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Rapid Estimation of Zero-Point Energies of Molecules Using Hartree−Fock Atomic Partial Charges

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Using a database of HF-SCF/6-31G(d) zero-point energies (scaled by 0.8929) and atomic partial charges of 117 closed-shell, neutral molecules containing H, C, N, O, and F atoms, relationships have been developed that permit the rapid estimation of zero-point energies from atomic partial charges (REZEP). The estimated zero-point energies have been compared to scaled HF-SCF/6-31G(d), B3LYP/6-31G(2df,p) (scaled by 0.9854), and to zero-point energies estimated from molecular stoichiometry. Sixty-nine experimental zero-point energies have also been used to check the quality of the various methods. The scaled HF-SCF and B3LYP zero-point energies show 0.4, and the stoichiometric and the proposed REZEP methods show a 1.0 kcal/mol average absolute deviation from the experimental results. New parameters have been developed for the stoichiometric method that reduces the average absolute deviation from the experimental results to 0.7 kcal/mol.

1. Introduction

For accurate calculations of the enthalpies of formation, a reliable method for the calculation of the zero-point energy (ZPE) and the thermal energy is necessary according to the usual methodology. This can be done by computing the ab initio molecular vibrational frequencies. However, such calculations can be very demanding in terms of computer time and disk space for large molecules. This fact has motivated Politzer et al.[1] to present a rapid, essentially immediate, and remarkably accurate estimation of the ZPE from the molecular stoichiometry. The relationship between the stoichiometry and the harmonic vibrational energy was rationalized on the basis of the kinetic molecular theory and the principle of the equipartition of energy. A database of 61 molecules was used to establish a linear relationship between the computed BP86/6-31G(d,p) vibrational energy and the stoichiometry of the molecule:[1]

$$\text{ZPE (kcal/mol)} = 7.06n_{\text{H}} + 3.66n_{\text{C}} + 3.41n_{\text{N}} + 2.76n_{\text{O}} + 1.90n_{\text{F}} + 2.49n_{\text{Cl}} - 3.97 \quad (1)$$

where n_i is the number of each kind of atom. A similar relationship with slightly different constants was established for the vibrational energy at 298 K.[1] In the original paper,[1] eq 1 was tested on eight new molecules (none of these molecules were in the database used to establish eq 1), and the average absolute (a.a.) deviation was less than 0.60 kcal/mol. Since eq 1 is based on stoichiometry, it cannot distinguish between structural isomers. A detailed investigation shows that the experimental ZPEs of structural isomers are similar. (Usually the difference is less than 1.0 kcal/mol.[1])

This simple relationship suggests that an implicit, parametrized treatment of ZPE if feasible. Such a treatment of ZPE is known in the literature. (For a recent example of such methods see ref 2.) A successful method for the implicit treatment of ZPE and thermal corrections was proposed by Wiberg,[3] who fitted nonrelativistic HF-SCF/6-31G(d)//HF-SCF/6-31G(d) total electronic energies for a variety of hydrocarbons to experimental enthalpies of formation (thus the relativistic effects were also treated implicitly) to derive five energy parameters for CH_3, CH_2, CH, C(saturated), and C(olefinic) groups. An estimate of the enthalpy of formation of any hydrocarbon may then be obtained as the difference in its calculated (HF-SCF/6-31G(d)//HF-SCF/6-31G(d)) total electronic energy from the sum of the appropriate groups. However, the definition of the group is not always straightforward (various definitions might lead to some ambiguity and arbitrariness), and such methods usually lead to a large number of parameters. Later on, this procedure was modified, and atomic energy parameters were proposed to correct nonrelativistic ab initio total energies leading to a.a. deviations of 2 kcal/mol for enthalpies of formation calculated in this manner. (In this way, again, the relativistic corrections are treated implicitly via atomic parameters.[4]) A total of 56 parameters were proposed originally for H, C, N, O, and F atoms in various molecular environments,[4] but that number was later reduced[5] to 14. The reasonable success of these methods also shows that a rapid estimation of ZPE and thermal corrections is feasible and that the error in the HF method can be treated systematically.

2. Rapid Estimation of Various Energy Factors from Atomic Charges

Recently, we have developed a method that is suitable for the rapid estimation of the basis set error and the correlation energy from partial charges (REBECEP).[6−9] This method uses the HF-SCF/6-31G(d)//B3LYP/6-31G(d) total electronic energy

