene(C_3H_4)	7	22	−115.8219	−0.6981	−0.7014	−115.8555	−0.6645	−0.6679
23	propylene(C_3H_6)	9	24	−117.0706	−0.7114	−0.7173	−117.1081	−0.6739	−0.6799
24	cyclopropane(C_3H_6)	9	24	−117.0581	−0.7106	−0.7171	−117.0912	−0.6775	−0.6840
25	propane(C_3H_8)	11	26	−118.2630	−0.7304	−0.7389	−118.2990	−0.6944	−0.7029
26	*trans*-1,3-butadiene (C_4H_6)	10	30	−154.9182	−0.9285	−0.9342	−154.9667	−0.8800	−0.8857
27	dimethylacetylene (C_4H_6)	10	30	−154.9075	−0.9265	−0.9310	−154.9535	−0.8806	−0.8850
28	methylenecyclopropane (C_4H_6)	10	30	−154.8863	−0.9254	−0.9315	−154.9300	−0.8817	−0.8878
29	bicyclo[1.1.0]butane (C_4H_6)	10	30	−154.8706	−0.9343	−0.9408	−154.9116	−0.8932	−0.8997
30	cyclobutene(C_4H_6)	10	30	−154.8986	−0.9294	−0.9360	−154.9421	−0.8859	−0.8924
31	cyclobutane (C_4H_8)	12	32	−156.0964	−0.9441	−0.9534	−156.1389	−0.9016	−0.9109
32	isobutene(C_4H_8)	12	32	−156.1097	−0.9493	−0.9574	−156.1574	−0.9015	−0.9096
33	*tran*s-butane(C_4H_{10})	14	34	−157.2976	−0.9666	−0.9775	−157.3442	−0.9200	−0.9309
34	isobutane(C_4H_{10})	14	34	−157.2982	−0.9693	−0.9803	−157.3447	−0.9227	−0.9338
35	spiropentane(C_5H_8)	13	38	−193.9166	−1.1632	−1.1721	−193.9667	−1.1131	−1.1220
36	benzene(C_6H_6)	12	42	−230.7019	−1.3515	−1.3581	−230.7631	−1.2902	−1.2969
37	difluoromethane(H_2CF_2)	5	26	−237.8948	−0.9670	−0.9698	−237.9780	−0.8838	−0.8867
38	trifluoromethane(HCF_3)	5	34	−336.7692	−1.3165	−1.3192	−336.8797	−1.2059	−1.2087
39	methylamine($H_3C{-}NH_2$)	7	18	−95.2089	−0.5529	−0.5586	−95.2470	−0.5147	−0.5204
40	acetonitrile($CH_3{-}CN$)	6	22	−131.9255	−0.7339	−0.7366	−131.9639	−0.6954	−0.6981
41	nitromethane($CH_3{-}NO_2$)	7	32	−243.6570	−1.2086	−1.2134	−243.7395	−1.1261	−1.1309
42	methylnitrite($CH_3{-}O{-}N{=}O$)	7	32	−243.6624	−1.2001	−1.2049	−243.7396	−1.1228	−1.1277
43	formic acid (HCOOH)	5	24	−188.7597	−0.8968	−0.8996	−188.8278	−0.8287	−0.8315
44	methyl formate ($HCOOCH_3$)	8	32	−227.7867	−1.1240	−1.1291	−227.8599	−1.0508	−1.0559
45	acetamide (CH_3CONH_2)	9	32	−207.9738	−1.0934	−1.0993	−208.0457	−1.0215	−1.0274
46	aziridine (C_2H_4NH)	8	24	−133.0370	−0.7658	−0.7720	−133.0797	−0.7231	−0.7294
47	cyanogen (NCCN)	4	26	−184.5863	−0.9820	−0.9813	−184.6340	−0.9342	−0.9336
48	dimethylamine ($(CH_3)_2NH$)	10	26	−134.2378	−0.7848	−0.7931	−134.2831	−0.7394	−0.7477
49	*trans*-ethylamine ($CH_3CH_2NH_2$)	10	26	−134.2465	−0.7870	−0.7953	−134.2950	−0.7386	−0.7468
50	ketene (CH_2CO)	5	22	−151.7228	−0.7830	−0.7843	−151.7725	−0.7331	−0.7345
51	oxirane (C_2H_4O)	7	24	−152.8655	−0.8051	−0.8098	−152.9138	−0.7568	−0.7616
52	acetaldehyde (CH_3CHO)	7	24	−152.9144	−0.8002	−0.8044	−152.9648	−0.7498	−0.7540
53	glyoxal (HCOCOH)	6	30	−226.5891	−1.1033	−1.1055	−226.6620	−1.0303	−1.0326
54	ethanol (CH_3CH_2OH)	9	26	−154.0743	−0.8303	−0.8371	−154.1320	−0.7725	−0.7794
55	dimethyl ether (CH_3OCH_3)	9	26	−154.0634	−0.8219	−0.8288	−154.1147	−0.7705	−0.7774
56	vinyl fluoride ($CH_2{=}CHF$)	6	24	−176.8809	−0.8298	−0.8328			
57	acrylonitrile($CH_2{=}CHCN$)	7	28	−169.7653	−0.9527	−0.9552	−169.8135	−0.9044	−0.9070
58	acetone (CH_3COCH_3)	10	32	−191.9606	−1.0365	−1.0427	−192.0215	−0.9755	−0.9817
59	acetic acid (CH_3COOH)	8	32	−227.8079	−1.1322	−1.1373	−227.8868	−1.0532	−1.0584
60	acetyl fluoride (CH_3COF)	7	32	−251.7959	−1.1546	−1.1583	−251.8779	−1.0726	−1.0763
61	2-propanol ($(CH_3)_2CHOH$)	12	34	−193.1138	−1.0678	−1.0771	−193.1819	−0.9998	−1.0091
62	methyl ethyl ether ($C_2H_5OCH_3$)	12	34	−193.1033	−1.0569	−1.0662	−193.1653	−0.9948	−1.0042
63	trimethylamine ($(CH_3)_3N$)	13	34	−173.2681	−1.0192	−1.0302	−173.3209	−0.9664	−0.9775
64	furan (C_4H_4O)	9	36	−228.6230	−1.2378	−1.2429	−228.6893	−1.1714	−1.1766
65	pyrrole (C_4H_5N)	10	36	−208.8061	−1.2009	−1.2072	−208.8677	−1.1392	−1.1456
66	pyridine (C_5H_5N)	11	42	−246.6940	−1.3991	−1.4056	−246.7599	−1.3331	−1.3397
67	methyl allene (C_4H_6)	10	30	−154.8984	−0.9287	−0.9340	−154.9453	−0.8818	−0.8871
68	isoprene (C_5H_8)	13	38	−193.9557	−1.1669	−1.1748	−194.0145	−1.1080	−1.1160

