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Reproducing Gaussian-3 Total Energy Using Fitted Atomic Correlation Parameters for the Rapid Estimation of Correlation Energy from Partial Charges Method and Hartree−Fock Results

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Gaussian-3 total energies has been approximated using single-point Hartree−Fock−self-consistent field (HF−SCF) total energies plus the correlation energy corrections calculated from the HF−SCF partial atomic charges according to the rapid estimation of correlation energy from partial charges (RECEP) method (*Chem. Phys. Lett.* **1999**, *307*, 469). Sixty-five closed-shell neutral molecules (composed of H, C, N, O, and F atoms) of the G2/97 thermochemistry database were used to obtain the fitted RECEP atomic correlation parameters. Four different mathematical definitions of partial charges were used to calculate the molecular correlation energies. The best results were obtained using the natural population analysis, although the other three are also recommended for use. The overall root-mean-square deviation of the RECEP-3 total energies from Gaussian-3 total energies for the 65 energies is 1.76 kcal/mol (the average absolute deviation is 1.43 kcal/mol). The root-mean-square deviation of fitted RECEP-3 enthalpies of formation from experimental enthalpies of formation for the 65 molecules is 2.17 kcal/mol (the average absolute deviation is 1.75 kcal/mol). The current fitted parameters of the RECEP method are recommended to estimate total correlation energies of closed-shell ground-state neutral molecules at stationary points of the potential-energy surface.

1. Introduction

The term "electron-correlation energy" (E_{corr}) for the electronic ground state is usually defined[1] as the difference between the exact nonrelativistic complete-CI (configurations interactions) electronic ground-state basis-set limit total energy [E_T(CI)] and the single-determinant ground-state HF−SCF (Hartree−Fock−self-consistent field) basis-set limit total energy [E_T(HF−SCF)] of a system:

$$E_{corr} = E_T(CI) - E_T(HF-SCF) \tag{1}$$

We use the well-defined unique restricted Hartree−Fock (RHF) total energy in our calculations where the spatial orbitals for α and β spins are identical for those of closed-shell molecules. Although the E_{corr} of an electron depends roughly (quasilinearly) on the number of other electrons, $N - 1$,[2,3] to obtain chemical accuracy, the effect of the potential of the nuclear frame must be considered.

The efficient calculation of correlation energy plays a central role in modern theoretical chemistry. The well-known, very expensive approximations for correlation energy are summarized elsewhere, e.g., in ref 4. The application of these methods is strictly limited by the large disk space demand, slow convergence, or divergence and by the huge computational demand. The very poor convergence and the $O(n^5) - O(n^7)$ scaling[4] with the basis-set increase led to development of the so-called composed (or extrapolation) methods, e.g., Gaussian-2 (G2)[5]

and Gaussian-3 (G3).[6] G3 theory achieves significantly improved accuracy compared to that of G2 theory. In addition, G3 theory requires fewer computational resources than G2 theory. For example, for benzene, it requires about one-half the CPU time, while giving a deviation from experiment of 0.6 kcal/mol, compared to 3.9 kcal/mol for G2 theory.[6] G3 theory uses the equilibrium geometries from second-order perturbation theory [MP2(FU)/6-31G(*d*)] and zero-point energies from HF−SCF theory [HF/6-31G(*d*)] followed by a series of single-point energy calculations at the second-order Møller−Plesset [MP2-(FU)/G3large], fourth-order Møller−Plesset [MP4(FC)/6-31G-(*d*), MP4(FC)/6-31+G(*d*), and MP4(FC)/6-31G(2*df*,*p*)], and quadratic configuration interaction [QCISD(T,FC)/6-31G(*d*)] levels of theory, where MP2(FU) denotes full second-order Møller−Plesset perturbation theory and FC denotes the frozen core approximation. The new basis set, referred to as G3large, includes functions necessary to core correlation. G3 theory approximates the QCISD(T,FU)/G3large level results, making assumptions about the additivity of the energies.[6] It also includes atomic spin−orbit correction and a higher-level empirical correction (HLC). G3 theory was assessed on a total of 299 energies (enthalpies of formation, ionization energies, electron affinities, and proton affinities) from the G2/97 test set.[7] The average absolute deviation from experiment of G3 theory for these energies is 1.01 kcal/mol. For the subset of 148 neutral enthalpies of formation, the average absolute deviation is 0.94 kcal/mol. The corresponding deviations for G2 theory are 1.48 and 1.56 kcal/mol, respectively.[5]