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and the HF-SCF/6-31G(d) atomic charges to predict enthalpies of formation. (The relativistic corrections are treated implicitly.) This method yields a REBECEP total electronic energy, noted as E_T(M, REBECEP), and a molecular enthalpy of formation, ΔH_f^0(M, REBECEP), is obtained from this energy after the usual Gaussian-3[10] (G3) ZPE and thermal corrections for molecule M as follows:

$$\Delta H_f{}^0(\mathrm{M, REBECEP}) = E_T(\mathrm{M, REBECEP}) + E_{ZP}(\mathrm{M, G3}) + E_{therm}(\mathrm{M, G3}) + \sum_{A \in M} [\Delta H_f{}^0(\mathrm{A, exptl}) - E_T(\mathrm{A, G3}) - E_{therm}(\mathrm{A, exptl})] \quad (2)$$

where E_T(M, REBECEP) is calculated from a HF-SCF/(basis set) total electronic energy, from a fitted atomic energy parameter set (the atomic parameters were fitted to the experimental, exptl, enthalpies of formation in a least-squares sense), and from the corresponding partial charges using a specific basis set and charge definition. Thus, the value of E_T(M, REBECEP) depends on the basis set quality, the partial-charge calculation method, and the fitting procedure. E_{ZP}(M, G3) is the explicit G3 ZPE of molecule M (scaled HF-SCF/6-31G(d) ZPE),[11] and 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 summation runs over all atoms (A) of the system: the ΔH_f^0(A, exptl) values are the experimental standard enthalpies of formation of the constituent atoms of molecule M, the E_T(A, G3) values are the G3 total energies of these atoms, and the E_{therm}(A, exptl) values are the differences between the enthalpies at $T = 298.15$ and 0 K (calculated from the elemental heat capacities). The actual values of E_{ZP}(M, G3), E_{therm}(M, G3), and E_T(A, G3) are method-dependent. For the cited studies, we used G3 values.

Earlier we investigated[9] the performance of the REBECEP method for using Mulliken, natural population analysis (NPA),[12] and stockholder[13] atomic charges. To test the performance of the method, we used the experimental enthalpies of formation of 117 molecules.[14] These closed-shell neutral molecules are composed of H, C, N, O, and F atoms. We selected 66 smaller molecules of the G2/97[15,16] molecular thermochemistry databases to obtaining the necessary energy parameters. The performance of these parameters was tested on 51 larger molecules of the G3/99[17] molecular thermochemistry database. The rms deviations from the experimental enthalpies of formation for the 51 test molecules are 1.15, 3.96, and 2.92 kcal/mol for Gaussian-3, B3LYP/6-311+G(3df, 2p), and REBECEP (NPA) enthalpies of formation, respectively. (The corresponding a.a. deviations are 0.94, 7.09, and 2.27 kcal/mol, respectively.) The REBECEP method performs considerably better for the 51 test molecules with a moderate 6-31G(d) basis set than the B3LYP method with a large 6−311+G(3df, 2p) basis set.

In our latest studies,[18,19] we have improved the applicability (made the calculations faster) and increased the precision of the REBECEP method in several ways. Among other modifications, we also provided a procedure for the implicit inclusion of the ZPE and thermal corrections into the REBECEP parametrization, yielding the so-called REBECZTEP parameters. Using these REBECZTEP parameters, the enthalpy of formation of a given molecule can be calculated without explicit HF-SCF/6-31G(d) frequency calculations. This procedure provides a considerable speed up compared to the original REBECEP method without losing precision in most of the cases. In some cases, even an improvement in the calculated results was observed. This method has some desirable features compared to group or atomic energy equivalent schemes. It does not require various definitions of groups and an extensive classification of various atom types depending on the molecular environment. Thus, the number of parameters remains limited, as the different chemical environments of the atoms are reflected in the atomic charges. (For molecules containing H, C, N, O, and F atoms, only 11−13 parameters are required, depending on the charge values of the molecules in the database.) Even a considerable extension of the molecular set would not influence the number of parameters if no extreme charges occur in the data set. The use of atomic charges to estimate correlation energy can also be rationalized on the basis of the dependence of the correlation energy on the number of electrons.

In the present study, we compare the explicit ZPEs for 117 molecules calculated at the HF-SCF/6-31G(d) and B3LYP/6−31G(2df, p) levels of theory (scaled by 0.8929 and 0.9854, respectively) and ZPEs calculated from the molecular stoichiometry using eq 1. The calculated ZPEs are compared to 69 available experimental data and to our new results. As mentioned, the ZPE can be estimated from molecular stoichiometry. Our proposed new method can be considered to be an extended stoichiometric method because it introduces a further refinement by atomic charges. We note that the stoichiometric method will result in the same zero-point energy for different ions with the same stoichiometry (e.g., according to the stoichiometric method, NO_2^+, NO_2, and NO_2^- would have the same ZPE), whereas our method is able to make differences between charged molecules with the same stoichiometry. In this way, a coherent method can be constructed that uses atomic charges for the estimation of the correlation energy, the basis set extension error, the relativistic corrections, and the ZPE (although the direct connection between the ZPE and atomic charges was not searched and the method relies on the observed insensitivity of the ZPE to structural changes in the molecules). The objective of this paper is to provide an extremely rapid method for the estimation of ZPEs from atomic partial charges to control the performance of eq 1 for a different set of molecules and to provide improved parameters for eq 1 for the current set of molecules. We also compare the enthalpies of formation obtained using an explicit estimation of the ZPE to earlier REBECZTEP[19] results.