TABLE 2 (Continued)

		no.		6-31G(d)			6-311+G(2d,p)		
no.	species	nuclei	elect	*E* (HF)	E_{corr} (ZPE)	E_{corr} (therm)	*E* (HF)	E_{corr} (ZPE)	E_{corr} (therm)
69	cyclopentane (C_5H_{10})	15	40	−195.1627	−1.1805	−1.1925	−195.2155	−1.1277	−1.1397
70	*n*-pentane (C_5H_{12})	17	42	−196.3321	−1.2032	−1.2165	−196.3892	−1.1461	−1.1593
71	neo-pentane (C_5H_{12})	17	42	−196.3328	−1.2103	−1.2238	−196.3897	−1.1534	−1.1670
72	1,3-cyclohexadiene (C_6H_8)	14	44	−231.8302	−1.3782	−1.3873	−231.8943	−1.3142	−1.3233
73	1,4-cyclohexadiene (C_6H_8)	14	44	−231.8321	−1.3769	−1.3860	−231.8971	−1.3119	−1.3210
74	cyclohexane (C_6H_{12})	18	48	−234.2069	−1.4163	−1.4313	−234.2700	−1.3532	−1.3682
75	*n*-hexane (C_6H_{14})	20	50	−235.3666	−1.4393	−1.4547	−235.4342	−1.3716	−1.3871
76	3-methyl pentane (C_6H_{14})	20	50	−235.3631	−1.4446	−1.4601	−235.4306	−1.3771	−1.3925
77	toluene ($C_6H_5CH_3$)	15	50	−269.7387	−1.5912	−1.5994	−269.8101	−1.5198	−1.5281
78	*n*-heptane (C_7H_{16})	23	58	−274.4011	−1.6755	−1.6932	−274.4793	−1.5973	−1.6150
79	cyclooctatetraene (C_8H_8)	16	56	−307.5215	−1.8125	−1.8208	−307.6058	−1.7282	−1.7365
80	*n*-octane (C_8H_{18})	26	66	−313.4356	−1.9119	−1.9320	−313.5243	−1.8232	−1.8433
81	naphthalene ($C_{10}H_8$)	18	68	−383.3526	−2.2336	−2.2425	−383.4489	−2.1372	−2.1462
82	acetic acid methyl ester (CH_3COOCH_3)	11	40	−266.8340	−1.3613	−1.3681	−266.9181	−1.2771	−1.2840
83	*t*-butanol $(CH_3)_3COH$	15	42	−232.1517	−1.3080	−1.3197	−232.2299	−1.2298	−1.2414
84	aniline ($C_6H_5NH_2$)	14	50	−285.7291	−1.6485	−1.6570	−285.8124	−1.5652	−1.5737
85	phenol (C_6H_5OH)	13	50	−305.5560	−1.6909	−1.6981	−305.6472	−1.5996	−1.6069
86	divinyl ether (C_4H_6O)	11	38	−229.7589	−1.2594	−1.2657	−229.8327	−1.1856	−1.1919
87	tetrahydrofuran (C_4H_8O)	13	40	−230.9748	−1.2709	−1.2811	−231.0431	−1.2024	−1.2127
88	cyclopentanone (C_5H_8O)	14	46	−268.8645	−1.4831	−1.4930	−268.9417	−1.4058	−1.4157
89	benzoquinone ($C_6H_4O_2$)	12	56	−379.2309	−1.9859	−1.9908	−379.3404	−1.8762	−1.8813
90	urea ($NH_2-CO-NH_2$)	8	32	−223.9822	−1.1452	−1.1514	−224.0646	−1.0628	−1.0690
91	pyrimidine($C_4H_4N_2$)	10	42	−262.6910	−1.4430	−1.4493	−262.7621	−1.3719	−1.3782
92	butanedinitrile ($N\equiv C-CH_2-CH_2\text{-}C\equiv N$)	10	42	−262.6861	−1.4448	−1.4490	−262.7580	−1.3729	−1.3770
93	pyrazine($C_4H_4N_2$)	10	42	−262.6805	−1.4535	−1.4597	−262.7513	−1.3826	−1.3889