The analysis of the effects of different modifications on G2 theory shows that the most important improvement occurs

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because of the introduction of MP2(FU)/G3large energy correction (the average absolute deviation of 148 neutral enthalpies decreases by 0.4 kcal/mol).[6] Further 0.15 kcal/mol improvement occurs because the HLC in G3 theory has been modified in several respects from that in G2 theory. The E(HLC) of G3 is defined as $-An_\beta - B(n_\alpha - n_\beta)$ for molecules and $-Cn_\beta - D(n_\alpha - n_\beta)$ for atoms and atomic ions, where n_α and n_β are the number of α and β valence electrons, respectively, with $n_\alpha \geq n_\beta$. A is the correction for pairs of valence electrons, B is the correction for unpaired electrons in molecules. C and D are the corresponding corrections in free atoms. The use of different corrections for atoms and molecules was supposed to account for the different importance of missing higher angular momentum basis functions in molecules and in atoms. The A, B, C, and D parameters for the E(HLC) were obtained from a fit to the full set of experimental energies of the G2/97 database. Thus, the E(HLC) per unpaired electron is optimized in G3 theory, whereas in G2 theory, it was set to 0.19 mhartree, i.e., 0.12 kcal/mol (the difference of the exact and calculated energy of the hydrogen atom). Optimization resulted that $A \cong C$ (6.39 vs 6.22 mhartree, i.e., 4.01 vs 3.90 kcal/mol) and $B \gg D$ (2.98 vs 1.18 mhartree, i.e., 1.87 vs 0.74 kcal/mol). Thus, the G3 ΔE(HLC) for breaking an electron pair in an atomization reaction is 4.03 mhartree, i.e., 2.53 kcal/mol (compared to 4.62 mhartree, i.e., 2.90 kcal/mol, in G2 theory, the smaller correction in G3 means better approximation). The G3 ΔE(HLC) for breaking an electron pair in a bond-separation reaction leading to two molecular radicals is only 0.44 mhartree, i.e., 0.28 kcal/mol (compared to the same 4.62 mhartree, i.e., 2.90 kcal/mol, in G2 theory). The origin of this surprising difference is the large difference between the B and D constants. The use of HLC in G3 theory is vital for chemical accuracy (cf. bond-separation reactions with electron pair breaking). It was experienced that these corrections must be different for atoms and molecules (any attempt to use the same HLC parameters for atoms and molecules caused degradation of the quality of the results).[6] The spin−orbit corrections of G3 theory are used in an additive manner for atomic species only.[6] This approach fits well into our method.

The density functional theory (DFT) methods use a considerably faster algorithm for the estimation of the correlation energy.[8,9] The recent functionals BPW91, B3PW91, and B3LYP[10,11,12,13] provide usually rather good results and show a basis-set convergence similar to that of the HF−SCF method. However, it should be noted that the DFT methods also introduce several new problems: There is no simple way to improve the results (cf. the use of semiempirical functionals), and numerical instabilities might occur as well (cf. numerical integrals).