3. Rapid Estimation of ZPE from Atomic Charges

According to our rapid estimation of zero-point energy from partial charges (REZEP) procedure, the ZPE is estimated for closed- or open-shell ground-state covalent molecules in the vicinity of their equilibrium geometry by an inexpensive atom-by-atom method:

$$\mathrm{ZPE(REZEP)} \equiv \sum_{A=1}^{M} E_{ZPE}(N_A, Z_A) \quad (3)$$

where ZPE(REZEP) approximates an accurate ZPE using a particular basis set and atomic partial-charge definition. The accurate ZPE can be a good-quality experimental result or a well-tested calculated ZPE. The summation in eq 3 is over all M atoms in the molecule. In eq 3, the REZEP-level ZPE energy is the sum of the M “atomic ZPE energies” noted as $E_{ZPE}(N_A,$

Z_A). The “quality” of the ZPE(REZEP) depends on the procedure used to obtain the atomic ZPE parameters (vide infra). N_A is the “electron content” of atom A, generally noninteger, and it is equal to (Z_A − partial charge on A), where Z_A is the nuclear charge of atom A. In the current study, we use atomic charges obtained from HF-SCF/6-31G(d) results at the given molecular geometry (vide infra). The $E_{ZPE}(N_A, Z_A)$ atomic ZPE energy terms of eq 3 are interpolated linearly as

$$E_{ZPE}(N_A, Z_A) = (N_A - N1)\,\mathrm{E}_{ZPEpar}(N2, Z_A) + (N2 - N_A)\,E_{ZPEpar}(N1, Z_A) \quad (4)$$

where $N1$ and $N2$ are integer numbers of electrons with $N1 \leq N_A \leq N2 = N1 + 1$ (i.e., the two closest integer numbers around the noninteger N_A). The $E_{ZPEpar}(N1 \text{ or } N2, Z_A)$ parameters in eq 4 are the “atomic ZPE parameters” that transform the atomic partial charge into an atomic ZPE energy estimation. The values of these parameters depend on the basis set and partial-charge calculation method and the target (HF-SCF, B3LYP, or experiment) of the fitting. For hydrogen atoms, we suggest using a single parameter, as in the REBECEP method:[7−9] $E_{ZPEpar}(N_A, Z_A = 1) = N_A\,E_{ZPEpar}(N2 = 2, Z_A = 1)/2$ for N_A between 0 and 2. Equations 3 and 4 show the simplicity of the suggested method. The two basic assumptions are the following: the ZPE energy is the sum of the atomic ZPE energies, and the value of the latter can be estimated from the partial charges by a linear equation.

How can E_{ZPEpar} atomic ZPE parameters be obtained for eq 4? The procedure is described in ref 7. These a posteriori parameters can be obtained from a multilinear fitting procedure that finds the minimum of

$$Y = \sum_{i=1,\mathrm{NM}} [\mathrm{ZPE(G3)}_i - \mathrm{ZPE(REZEP)}_i]^2 \quad (5)$$

in a set of NM molecules. $\mathrm{ZPE(G3)}_i$ is taken from the G3 results (actually it is an empirically corrected, fitted HF-SCF/6-31G(d) ZPE), and $\mathrm{ZPE(REZEP)}_i$ is calculated with 6-31G(d) basis set and with several charge definitions according to eqs 3 and 4.

Let us denote the k^{th} $E_{ZPEpar}(N1, Z_A)$ parameter of eq 4 by a_k and regroup the terms to yield

$$\mathrm{ZPE(REZEP)}_i = \sum_{k=1,L} x_{ki} a_k$$

where the x_{ki}’s are the charge factors ($N_A - N1$ and $N_2 - N_A$, cf. eq 4) arising from the summation of fractional electron numbers requiring the same a_k parameter in the molecule and L is the number of parameters necessary to calculate ZPE. The

$$\partial Y / \partial a_k = 0 \quad (6)$$

minimization yields a system of linear equations

$$a_1 \sum_{i=1,\mathrm{NM}} x_{1i} x_{ki} + a_2 \sum_{i=1,\mathrm{NM}} x_{2i} x_{ki} + \ldots + a_L \sum_{i=1,\mathrm{NM}} x_{Li} x_{ki} = \sum_{i=1,\mathrm{NM}} y_i x_{ki} \quad (7)$$

with $k = 1, 2, \ldots, L$, and $y_i \equiv \mathrm{ZPE(G3)}_i$. The solution yields the desired a_k (i.e., $E_{ZPEpar}(N1, Z_A)$) fitted values.