94	acetyl acetylene ($CH_3-CO-C\equiv CH$)	9	36	−228.5861	−1.2384	−1.2415	−228.6555	−1.1691	−1.1721
95	crotonaldehyde ($CH_3-CH=CH-CHO$)	11	38	−229.8016	−1.2499	−1.2559	−229.8727	−1.1787	−1.1848
96	acetic anhydride ($CH_3-CO-O-CO-CH_3$)	13	54	−379.5790	−1.9011	−1.9083	−379.6956	−1.7844	−1.7916
97	isobutane nitrile ($(CH_3)_2CH-C\equiv N$)	12	38	−209.9956	−1.2090	−1.2167	−210.0552	−1.1493	−1.1571
98	methyl ethyl ketone ($CH_3-CO-CH_2-CH_3$)	13	40	−230.9962	−1.2719	−1.2805	−231.0671	−1.2010	−1.2096
99	isobutanal($(CH_3)_2CH-CHO$)	13	40	−230.9839	−1.2753	−1.2840	−231.0550	−1.2040	−1.2130
100	1,4-dioxane($C_4H_8O_2$)	14	48	−305.8227	−1.5967	−1.6084	−305.9163	−1.5029	−1.5148
101	tetrahydropyrrole(C_4H_8NH)	14	40	−211.1440	−1.2332	−1.2450	−211.2065	−1.1706	−1.1825
102	nitro-s-butane ($CH_3-CH_2-CH(CH_3)\text{-}NO_2$)	16	56	−360.7691	−1.9189	−1.9309	−360.8821	−1.8059	−1.8179
103	diethyl ether ($CH_3-CH_2-O-CH_2-CH_3$)	15	42	−232.1432	−1.2936	−1.3051	−232.2158	−1.2209	−1.2325
104	dimethyl acetal ($CH_3-CH(OCH_3)_2$)	16	50	−306.9912	−1.6224	−1.6347	−307.0873	−1.5261	−1.5386
105	*tert*-butylamine($(CH_3)_3C-NH_2$)	16	42	−212.3203	−1.2668	−1.2799	−212.3895	−1.1977	−1.2108
106	*N*-methyl pyrrole (cyc-$C_4H_4N-CH_3$)	13	44	−247.8369	−1.4352	−1.4437	−247.9061	−1.3659	−1.3745
107	tetrahydropyran ($C_5H_{10}O$)	16	48	−270.0161	−1.5066	−1.5200	−270.0943	−1.4283	−1.4418
108	diethyl ketone($CH_3-CH_2-CO-CH_2-CH_3$)	16	48	−270.0316	−1.5066	−1.5174	−270.1124	−1.4257	−1.4366
109	isopropyl acetate ($CH_3-CO-O-CH(CH_3)_2$)	17	56	−344.9123	−1.8354	−1.8471	−345.0173	−1.7304	−1.7420
110	piperidine (cyc-$C_5H_{10}NH$)	17	48	−250.1859	−1.4702	−1.4849	−250.2582	−1.3978	−1.4125
111	*tert*-butyl methyl ether($(CH_3)_3C-O-CH_3$)	18	50	−271.1737	−1.5380	−1.5519	−271.2563	−1.4553	−1.4693
112	1,3-difluorobenzene($C_6H_4F_2$)	12	58	−428.4033	−2.0614	−2.0666	−428.5294	−1.9352	−1.9405
113	1,4-difluorobenzene($C_6H_4F_2$)	12	58	−428.4017	−2.0620	−2.0672	−428.5278	−1.9357	−1.9411
114	fluorobenzene (C_6H_5F)	12	50	−329.5531	−1.7069	−1.7130	−329.6467	−1.6132	−1.6193
115	di-isopropyl ether ($(CH_3)_2CH-O-CH(CH_3)_2$)	21	58	−310.2167	−1.7714	−1.7875	−310.3098	−1.6782	−1.6944
116	ethane-hexafluoro- (C_2F_6)	8	66	−672.3791	−2.6089	−2.6119	−672.5913	−2.3966	−2.3998
117	azulene ($C_{10}H_8$)	18	68	−383.2806	−2.2531	−2.2618	−383.3792	−2.1545	−2.1633