In our earlier works,[3,14] we analyzed the applicability of a radically different approach to calculate correlation energy very rapidly and effectively. This method requires a simple HF−SCF energy calculation in the equilibrium geometry. Next the atomic correlation energy for all atoms in a molecule is estimated from complete CI or B3LYP atomic correlation energies and atomic partial charges. Finally, the sum of the atomic correlation energies yields the molecular correlation energy. This procedure is called rapid estimation of correlation energy from partial charges (RECEP).[3] The results showed that, although the G2 total energy was approximated qualitatively correctly, the chemical accuracy (1−2 kcal/mol) was not reached using the "so-called" RECEP-c and RECEP-d parameters.[3,14] Next we developed a multilinear fitting procedure for the RECEP atomic correlation parameters (called RECEP-2 pa-

rameters[14] throughout this paper) in order to reproduce the G2 total energies from HF−SCF/6-311+G(2d,p) single-point total energies and from the partial charges of 41 closed-shell neutral molecules (composed of H, C, N, O, and F atoms) of the G2/97 thermochemistry database.[7] The MP2(FU)/6-31G(d) equilibrium geometries were used in these calculations. The best results were obtained using the partial charges calculated from natural population analysis (NPA).[15] The other three partial charge definitions ChelpG,[16] Merz−Kollman (MK),[17] and Mulliken[13] provide slightly worse results. The root-mean-square deviation of the RECEP-2(NPA) total energies from the G2 total energies was 1.8 kcal/mol (the average absolute deviation was 1.5 kcal/mol) for the 41 molecules.[14] The quality of the RECEP-2(NPA) atomic correlation parameters was also tested on a different set of 24 molecules of the G2/97 thermochemistry database. For these 24 molecules, the root-mean-square deviation of the RECEP-2(NPA) total energies from the G2 total energies was 2.3 kcal/mol (the average absolute deviation was 1.9 kcal/mol).[14] Comparison of approximate correlation energies defined as a difference of the G2 total energy and the HF/6-311+G-(2d,p) total energy with another approximation defined as a difference of the core correlated CCSD(T) infinite basis-set total energy and HF infinite basis-set total energy shows that the G2 correlation energy is about the 79% of the latter one. Although the G2 method provides reliable thermochemistry, the G2 total energies should be improved. This is in line with our nonfitted RECEP-c and -d results[14] and with the recently published G3 total energies.[6]

The impressing superiority of the results of G3 theory[6] over the results of G2 theory[5] inspired us to provide what we call RECEP-3 parameters obtained from G3 total energies. To achieve this goal, we have selected 65 closed-shell neutral molecules (composed of H, C, N, O, and F atoms) from the G2/97 test set.[7] We used the MP2(FU)/6-31G(d) geometries and performed the necessary single-point HF−SCF/6-311+G(2d,p) total energy and partial charge calculations (these calculations require several orders of magnitude less CPU time than the G3 calculations). We have also calculated the enthalpies of formation of the selected molecules and compared the results to the experimental results.

2. RECEP Method

For various atomic correlation energy parameters, we use the following notation: The correlation energy parameters $E_{par}(N, Z, \text{method})$ with three arguments denote the atomic RECEP parameters obtained from various methods without fit, where N is the number of the electrons and Z is the nuclear charge. Methods can be complete-CI,[18] corrected low-spin CI,[14] or low-spin B3LYP[13] (cf. Table 1, CI, low-spin CI and low-spin B3LYP parameters). The fitted parameters are noted as $E_{fitpar}(N, Z, \text{method}, \text{charge definition}, L)$, with five arguments, where N is the number of the electrons; Z is the nuclear charge; method can be G2 or G3; charge definition can be NPA,[15] ChelpG,[16] MK,[17] or Mulliken;[13] and L denotes the number of molecules used for the fit (cf. Table 1 for various fitted parameters).