TABLE 1: Fitted Energy Parameters E_{ZPEpar} (N1, Z_A) (kcal/mol) for Rapid Estimation of the ZPE from HF-SCF/6-31G(d) Mulliken, NPA, and Stockholder Partial Charges to Be Used in Equation 4[a]

	Z_A	$N1$	Mulliken	NPA	stockholder
H	1	2	15.08	14.65	13.45
C	6	4	2.48	−4.40	
C	6	5	1.99	−1.00	−2.23
C	6	6	3.99	3.61	4.02
C	6	7	3.81	7.05	−9.20
N	7	6	5.74	1.64	−3.41
N	7	7	−0.39	0.99	3.40
N	7	8	7.79	8.79	1.25
N	7	9		−7.31	
O	8	8	0.18	0.86	2.58
O	8	9	6.22	7.27	4.55
F	9	9	−1.70	0.02	2.29
F	9	10	9.45	8.62	2.17

[a] This parameter set was fitted in a least-squares sense to approximate the G3 ZPE, which is an empirically-corrected (scaled by 0.8929) HF-SCF/6-31G(d) ZPE, for the molecules listed in Table 2.

4. Results and Discussion

Table 1 shows the fitted ZPE parameters obtained for various HF-SCF/6-31G(d) charges. Table 2 shows the 117 molecules used to obtain the parameters in Table 1 and the performance of the proposed method. We used the HF-SCF/6-31G(d) ZPEs (scaled by 0.8929) of the G3 method as a reference because reliable experimental ZPEs are not available for 48 molecules in our database. For consistency, we used the B3LYP/6-31G(d) geometries for the charge calculations because these geometries were used for REBECEP calculations. (However, HF-SCF/6-31G(d) geometries can be proposed for independent calculations. The subtle differences between the two types of optimized geometries certainly have an influence on the total electronic energies; however, the influence on the atomic charges was negligible for the 117 molecules in this study). Table 3 shows the results of the statistical analysis of the deviation of the various REZEP values from the scaled HF-SCF/6-31G(d) ZPEs. The deviations are in the −3.5 and +2.7 kcal/mol range (cf. Table 3). The best results were obtained by using the stockholder charges; however, using Mulliken or NPA charges provides only slightly worse results.

A comparison of all available experimental ZPEs from ref 20 to scaled HF-SCF/6-31G(d) and B3LYP/6-31G(2df, p) (scaled by 0.9854) results shows that the scaled HF-SCF/6-31G(d) ZPE is rather reliable (a.a. deviation is 0.4 kcal/mol in Table 4), and using B3LYP ZPEs instead of HF-SCF ZPEs does not provide an improvement for the 69 molecules in this study (cf. Table 4). On the contrary, the center of the distribution of the B3LYP results is shifted by 0.5 kcal/mol compared to that of the HF-SCF/6-31G(d). Otherwise, the a.a. and root-mean-square (rms) deviations of the two methods are practically the same. This is why we currently use the less-expensive scaled HF-SCF/6-31G(d) ZPEs. B3LYP/6-31G(2df, p) frequencies are clearly superior to HF-SCF/6-31G(d) frequencies, and the better quality of the former is clear from the scaling factor, which is considerably closer to unity. However, this advantage is effectively compensated by the scaling factor applied to HF-SCF/6-31G(d) ZPEs.

The stoichiometric method proposed by Politzer et al.[1] shows a considerably poorer performance than in the original paper. The rms and a.a. deviations from the experiment are 1.3 and 1.0 kcal/mol, respectively (cf. Table 4). It can also be observed that eq 1 fits considerably better to B3LYP ZPEs than to HF-

TABLE 2: Species, Number of Atoms, Electrons, the G3 ZPE and the Deviations between the Experimental and G3 ZPE, G3, and REZEP ZPE (kcal/mol) Using Various Partial Charges Calculated from the HF-SCF/6-31G(d) Wave Function for 117 Molecules