energy in this molecule. Our analysis of charges showed that it is not possible to obtain good quality results with the same parameter set for azulene and the rest of the 116 molecules of the database. Three other notoriously problematic molecules can be identified in Table 3: namely, carbonic difluoride (15), cyclopropene (22), and bicyclo[1.1.0]butane (29). We note that the G3[9] and G3SX[16] enthalpies of formation show considerable −3.5 kcal/mol deviation from experiment for carbonic difluoride (15) molecule. The experimental error is also fairly large for this molecule (cf. 1.4 kcal/mol error in Table 4 and in ref 17). The uncertainties about the enthalpy of formation and the large deviation from the best theoretical results suggest removing this molecule from the database; however, we kept it for the current comparison with G3 results. The enthalpy of formation of carbonic difluoride has been deleted recently from the G2/97 test set because a new experimental upper limit[18] has been reported that casts doubt on the value in the database.

The cyclopropene (22) and the bicyclo[1.1.0]butane (29) have rather strained structures, and our method fails to provide good quality results for such molecules (the error range is from −3.1 to −6.3 kcal/mol, cf. Table 3). As it was already mentioned, the calculated enthalpy of formation of the butanedinitrile (92) shows the largest positive deviation from the experiment if NPA charges are used (independent of basis set). Inspection of the values in Table 3 shows that this problem can be solved by using stockholder charges. Leaving out these five most problematic molecules yielded 1.22 kcal/mol a.a. deviation respectively for the remaining 110 molecules if the calculation is performed with NPA charges and 6-311+G(2d,p) basis set.

Inspection of the results in the Table 3 shows that the stockholder results are rather poor for the small hydrides that contain a heavy atom with large electronegativity. More than 4 kcal/mol deviation from the experimental enthalpy of formation can be observed for ammonia (2), water (3), hydrogen-fluoride

TABLE 3: Experimental Enthalpies of Formation (kcal/mol) and Deviation (kcal/mol) between Experimental Enthalpies of Formation and Calculated REBECZTEP Enthalpies of Formation Depending on the Basis Sets [6-31G(d) or 6-311+G(2d,p)] and Partial Charge Calculation Methods [NPA or Stockholder][a]