For various estimations of the molecular correlation energy, we use the following notation: E_{corr} without argument notes the accurate complete-CI correlation energy (cf. eq 1). At the G2 or G3 level of theory, we define the correlation energy in the following way: $E_{corr}(\text{method}) = E_T(\text{method}) - E_T(\text{HF−SCF/basis})$. Although the $E_T(\text{method})$ (e.g., $E_T(G3)$ for G3 ground-state total energy) is well-defined for a given molecule, the $E_{corr}(\text{method})$ correlation energy depends on the basis set used for the $E_T(\text{HF−SCF/basis})$ total energy calculation. Our

TABLE 1: $E_{par}(N, Z, Method)$ and $E_{fitpar}(N, Z, Method, Charge Definition, L)$ RECEP Atomic Correlation Parameters (hartree) for E_{corr}(RECEP, Method, Charge Definition, L) Estimation for Molecular Correlation Energies

| | | | | low-spin | low-spin | Fitted parameters[a] | | | | | |
atom	N[b]	Z[b]	CI[c]	CI[d]	B3LYP[e]	G2, NPA, 41[f]	G3, MK, 41	G3, ChelpG, 41	G3, Mulliken, 41	G3, NPA, 41	G3, NPA, 65
H	2	1	−0.0395	−0.0395	−0.0432	−0.0376	−0.0419	−0.0417	−0.0398	−0.0374	−0.0381
C	4	6	−0.1264	−0.1264	−0.1079	−0.1105	n.a.	n.a.	−0.1515	−0.1466	−0.1487
	5	6	−0.1388	−0.1388	−0.1400	−0.1387	−0.1802	−0.1808	−0.1821	−0.1796	−0.1783
	6	6	−0.1564	−0.1754	−0.1911	−0.1659	−0.2094	−0.2098	−0.2106	−0.2103	−0.2111
	7	6	−0.1827	−0.2087	−0.2258	−0.1909	−0.2322	−0.2323	−0.2357	−0.2392	−0.2361
N	6	7	−0.1666	−0.1856	−0.2005	−0.2227	−0.2700	−0.2696	−0.2659	−0.2640	−0.2641
	7	7	−0.1883	−0.2143	−0.2373	−0.2259	−0.2740	−0.2741	−0.2690	−0.2721	−0.2721
	8	7	−0.2617	−0.2877	−0.3035	−0.2351	−0.2805	−0.2805	−0.2801	−0.2833	−0.2850
O	8	8	−0.2579	−0.2839	−0.3079	−0.2703	−0.3161	−0.3163	−0.3184	−0.3181	−0.3171
	9	8	−0.3314	−0.3314	−0.3619	−0.2790	−0.3237	−0.3240	−0.3265	−0.3295	−0.3298
F	9	9	−0.3245	−0.3245	−0.3599	−0.2892	−0.3399	−0.3397	−0.3373	−0.3396	−0.3399
	10	9	−0.3995	−0.3995	−0.4430	−0.3061	−0.3446	−0.3460	−0.3588	−0.3575	−0.3572

[a] The multilinear fitting procedure is described in ref 14 for 6-311+G(2d,p) basis set. [b] N is the number of electrons, and Z is the nuclear charge. [c] CI correlation energies for ground-state atoms in free space, cf. ref 18. [d] Estimated low-spin atomic CI correlation energies: a −0.019 hartree correction for 6 electronic systems and a −0.026 hartree correction for 7 and 8 electronic systems, cf. ref 3. [e] Atomic correlation energies for low-spin states (e.g., for carbon, the $1s^2 2s^2 2p_x^2$ singlet low-spin state) calculated as a difference of B3LYP/6-311+G(3df,2pd) and HF/6-311+G(3df,2pd) energies. n.a. = it was not necessary to calculate for the molecules used in ref 14 and here. [f] G2 results from ref 14.

experience shows that a difference of G2 and HF/6-311+G-(2d,p) total energies, i.e., E_{corr}(G2), can be used in RECEP with success (vide infra).

E_{corr}(RECEP, method, charge definition) denotes the correlation energy calculated using the $E_{par}(N, Z, method)$ parameters and the given partial charge definition. E_{corr}(RECEP fit, method, charge definition, L) denotes the correlation energy calculated using the $E_{fitpar}(N, Z, method, charge definition, L)$ parameters and the given partial charge definition, fitted to the correlation energy of the number L of molecules.