		no.			deviation of ZPEs			
					exptl[a]	G3-REZEP		
no.	species	nuclei	electron	G3 ZPE	G3	Mulliken	NPA	stockholder
1	methane (CH_4)	5	10	26.77	0.34	−2.3	−2.8	−2.1
2	ammonia (NH_3)	4	10	20.73	−0.10	−2.1	0.0	−0.3
3	water (H_2O)	3	10	12.87	0.01	−1.1	−1.8	−1.6
4	hydrogenfluoride (HF)	2	10	5.56	0.36	−2.1	−2.5	−1.8
5	acetylene (C_2H_2)	4	14	16.50	−0.31	−2.2	−3.5	−1.0
6	ethylene ($H_2C{=}CH_2$)	6	16	30.68	0.21	−2.0	−2.6	−1.4
7	ethane ($H_3C{-}CH_3$)	8	18	44.68	0.64	−1.2	−1.5	−1.3
8	hydrogencyanide (HCN)	3	14	10.08	−0.31	−1.7	−2.3	−2.3
9	formaldehyde ($H_2C{=}O$)	4	16	16.36	−0.22	−3.0	−3.1	−2.5
10	methanol ($CH_3{-}OH$)	6	18	31.00	0.01	−0.9	−1.1	−1.2
11	hydrazine($H_2N{-}NH_2$)	6	18	32.53	−0.49	2.3	0.6	2.1
12	hydrogenperoxide ($HO{-}OH$)	4	18	16.42	−0.51	2.4	1.0	−0.5
13	carbon dioxide (CO_2)	3	22	7.14	0.03	−0.9	−0.7	−0.2
14	carbon tetrafuoride (CF_4)	5	42	10.74	0.03	0.2	−0.2	0.4
15	carbonic difluoride (COF_2)	4	32	8.85	−0.09	0.5	−0.4	−0.1
16	dinitrogen monoxide (N_2O)	3	22	6.90	−0.19	−0.3	0.4	−0.8
17	nitrogen trifluoride (NF_3)	4	34	7.15	−0.75	−2.0	−1.3	−1.1
18	ethene, tetrafluoro-($F_2C{=}CF_2$)	6	48	13.43	−0.09	0.3	0.2	−1.2
19	acetonitrile, trifluoro-(CF_3CN)	6	46	14.29	−0.27	−0.8	0.3	−0.7
20	propyne (C_3H_4)	7	22	33.67	0.12	−1.4	−2.6	−0.9
21	allene (C_3H_4)	7	22	33.31	0.03	−2.2	−3.1	−1.8
22	cyclopropene (C_3H_4)	7	22	33.90	−0.12	−2.7	−2.9	−1.9
23	propylene (C_3H_6)	9	24	47.88	0.32	−1.4	−1.9	−1.1
24	cyclopropane (C_3H_6)	9	24	48.89	0.49	−0.1	−0.6	0.1
25	propane (C_3H_8)	11	26	61.96	0.99	−0.7	−0.8	−1.0
26	*trans*-1,3-butadiene (C_4H_6)	10	30	51.29	0.18	−1.5	−2.1	−0.9
27	dimethylacetylene (C_4H_6)	10	30	50.75		−1.5	−2.0	−1.0
28	methylenecyclopropane (C_4H_6)	10	30	51.40	0.16	−0.8	−1.7	−0.8
29	bicyclobutane (C_4H_6)	10	30	52.17	−0.01	−0.6	−1.0	−0.3
30	cyclobutene (C_4H_6)	10	30	52.24	0.66	−1.0	−1.1	−1.2
31	cyclobutane (C_4H_8)	12	32	66.56	0.51	0.3	0.2	−0.5
32	isobutene (C_4H_8)	12	32	64.80	1.23	−0.9	−1.4	−0.5
33	*trans*-butane (C_4H_{10})	14	34	79.09	0.64	−0.3	−0.3	−0.8
34	isobutane (C_4H_{10})	14	34	78.87		−0.5	−0.5	−0.6
35	spiropentane (C_5H_8)	13	38	69.32	−0.18	0.2	−0.3	0.2
36	benzene (C_6H_6)	12	42	60.33	0.84	0.4	0.1	0.3
37	difluoromethane (H_2CF_2)	5	26	20.16	−0.12	−0.8	−0.7	0.2
38	trifluoromethane (HCF_3)	5	34	15.76	−0.16	0.4	0.0	0.8
39	methylamine ($H_3C{-}NH_2$)	7	18	38.61	0.56	−0.9	−1.4	−0.1
40	acetonitrile ($CH_3{-}CN$)	6	22	27.40	0.12	−0.7	−0.9	−1.8
41	nitromethane ($CH_3{-}NO_2$)	7	32	30.57		0.7	−0.1	0.4
42	methylnitrite ($CH_3{-}O{-}N{=}O$)	7	32	30.08		0.1	−0.4	−1.1
43	formic acid (HCOOH)	5	24	20.76	−0.31	0.1	−0.1	0.5
44	methyl formate ($HCOOCH_3$)	8	32	37.86	0.00	−0.6	−0.4	0.0
45	acetamide (CH_3CONH_2)	9	32	44.23		−0.5	−0.7	0.9
46	aziridine (C_2H_4NH)	8	24	42.56	0.12	0.3	−0.6	0.0
47	cyanogen (NCCN)	4	26	10.20	−0.46	−1.8	−0.4	−2.5
48	dimethylamine ($(CH_3)_2NH$)	10	26	55.72		−0.6	−0.9	−0.6
49	*trans*-ethylamine ($CH_3CH_2NH_2$)	10	26	55.78	0.24	−0.4	−0.7	0.7
50	ketene (CH_2CO)	5	22	19.16	0.02	−2.0	−2.1	−0.7
51	oxirane (C_2H_4O)	7	24	34.90	0.19	−1.2	−1.2	−1.5
52	acetaldehyde (CH_3CHO)	7	24	33.58	−0.01	−1.4	−1.7	−1.5
53	glyoxal (HCOCOH)	6	30	22.88	−0.39	−1.8	−1.8	−1.6
54	ethanol (CH_3CH_2OH)	9	26	48.20		−0.4	−0.4	−0.3
55	dimethyl ether (CH_3OCH_3)	9	26	48.26	0.28	−1.7	−1.4	−1.7
56	vinyl fluoride ($CH_2{=}CHF$)	6	24	26.70	−0.01	−1.3	−1.8	−0.9
57	acrylonitrile ($CH_2{=}CHCN$)	7	28	30.79	0.01	−1.3	−1.4	−2.4
58	acetone (CH_3COCH_3)	10	32	50.37	0.47	−0.3	−0.8	−0.7
59	acetic acid (CH_3COOH)	8	32	37.46	0.42	1.1	0.8	0.9
60	acetyl fluoride (CH_3COF)	7	32	29.72	0.17	0.2	−0.3	−0.2
61	2-propanol ($(CH_3)_2CHOH$)	12	34	64.98		0.2	0.2	0.5
62	methyl ethyl ether ($C_2H_5OCH_3$)	12	34	65.30		−1.4	−0.8	−0.9
63	trimethylamine ($(CH_3)_3N$)	13	34	72.56	0.44	−0.6	−0.7	−1.3
64	furan (C_4H_4O)	9	36	42.43	0.22	−0.1	0.1	0.5
65	pyrrole (C_4H_5N)	10	36	49.74	0.31	−0.2	0.2	1.9
66	pyridine (C_5H_5N)	11	42	53.48	0.59	0.2	0.2	0.1