				deviation (expt.-REBECZTEP)			
		expt. ΔH_f^0		6-31G(d)		6-311+G(2d,p)	
no.	species	value	error	NPA	Stockh.	NPA	Stockh.
1	methane(CH_4)	−17.9	0.1	−1.3	0.4	0.1	0.2
2	ammonia(NH_3)	−11.0	0.1	0.0	−4.3	0.0	−2.8
3	water(H_2O)	−57.8	0.01	−2.6	−4.0	−0.3	−1.8
4	hydrogenfluoride(HF)	−65.1	0.2	−3.4	−5.3	−0.1	−2.5
5	acetylene(C_2H_2)	54.2	0.2	−2.9	1.7	1.1	1.9
6	ethylene($H_2C{=}CH_2$)	12.5	0.1	−1.4	1.8	2.5	3.0
7	ethane($H_3C{-}CH_3$)	−20.1	0.1	0.5	1.6	1.4	1.6
8	hydrogencyanide(HCN)	31.5	1.0	0.2	1.9	1.8	1.4
9	formaldehyde($H_2C{=}O$)	−26.0	0.1	−2.8	−0.9	0.4	0.6
10	methanol($CH_3{-}OH$)	−48.0	0.1	−0.1	0.3	2.2	1.8
11	hydrazine($H_2N{-}NH_2$)	22.8	0.2	−0.7	−0.9	0.9	0.0
12	hydrogenperoxide(HO−OH)	−32.5	0.04	−0.6	−2.7	−0.9	−3.4
13	carbon dioxide (CO_2)	−94.1	0.01	−2.4	−3.6	1.2	0.0
14	carbon tetrafuoride (CF_4)	−223.0	0.3	3.4	3.1	2.6	0.2
15	carbonic difluoride (COF_2)	−149.1	1.4	−5.7	−6.4	−3.5	−4.9
16	dinitrogen monoxide (N_2O)	19.6	0.1	−4.1	0.2	−2.1	2.3
17	nitrogen trifluoride (NF_3)	−31.6	0.3	−0.5	−0.7	0.3	−0.5
18	ethene, tetrafluoro- ($F_2C{=}CF_2$)	−157.4	0.7	−2.5	−2.0	0.0	2.9
19	acetonitrile, trifluoro- (CF_3CN)	−118.4	0.7	0.8	−0.4	−0.3	−0.4
20	propyne(C_3H_4)	44.2	0.2	0.6	3.3	3.1	3.4
21	allene(C_3H_4)	45.5	0.3	−1.4	1.3	1.9	2.4
22	cyclopropene(C_3H_4)	66.2	0.6	−5.6	−3.1	−3.5	−3.1
23	propylene(C_3H_6)	4.8	0.2	−0.2	1.8	2.7	2.9
24	cyclopropane(C_3H_6)	12.7	0.1	0.8	2.3	0.4	0.4
25	propane(C_3H_8)	−25.0	0.1	0.9	1.5	1.5	1.6
26	*trans*-1,3-butadiene (C_4H_6)	26.3	0.3	−1.8	1.4	2.8	3.3
27	dimethylacetylene (C_4H_6)	34.8	0.3	3.4	4.3		4.1
28	methylenecyclopropane (C_4H_6)	47.9	0.4	1.5	3.1	2.1	2.0
29	bicyclo[1.1.0]butane (C_4H_6)	51.9	0.2	−4.6	−3.4	−5.6	−5.6
30	cyclobutene(C_4H_6)	37.4	0.4	−2.5	−2.2	−1.4	−1.6
31	cyclobutane (C_4H_8)	6.8	0.1	1.5	0.7	0.4	0.1
32	isobutene(C_4H_8)	−4.0	0.2	−0.5	0.6	1.7	1.5
33	*trans*-butane(C_4H_{10})	−30.0	0.2	0.9	1.2	1.3	1.4