The RECEP formula for the E_{corr} value of ground-state neutral covalent molecules in the vicinity of stationary points is the following:

$$E_{corr}(\text{RECEP, method, charge definition}) \equiv$$
$$\sum_{A=1}^{M} E_{corr}(N_A, Z_A, \text{method, charge definition}) \quad (2)$$

In eq 2, N_A is the electron content on atom A, defined as Z_A minus the partial charge on atom A, and Z_A is the nuclear charge of atom A. The summation in eq 2 runs for all M atoms in the molecule. The two basic assumptions of eq 2 are that the correlation energy is the sum of the RECEP atomic correlation energies and the value of these atomic correlation energies can be estimated from the atomic partial charges in the molecule and from atomic correlation parameters.[3,14] Partial charges are essentially mathematical constructions that serve to reflect the electron content around the selected atom of the molecule. These partial charges are not physically measurable quantities, because they depend on the definition of the partition scheme of the electron density. The primary use of partial charges is to help chemists to establish empirical rules, e.g., for describing chemical bonds. However, partial charges can be defined to reproduce the measurable dipole moment and electrostatic potential of the molecule for example. The partial charges were successfully applied to identify the electron-rich (nucleophile) and electron-poor (electrophile) functional groups of molecules. Thus, partial charges in an ideal case are able to represent (in a simplified manner) the electron distribution in a molecule.

The $E_{corr}(N_A, Z_A, \text{method, charge definition})$ atomic electron-correlation terms in eq 2 are estimated as following (N_A is generally noninteger):

$$E_{corr}(N_A, Z_A, \text{method, charge definition}) =$$
$$(N_A - N1)E_{par}(N2, Z_A, \text{method}) +$$
$$(N2 - N_A)E_{par}(N1, Z_A, \text{method}) \quad (3)$$

where N1 and N2 are integer numbers of electrons, with N1 ≤ N_A ≤ N2, and N_A is the electron content around atom A. For hydrogen atoms, N1 = 0, $E_{par}(0, 1, \text{method}) = 0$, and N2 = 2. Thus, for hydrogen atoms, $E_{corr}(N_A, 1, \text{method, charge definition}) = N_A E_{par}(2, 1, \text{method})/2$. Similar equations hold for E_{fitpar} parameters (vide infra).

The atomic correlation parameters derived from CI atomic correlation energies in free space[18] $E_{par}(N, Z_A, \text{full-CI})$ are not the best choice for eq 3. The reason for this is that the correlation energy depends on spin pairing. Thus, high-spin atomic correlation energies are not the optimal choice in a low-spin (singlet) molecular environment. This is why low-spin CI and low-spin B3LYP atomic parameters were used in our earlier works[3,14] (cf. Table 1). For 6, 7, and 8 electronic systems, the differences between the high-spin and low-spin correlation energies are approximately −19, −26, and −26 mhartree, respectively.[3,14] These corrections were used to obtain low-spin CI atomic correlation parameters from atomic full-CI energies in Table 1. Our experience shows that chemical accuracy cannot be reached using such parameters. Figure 1 shows the quality of the linear fit between the G3 correlation energy and RECEP low-spin B3LYP correlation energy (called RECEP-d). Figure 2 shows the fit between the G3 correlation energy and RECEP low-spin CI correlation energy (called RECEP-c). We used the HF/6-311+G(2d,p) NPA charges in the RECEP calculations. The Gaussian 98 program[19] was used for the partial-charge and HF−SCF calculations throughout this paper. The agreement between the G3 and the low-spin RECEP-c and -d correlation energy is considerably better than the agreement between the G2 and the low-spin RECEP-c and -d correlation energy (for G2 regression analysis, see ref 14). However, these figures illustrate that the chemical accuracy cannot be reached using these RECEP parameters, the root-mean-square deviation of RECEP total energies from G3 total energies for the selected 65 molecules is about 29 kcal/mol.
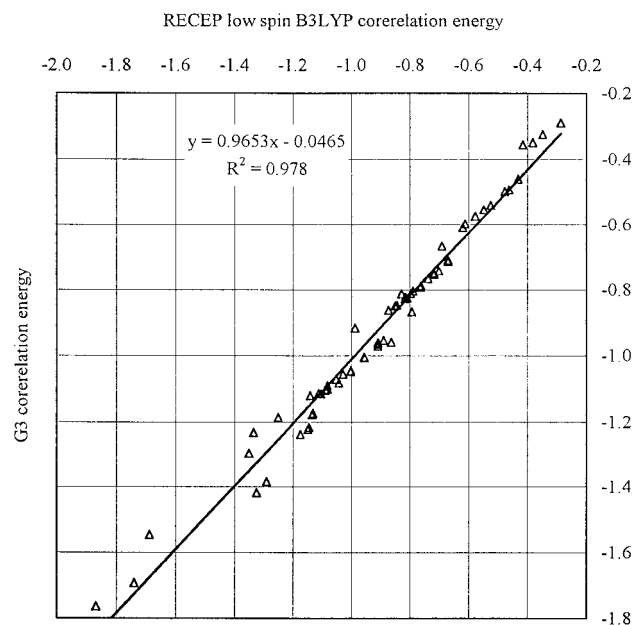
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RECEP low spin B3LYP corerelation energy