TABLE 2 (Continued)

		no.			deviation of ZPEs			
						G3-REZEP		
no.	species	nuclei	electron	G3 ZPE	exptl[a] G3	Mulliken	NPA	stockholder
67	methyl allene (C_4H_6)	10	30	50.61		−1.6	−2.4	−1.6
68	isoprene (C_5H_8)	13	38	68.34		−0.7	−1.5	−0.3
69	cyclopentane (C_5H_{10})	15	40	84.44		1.4	1.6	0.2
70	*n*-pentane (C_5H_{12})	17	42	96.21	1.20	0.0	0.2	−0.6
71	neopentane (C_5H_{12})	17	42	95.61	0.54	−0.4	−0.3	0.2
72	1,3-cyclohexadiene (C_6H_8)	14	44	73.76		0.6	0.5	0.1
73	1,4-cyclohexadiene (C_6H_8)	14	44	73.69	1.35	0.3	0.4	0.0
74	cyclohexane (C_6H_{12})	18	48	102.21	1.42	2.1	2.7	0.9
75	*n*-hexane (C_6H_{14})	20	50	113.31	1.12	0.4	0.6	−0.5
76	3-methyl pentane (C_6H_{14})	20	50	113.18		0.5	0.6	−0.2
77	toluene ($C_6H_5CH_3$)	15	50	76.71		0.2	−0.1	0.1
78	*n*-heptane (C_7H_{16})	23	58	130.40		0.7	1.1	−0.4
79	cyclooctatetraene (C_8H_8)	16	56	80.34		−0.3	−0.2	−0.4
80	*n*-octane (C_8H_{18})	26	66	147.49		1.0	1.5	−0.2
81	naphthalene ($C_{10}H_8$)	18	68	88.62		1.0	1.0	0.7
82	acetic acid methyl ester (CH_3COOCH_3)	11	40	54.39	0.35	0.1	0.3	0.2
83	*t*-butanol ($(CH_3)_3COH$)	15	42	81.56		0.5	0.5	1.1
84	aniline ($C_6H_5NH_2$)	14	50	70.38		0.3	0.3	2.7
85	phenol (C_6H_5OH)	13	50	62.92		1.1	1.1	1.7
86	divinyl ether (C_4H_6O)	11	38	53.83		−1.6	−1.9	0.0
87	tetrahydrofuran (C_4H_8O)	13	40	70.56		0.4	1.2	0.5
88	cyclopentanone (C_5H_8O)	14	46	73.14		2.1	1.9	0.6
89	benzoquinone ($C_6H_4O_2$)	12	56	51.79		0.6	1.0	−0.8
90	urea ($NH_2{-}CO{-}NH_2$)	8	32	38.71	−0.05		3.0	
91	pyrimidine ($C_4H_4N_2$)	10	42	46.65	−0.54	0.4	0.3	1.5
92	butanedinitrile ($N{\equiv}C{-}CH_2{-}CH_2{-}C{\equiv}N$)	10	42	44.59		0.9	0.9	−1.2
93	pyrazine ($C_4H_4N_2$)	10	42	46.47	0.16	0.2	0.3	−0.5
94	acetyl acetylene ($CH_3{-}CO{-}C{\equiv}CH$)	9	36	39.70		−1.3	−2.1	−1.0
95	crotonaldehyde ($CH_3{-}CH{=}CH{-}CHO$)	11	38	54.15	0.29	−1.1	−1.4	−1.3
96	acetic anhydride ($CH_3{-}CO{-}O{-}CO{-}CH_3$)	13	54	59.64		0.6	0.9	0.9
97	isobutane nitrile ($(CH_3)_2CH{-}C{\equiv}N$)	12	38	61.73		0.3	0.1	−0.5
98	methyl ethyl ketone ($CH_3{-}CO{-}CH_2{-}CH_3$)	13	40	67.65		0.2	−0.1	−0.4
99	isobutanal ($(CH_3)_2CH{-}CHO$)	13	40	67.85		−0.2	−0.6	−0.9
100	1,4-dioxane ($C_4H_8O_2$)	14	48	74.38	0.22	0.2	2.0	1.4
101	tetrahydropyrrole (C_4H_8NH)	14	40	78.17	−0.68	1.4	1.6	1.0