34	isobutane(C_4H_{10})	−32.1	0.2	−0.6	−0.5	−0.2	−0.3
35	spiropentane(C_5H_8)	44.3	0.2	0.6	1.6	−1.8	−2.1
36	benzene(C_6H_6)	19.7	0.2	3.8	3.8	4.1	3.6
37	difluoromethane(H_2CF_2)	−107.7	0.4	−1.5	−0.1	0.7	1.0
38	trifluoromethane(HCF_3)	−166.6	0.8	0.1	1.3	0.0	0.2
39	methylamine($H_3C{-}NH_2$)	−5.5	0.1	−1.0	−1.0	0.9	0.1
40	acetonitrile($CH_3{-}CN$)	18.0	0.1	3.2	2.8	3.3	1.9
41	nitromethane($CH_3{-}NO_2$)	−17.8	0.1	0.6	0.9	1.3	0.6
42	methylnitrite($CH_3{-}O{-}N{=}O$)	−15.9	0.2	2.0	1.3	0.9	0.2
43	formic acid (HCOOH)	−90.5	0.1	−0.8	0.8	−0.2	0.6
44	methyl formate ($HCOOCH_3$)	−85.0	0.2	−0.2	2.5	0.2	1.7
45	acetamide (CH_3CONH_2)	−57.0	0.2	−0.1	0.4	−0.5	−0.4
46	aziridine (C_2H_4NH)	30.2	0.2	−1.7	−0.6	−1.3	−1.4
47	cyanogen (NCCN)	73.3	0.2	−3.0	−4.6	−2.7	−2.7
48	dimethylamine ($(CH_3)_2NH$)	−4.4	0.2	−1.7	0.3	0.0	0.9
49	*trans*-ethylamine ($CH_3CH_2NH_2$)	−11.3	0.2	0.9	−0.1	1.9	0.8
50	ketene (CH_2CO)	−11.4	0.4	−3.6	−2.0	−0.8	0.0
51	oxirane (C_2H_4O)	−12.6	0.1	−0.7	−0.3	−0.7	−1.2
52	acetaldehyde (CH_3CHO)	−39.7	0.1	−0.6	0.2	1.1	0.9
53	glyoxal (HCOCOH)	−50.7	0.2	0.2	−0.8	2.2	1.0
54	ethanol (CH_3CH_2OH)	−56.2	0.1	1.3	0.3	2.3	1.7
55	dimethyl ether (CH_3OCH_3)	−44.0	0.1	0.0	2.0	1.9	2.6
56	vinyl fluoride ($CH_2{=}CHF$)	−33.2	0.4	−1.0	1.4		
57	acrylonitrile($CH_2{=}CHCN$)	43.2	0.4	−0.3	0.1	1.3	0.4
58	acetone (CH_3COCH_3)	−51.9	0.2	0.9	0.9	1.4	0.7
59	acetic acid (CH_3COOH)	−103.4	0.4	1.5	1.6	0.6	0.8
60	acetyl fluoride (CH_3COF)	−105.7	0.8	−0.6	−0.9	−0.4	−0.9
61	2-propanol ($(CH_3)_2CHOH$)	−65.2	0.1	0.3	−0.6	0.8	0.3
62	methyl ethyl ether ($C_2H_5OCH_3$)	−51.7	0.2	1.6	2.3	2.4	3.0
63	trimethylamine ($(CH_3)_3N$)	−5.7	0.2	−3.9	0.1	−2.2	0.3
64	furan (C_4H_4O)	−8.3	0.2	−3.0	−0.1	−3.1	−1.2
65	pyrrole (C_4H_5N)	25.9	0.1	−2.8	1.2	−2.4	0.0
66	pyridine (C_5H_5N)	33.6	0.2	3.1	2.8	2.2	2.4
67	methyl allene (C_4H_6)	38.8	0.1	−0.4	1.4	2.1	2.4