Figure 1. RECEP low-spin B3LYP correlation energy vs G3 correlation energy E_{corr}(G3), where E_{corr}(G3) = E_T(G3) − E_T(HF/6-311+G-(2d,p)). The RECEP low-spin B3LYP correlation energy (RECEP-d in text) is calculated from low-spin B3LYP correlation energy parameters in Table 1 and HF/6-311+G(2d,p) NPA[15] partial atomic charges using eqs 2 and 3.

RECEP low spin CI corerelation energy

Figure 2. RECEP low-spin CI correlation energy vs G3 correlation energy E_{corr}(G3), where E_{corr}(G3) = E_T(G3) − E_T(HF/6-311+G(2d,p)). The RECEP low-spin CI correlation energy (RECEP-c in text) is calculated from low-spin CI correlation energy parameters in Table 1 and HF/6-311+G(2d,p) NPA[15] partial atomic charges using eqs 2 and 3.
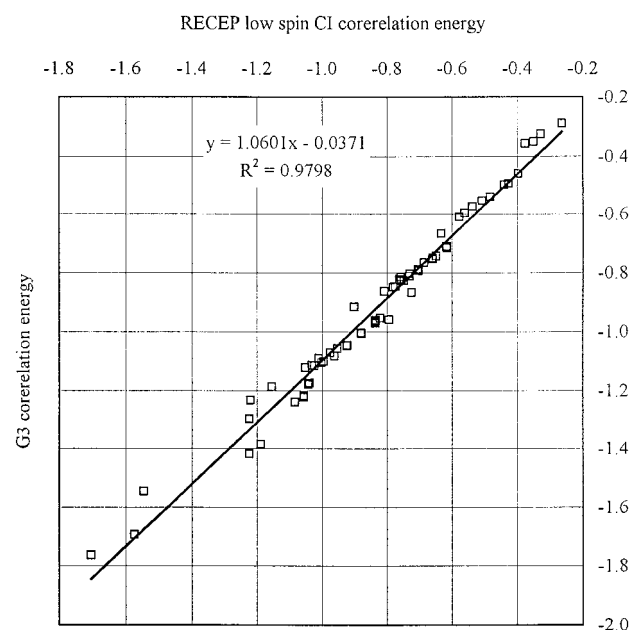
3. Fitting the RECEP Atomic Correlation Parameters