102	nitro-*s*-butane ($CH_3{-}CH_2{-}CH(CH_3){-}NO_2$)	16	56	81.88	0.34	2.7	1.7	2.0
103	diethyl ether ($CH_3{-}CH_2{-}O{-}CH_2{-}CH_3$)	15	42	82.30	−0.10	−1.1	−0.3	−0.2
104	dimethyl acetal ($CH_3{-}CH(OCH_3)_2$)	16	50	85.55	0.01	−0.2	0.6	0.4
105	*tert*-butylamine ($(CH_3)_3C{-}NH_2$)	16	42	89.32	0.36	0.2	−0.1	2.1
106	*N*-methyl pyrrole (cyc-$CH{=}CH{-}N(CH_3){-}CH{=}CH$)-	13	44	66.46	−0.31	−0.2	0.2	1.0
107	tetrahydropyran ($C_5H_{10}O$)	16	48	88.32	0.21	1.3	2.4	1.3
108	diethyl ketone ($CH_3{-}CH_2{-}CO{-}CH_2{-}CH_3$)	16	48	84.92	0.64	0.7	0.5	−0.2
109	isopropyl acetate ($CH_3{-}C({=}O){-}O{-}CH(CH_3)_2$)	17	56	88.07	−0.31	1.0	1.2	1.5
110	piperidine (cyc-$C_5H_{10}NH$)	17	48	95.78	−0.22	2.3	2.7	2.0
111	*tert*-butyl methyl ether ($(CH_3)_3C{-}O{-}CH_3$)	18	50	98.64	0.01	−0.3	0.1	0.5
112	1,3-difluorobenzene ($C_6H_4F_2$)	12	58	50.76		0.5	0.8	0.9
113	1,4-difluorobenzene ($C_6H_4F_2$)	12	58	50.74		0.3	0.7	0.1
114	fluorobenzene (C_6H_5F)	12	50	55.57		0.4	0.4	0.4
115	di-isopropyl ether ($(CH_3)_2CH{-}O{-}CH(CH_3)_2$)	21	58	115.75		−0.1	0.6	1.3
116	ethane, -hexafluoro-(C_2F_6)	8	66	18.46		1.2	1.0	1.0
117	azulene ($C_{10}H_8$)	18	68	87.62		−0.1	0.1	0.1

[a] Experimental data are taken from ref 20.

TABLE 3: Statistical Analysis of the Results Obtained for the 117 ZPEs (kcal/mol) Calculated Using the Parameters in Table 1 and the Corresponding HF-SCF/6-31G(d) Mulliken, NPA, and Stockholder Charges[a]

	Mulliken	NPA	stockholder
root-mean-square deviation	1.1	1.3	1.1
average deviation	−0.3	−0.3	−0.2
average absolute deviation	0.9	1.0	0.9
largest positive deviation	2.7	2.7	2.7
largest negative deviation	−3.0	−3.5	−2.5

[a] For the (G3-REZEP) values listed in Table 2.

SCF ZPEs. The parameters of eq 1 were obtained from a fitting procedure using the BP86/6-31G(d, p) ZPEs; this can explain the better agreement with B3LYP ZPEs. Because no experimental results were used in the parametrization of eq 1, fitting eq 1 to the currently used experimental ZPEs improves the agreement. The new equation obtained after fitting is the following:

$$\text{ZPE (kcal/mol)} = 6.99n_\text{H} + 3.74n_\text{C} + 3.98n_\text{N} + 3.45n_\text{O} + 2.79n_\text{F} - 4.63 \quad (8)$$