TABLE 3 (Continued)

				deviation (expt.-REBECZTEP)			
		expt. ΔH_f^0		6-31G(d)		6-311+G(2d,p)	
no.	species	value	error	NPA	Stockh.	NPA	Stockh.
68	isoprene (C_5H_8)	18.0	0.3	−2.3	−0.2	1.6	1.6
69	cyclopentane (C_5H_{10})	−18.3	0.2	2.0	−0.3	−0.2	−0.7
70	*n*-pentane (C_5H_{12})	−35.1	0.2	0.7	0.6	0.8	0.9
71	neo pentane (C_5H_{12})	−40.2	0.2	−3.3	−3.7	−3.3	−4.1
72	1,3-cyclohexadiene (C_6H_8)	25.4	0.2	0.4	−0.6	1.0	0.4
73	1,4-cyclohexadiene (C_6H_8)	25.0	0.1	1.3	0.2	2.4	1.9
74	cyclohexane (C_6H_{12})	−29.5	0.2	1.6	−1.2	−1.0	−1.3
75	*n*-hexane (C_6H_{14})	−39.9	0.2	0.9	0.4	0.8	0.9
76	3-methyl pentane (C_6H_{14})	−41.1	0.2	−2.0	−2.6	−2.3	−2.5
77	toluene ($C_6H_5CH_3$)	12.0	0.1	2.4	1.9	2.1	1.4
78	*n*-heptane (C_7H_{16})	−44.9	0.3	1.0	0.1	0.6	0.7
79	cyclooctatetraene (C_8H_8)	70.7	0.4	−2.1	−2.6	0.4	−0.2
80	*n*-octane (C_8H_{18})	−49.9	0.3	0.9	−0.4	0.2	0.3
81	naphthalene ($C_{10}H_8$)	35.9	0.4	3.9	2.2	2.4	1.3
82	acetic acid methyl ester (CH_3COOCH_3)	−98.4	0.4	1.0	2.5	0.2	1.3
83	*t*-butanol $(CH_3)_3COH$	−74.7	0.2	−2.7	−3.0	−2.2	−2.8
84	aniline ($C_6H_5NH_2$)	20.8	0.2	0.4	0.4	0.4	0.1
85	phenol (C_6H_5OH)	−23.0	0.2	0.4	0.5	0.1	0.3
86	divinyl ether (C_4H_6O)	−3.3	0.2	−4.5	0.5	−0.5	2.2
87	tetrahydrofuran (C_4H_8O)	−44.0	0.2	3.6	0.9	0.9	0.6
88	cyclopentanone(C_5H_8O)	−45.9	0.4	3.7	1.2	1.1	0.1
89	benzoquinone($C_6H_4O_2$)	−29.4	0.8	0.8	−2.7	0.4	−1.6
90	urea(CH_4ON_2)	−56.3	0.3	1.6	1.8	0.4	0.5
91	pyrimidine($C_4H_4N_2$)	46.8	0.3	2.1	2.8	1.1	2.3
92	butanedinitrile($N{\equiv}C-CH_2-CH_2-C{\equiv}N$)	50.1	0.2	6.1	2.7	4.7	1.8
93	pyrazine($C_4H_4N_2$)	46.9	0.3	0.5	−0.6	−1.7	−0.8
94	acetyl acetylene($CH_3-CO-C{\equiv}CH$)	15.6	0.2	−3.6	−3.0	−1.7	−2.5
95	crotonaldehyde($CH_3-CH{=}CH-CHO$)	−24.0	0.3	1.1	1.6	3.3	2.8
96	acetic anhydride ($CH_3-CO-O-CO-CH_3$)	−136.8	0.4	0.0	1.1	−2.4	−0.6
97	isobutane nitrile($(CH_3)_2CH-C{\equiv}N$)	5.6	0.3	1.5	−0.1	1.1	−0.9
98	methyl ethyl ketone($CH_3-CO-CH_2-CH_3$)	−57.1	0.2	1.5	1.0	1.2	0.6
99	isobutanal($(CH_3)_2CH-CHO$)	−51.6	0.2	−1.8	−1.7	−1.0	−1.3
100	1,4-dioxane($C_4H_8O_2$)	−75.5	0.2	5.3	1.9	2.1	1.6
101	tetrahydropyrrole(C_4H_8NH)	−0.8	0.2	1.0	−0.9	−0.1	−0.2
102	nitro-s-butane ($CH_3-CH_2-CH(CH_3)\text{-}NO_2$)	−39.1	0.4	1.6	−1.2	−0.6	−2.2
103	diethyl ether($CH_3-CH_2-O-CH_2-CH_3$)	−60.3	0.2	2.2	1.6	1.8	2.3
104	dimethyl acetal($CH_3-CH(OCH_3)_2$)	−93.1	0.2	−0.8	1.8	−1.6	0.5
105	*tert*-butylamine($(CH_3)_3C-NH_2$)	−28.9	0.2	−3.9	−5.2	−3.4	−4.9
106	*N*-methyl pyrrole (cyc-$C_4H_4N-CH_3$)	24.6	0.1	−5.0	0.9	−4.4	−0.4
107	tetrahydropyran($C_5H_{10}O$)	−15.2	0.2	3.4	0.3	0.0	−0.1
108	diethyl ketone ($CH_3-CH_2-CO-CH_2\text{-}CH_3$)	−61.6	0.2	2.6	1.6	1.6	1.1
109	isopropyl acetate ($CH_3-CO-O-CH(CH_3)_2$)	−115.1	0.2	0.8	0.8	−1.8	−0.8
110	piperidine(cyc-$C_5H_{10}NH$)	−11.3	0.1	0.6	−1.7	−1.6	−1.7
111	*tert*-butyl methyl ether($(CH_3)_3C-O-CH_3$)	−67.8	0.3	−4.1	−2.7	−4.1	−3.4
112	1,3-difluorobenzene($C_6H_4F_2$)	−73.9	0.2	0.2	0.5	−0.2	0.5
113	1,4-difluorobenzene($C_6H_4F_2$)	−73.3	0.2	0.7	0.6	0.1	0.3
114	fluorobenzene (C_6H_5F)	−27.7	0.3	2.0	2.0	1.8	1.7
115	di-isopropyl ether ($(CH_3)_2CH-O-CH(CH_3)_2$)	−76.3	0.4	−1.5	−1.6	−2.8	−2.1
116	ethane,-hexafluoro- (C_2F_6)	−321.3	0.8	1.9	1.4	−1.0	−0.4
117	azulene ($C_{10}H_8$)	69.1	0.8	−8.0	−9.9	−8.3	−9.5