To obtain increased precision, a fitting procedure was applied to replace the E_{par}(N, Z, method) parameters in eq 3 by E_{fitpar}-(N, Z, method, charge definition, L) atomic correlation parameters. The fitting procedure yields the optimal values for the RECEP atomic correlation parameters that reproduce the known (e.g., G3) molecular correlation energies for a larger set of molecules.[14] Using these fitted parameters, eq 2 approaches chemical accuracy. Figure 3 shows the improvements because
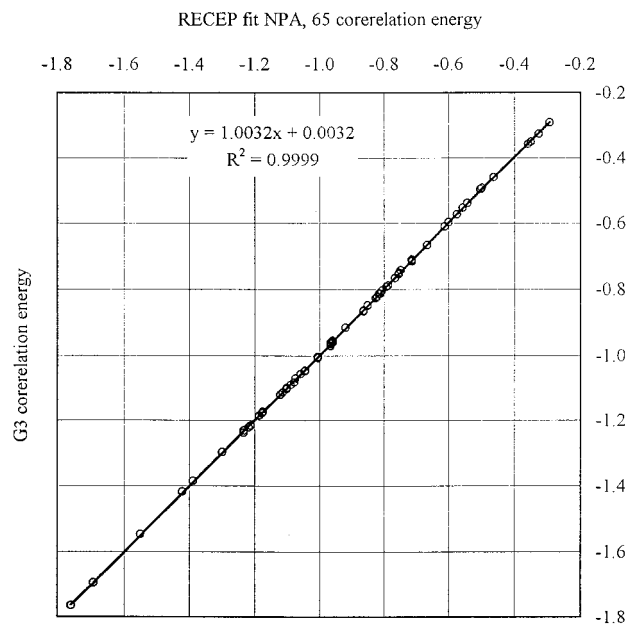
RECEP fit NPA, 65 corerelation energy

Figure 3. RECEP fit, NPA, 65 correlation energy vs G3 correlation energy E_{corr}(G3), where E_{corr}(G3) = E_T(G3) − E_T(HF/6-311+G(2d,p)). The RECEP fit, NPA, 65 correlation energy is calculated from corresponding correlation energy parameters in Table 1 and HF/6-311+G(2d,p) NPA[15] partial atomic charges using eqs 2 and 3.

of the fitting. Table 1 shows fitted atomic correlation parameter sets that can be used to obtain G2 or G3 quality correlation energies. Inspection of the values of the correlation energy parameters in Table 1 shows the following:

The low-spin B3LYP parameters are more negative than that of the low-spin CI values.

The fitted RECEP-2 (G2) parameters from ref 14 (G2, NPA, and 41 in Table 1) are usually closer to the more negative low-spin CI values than to the high-spin CI values (i.e., to the correlation energy in the free atom).

The fitted RECEP-3 (G3) parameters are more negative than the corresponding RECEP-2 parameters. This is the consequence of the lower G3 energy.

The E_{fitpar}(N, Z, NPA, 41) and E_{fitpar}(N, Z, NPA, 65) parameters are similar, this shows convergence with respect to the increase of the size of the molecule set.

The G3 correlation parameters are similar for the MK and ChelpG partial charges.

The G3 correlation parameters are similar for the Mulliken and NPA partial charges.

Somewhat larger difference can be observed between the ChelpG and NPA charges.

The values of the fitted RECEP correlation energy parameters (and the quality of the results) depend very slightly on the charge definition, thus the method is not sensitive to the partial charges used in the fitting procedure. This is valid for the present set of molecules and the charge definitions used in this paper.