These new parameters provide considerably better rms and a.a. deviations from the 69 experimental results in this study (0.8 and 0.7 kcal/mol, respectively; cf. Table 4); however, the quality of the results remains slightly worse than it was in the original paper (a.a. deviation of 0.6 kcal/mol, cf. ref 1). We analyzed the sensitivity of the rms deviation from the experimental values on the variation of the multiplicative factors of eq 8. It was observed that the rms deviation is the most sensitive to the multiplicative factor of the hydrogen and carbon atoms; however, the rms deviation is stable for three decimal places against a ±0.01 kcal/mol change in the multiplicative factors. We note that whereas eq 1 provides similar-quality results compared to the quality of results obtained by the currently proposed method, eq 8 provides superior-quality results and shows better agreement with the 69 experimental values. Refitting our parameters using experimental ZPEs instead of scaled HF-SCF/6-31G(d) ZPEs would result in similar improvement. A comparison of the constants of eqs 1 and 8 with the energy parameters in Table 1 shows some agreement (although a simple comparison is not always sensible because the influence of the atomic charges makes such a comparison difficult). For example, comparing the values of $E_\text{ZPEpar}(N = 2, Z = 1$, 6-31G-(d), charge def., G3)/2 (half of the ZPE parameter for the hydrogen atom, 6.8−7.5 kcal/mol depending on the charge calculation method) with 7.06 (cf. eq 1) or 6.99 (cf. eq 8) kcal/mol shows good agreement. (Usually, the hydrogen atoms have positive partial charges, thus the average ZPE contribution of the hydrogen atoms is less than half of the corresponding parameter.)

Combining the REZEP ZPEs in Table 2 with the REBECEP energies yields a worsening of the calculated enthalpies of formation by increasing the a.a. deviations by about 0.2 kcal/mol compared to the original proposition where a scaled HF-SCF/6-31G(d) ZPE was used. So the worsening of the results is relatively small (because of random error compensations); however, the implicit ZPE and thermal correction calculations do not have such a negative effect on the quality of the results, thus an explicit ZPE calculation combined with the REBECEP method has no advantage over the REBECZTEP method for calculating the enthalpies of formation.[19] However, the REZEP method can be useful if explicit knowledge of ZPE is required.

5. Conclusions

We propose a new method for the rapid estimation of the ZPEs of the covalent molecules containing the H, C, N, O, and F atoms. This method uses HF-SCF/6-31G(d) atomic charges and fitted parameters to estimate the ZPE practically instantly after a HF calculation without performing an expensive frequency analysis. We used scaled HF-SCF/6-31G(d) ZPEs of 117 of molecules to obtain a fitted parameter set in the least-squares sense. This way the rather expensive frequency calculation can be replaced for enthalpy calculations. Our method is a refined version of the rapid ZPE estimation method proposed by Politzer et al. In that method, the molecular stoichiometry was used to estimate the ZPE using a simple equation.

A comparison of 69 experimental ZPEs with the HF-SCF/6-31G(d) (scaled by 0.8929), B3LYP/6-31G(2df,p) (scaled by 0.9854), and the two types of estimated ZPEs yields the following:

(1) The scaled HF-SCF ZPEs agree best with the experiment, and the B3LYP method provides similar-quality results: an ∼0.4 kcal/mol a.a. deviation from the experiment.

(2) The stoichiometric method and the REZEP method provide similar agreement with the experiment: an ∼1.0 kcal/mol a.a. deviation from the experiment.

(3) We reoptimized the parameters of the stoichiometric method and obtained a 0.7 kcal/mol a.a. deviation from the experiment.

(4) Using REZEP ZPEs instead of scaled HF ZPEs with REBECEP energies yields a 0.2 kcal/mol worsening of the a.a. deviation compared to the experimental enthalpies of formation, whereas implicit parametrization of the ZPE does not lead to a worsening of the a.a. deviation of the calculated enthalpies from the experimental enthalpies of formation, thus implicit ZPE calculations are advantageous.

TABLE 4: Deviations (kcal/mol) of the Various ZPE Calculation Methods Compared to 69 Experimental ZPE Values Given in Table 2[a]

					REZEP		
method	G3[b]	G3SX[c]	stoichiometry[d]	stoichiometry[e]	Mulliken	NPA	stockholder
root-mean-square deviation	0.47	0.55	1.30	0.83	1.28	1.45	1.17
average deviation	0.18	0.73	−0.04	0.00	−0.41	−0.52	−0.37
average absolute deviation	0.35	0.40	1.04	0.69	1.02	1.10	0.95
largest positive deviation	1.4	2.5	2.9	1.8	3.5	4.1	2.3
largest negative deviation	−0.8	−0.2	−3.5	−1.9	−3.2	−3.8	−3.0

[a] Experimental data are taken from ref 20. [b] HF-SCF/6-31G(d) ZPEs (scaled by 0.8929). [c] B3LYP/6-31G(2df,p) ZPEs (scaled by 0.9854). [d] Using the parameters of eq 1 published in ref 1. [e] Using new parameters optimized for experimental values (cf. eq 8).

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