[a] Corresponds to eq 5.

(4), acetonitrile (40), and *tert*-butylamine (105) if the 6-31G(d) basis set was used in the calculations. Calculations that use NPA charges fail for dinitrogen monoxide (16) and dimethylacetylene (27). It can be observed that the results show negative deviation for *tert*-butyl group containing molecules, e.g., *tert*-butyl alcohol (83), *tert*-butylamine (105), and *tert*-butyl-methyl-ether (111).

Improving the basis set quality improves the results in general; however, the most problematic molecules remain the same. The molecules with more than 4 kcal/mol deviation from the experiment are the COF_2, bicyclo[1.1.0]butane, and *tert*-butylamine if stockholder charges are used. Using NPA charges would provide poor results for more molecules: cyclopropene, bicyclo[1.1.0]butane, benzene, butanedinitrile, and *N*-methylpyrrole. Further analysis of the components of the thermal correction could probably lead to further improvement of the current method; however, this falls outside the present scope.

It is not easy to understand why the implicit treatment of ZPE and thermal corrections provide such good results for the REBECZTEP method. It is known that the ZPE and thermal corrections calculated from scaled, harmonic HF−SCF/6-31G(d) results are in error. These errors are present in the G3 method and also in the REBECEP method, and they are seemingly well absorbed by the fitted REBECZTEP energy parameters obtained from experimental results. Implicit treatment of ZPE can be found in the literature.[19] However, it is considerably more difficult to understand how ZPE and thermal corrections should depend on atomic charges. We have started studies in this direction, and the results will be published elsewhere.[15] Our

TABLE 4: Statistics for the Deviation (kcal/mol) between Experimental Enthalpies of Formation and Calculated REBECZEP or REBECZTEP Enthalpies of Formation Depending on the Basis Sets [6-31G(d) or 6-311+G(2d,p)] and Partial Charge Calculation Methods [NPA or Stockholder]

	deviation (expt.-REBECEP)							
	6-31G(d)				6-311+G(2d,p)			
	REBECZEP[a]		REBECZTEP[b]		REBECZEP[a]		REBECZTEP[b]	
	NPA	Stockh.	NPA	Stockh.	NPA	Stockh.	NPA	Stockh.
number of molecules	117	117	117	117	115	116	115	116
root-mean-square deviation	2.58	2.26	2.40	2.23	1.96	2.02	2.03	2.08
average deviation	−0.30	−0.05	−0.21	0.01	0.08	0.07	0.16	0.13
average absolute deviation	2.04	1.68	1.85	1.67	1.48	1.50	1.55	1.54

[a] Only ZPE correction is applied in eq 5. [b] Corresponds to eq 5.

preliminary results show that the ZPE shows correlation with the sum of the inverse square root of the atomic masses of the constituent atoms of a selected molecule.[20] We have already obtained several atomic parameter sets for various atomic charges for the explicit ZPE calculation of set of molecules. Analysis of those atomic parameters is in progress.

Conclusions

The enthalpies of formations obtained with 12 new fitted parameter sets were compared to our previous REBECEP, to G3, and to B3LYP/6-311+G(3df,2p) results. These new parameter sets were developed using the implicit inclusion of the ZPE and the thermal corrections into the REBECEP parameters. This leads to two new class of parameter sets, namely, the REBECZEP and the REBECZTEP parameter sets, which were developed for HF/6-31G(d) or HF/6-311+G(2d,p) energies and the corresponding NPA, stockholder, or Mulliken charges. All parameter sets were developed and tested on the same molecular database, a set of 117 closed shell molecules composed of H, C, N, O, and F atoms. We used the B3LYP/6-31G(d) equilibrium geometries in the calculations.

The six parameter sets developed for the HF/6-31G(d) method yield the following results:

(1) The implicit inclusion of the ZPE into the REBECEP parametrizations, the REBECZEP parameters provide worsening for the results obtained by the use of NPA charges (e.g., the a.a. deviation increases from 1.65 to 2.04 kcal/mol). The inclusion of the thermal corrections, the REBECZTEP parametrization improves these results (a.a. deviation is decreased to 1.85 kcal/mol).

(2) The stockhholder charges provide better REBECZEP or REBECZTEP results than REBECEP results. The stockholder REBECZTEP a.a. deviation (1.67 kcal/mol) is smaller than the corresponding REBECEP deviation (1.79 kcal/mol).

(3) The use of Mulliken charges provides a.a. deviation of 1.93, 1.95, and 1.88 kcal/mol for REBECEP, REBECZEP, and REBECZTEP parametrizations, respectively. This shows that the latter two approximations do not influence the quality of the results obtained with Mulliken population analysis.

The six parameter sets developed for the HF/6-311+G(2d,p) method yield the following results:

(4) The current REBECZEP parametrization for 115 molecules yields a considerable improvement for the combination of NPA charges with this larger basis set. The 1.86 a.a. deviation from the experiment of the original REBECEP method is decreased to 1.48 kcal/mol. Leaving out the five most problematic molecules yielded 1.22 kcal/mol a.a. deviation for 110 molecules.

(5) The molecules with consistently large deviations are azulene, carbonic difluoride, cyclopropene, and bicyclo[1.1.0]-butane.

(6) The use of stockholder charges or the thermal corrections (REBECZTEP parameters) provide only very small changes in a.a. deviations from the experiment.

(7) The use of Mulliken charges with this large basis set yields 1.82 kcal/mol a.a. deviation.

(8) The best results we could obtain with the current REBECZEP and REBECZTEP methods compare rather favorably to Gaussian-3 and B3LYP/6-311+G(3df,2p) enthalpies of formation (the corresponding a.a. deviations are 0.94, 7.09 kcal/mol, respectively).

The implicit inclusion of the ZPE and the thermal corrections into the REBECEP method slightly improve further the performance of the method. This can be attributed to the fact that, by the implicit treatment of the ZPE and the thermal corrections, the errors arising from the explicit ZPE and thermal correction calculations are compensated partly by the parametrization. Another important advantage of the new method is that it makes superfluous the very costly HF/6-31G(d) frequency calculation in the proposed procedure. This new method is considerably faster than the previous REBECEP method, without losing the precision.

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