The use of the HF−SCF partial charges, derived from the one-electron density, $\rho_{HF-SCF}(\mathbf{r})$, for electron-correlation effects can be justified readily. It was observed that DFT correlation energy functionals provide adequate correlation energy using a relatively low-quality basis set $\rho_{HF-SCF}(\mathbf{r})$.[8] A similar argument[3,14] holds for the HF−SCF level partial charges used in eq 3. This observation originates in the fact that the E_{corr} in DFT is an integrated quantity with respect to the $\rho(\mathbf{r})$, and the one-electron density integrates to the number of electrons in any case. Thus, more accurate electron density causes a relatively small change in E_{corr}. We also experienced that different partial

charge definitions provide only slight differences in the correlation energy. The best results were obtained with NPA charges, so these results will be discussed in the subsequent sections (the results obtained with MK, ChelpG, and Mulliken charges are not shown).

In Table 2, we show the HF/6-311+G(2d,p) total energies, E_T(HF/6-311+G(2d,p)), and the G3 correlation energies, E_{corr}-(G3), defined as E_T(G3) − E_T(HF/6-311+G(2d,p)), the energy deviations between E_{corr}(G2)[14] or E_{corr}(G3) and E_{corr}(RECEP) for the set of 65 closed-shell molecules composed of H, C, N, O, and F atoms. These molecules were selected from the G2/97 thermochemistry database.

The total energy of a RECEP parameter set is given by

$$E_T(\text{RECEP, method, charge definition, } L) =$$
$$E_T(\text{HF/6-311+G(2d,p)}) +$$
$$E_{corr}(\text{RECEP, method, charge definition, } L) \quad (4)$$

Our previous experience has shown that the sum of these correlation energies and HF/6-311+G(2d,p) total energies approximate the G2 total energies within a few kcal/mol error.[14] The same method is used to approximate the G3 total energies. Statistical analysis of the results in Table 2 provides that the root-mean-square deviation of fitted RECEP, G3, NPA, and 41 total energies from G3 total energies for the selected 41 molecules is 1.72 kcal/mol (the average absolute deviation is 1.38 kcal/mol). The root-mean-square deviation of the same type RECEP total energies from G3 total energies for the 24 test molecules is 2.32 kcal/mol (the average absolute deviation is 1.97 kcal/mol; cf. Table 2, data in italic, i.e., molecules from 42 to 65). Finally we used all of the 65 G3 total energies in the fitting procedure. The overall root-mean-square deviation of fitted RECEP-3 total energies from G3 total energies for the 65 energies is 1.76 kcal/mol (the average absolute deviation is 1.43 kcal/mol).

The atomization energies of the 65 molecules (ΣD_0) were obtained from the E_T(RECEP, G3, NPA, 65) total energies, from the G3 atomic energies,[6] and from the corrected HF/6-31G(d) zero-point vibration energies (ZPVE).[20] The enthalpy of formation at 0 K, ΔH_f^0(0 K), was calculated as a difference of the sum of the atomic enthalpies of formation and the atomization energy of the molecule. The necessary thermal corrections for ΔH_f^0(298 K) were calculated from HF/6-31G(d) vibration analysis.[20] Table 2 shows the experimental ΔH_f^0(298 K) values for the 65 molecules[6] and the deviation between the experimental and calculated values. Because the current parameter set was fitted to G3 results, the ΔH_f^0(298 K) values calculated from the RECEP energies include the G3 errors. The root-mean-square deviation of the G3 ΔH_f^0(298 K) values from the experimental values is 1.15 kcal/mol (the average absolute deviation is 0.74 kcal/mol) for the 65 selected molecules.[6] The root-mean-square deviation of the best RECEP ΔH_f^0(298 K) values from the experimental values is 2.17 kcal/mol (the average absolute deviation is 1.75 kcal/mol) for the same set of molecules. Our preliminary results show that the elimination of the errors arising from the G3 method is feasible and the average absolute deviation of the RECEP ΔH_f^0(298 K) values from the experimental values can be reduced to 1.6−1.4 kcal/mol. This idea will be developed further in subsequent papers. Such a degree of precision using simple HF−SCF results seems to be rather useful. Analysis of the results in Table 2 provides that the RECEP method has difficulties with the HCN, N$_2$O, COF$_2$, bicyclobutane (−6.7 kcal/mol deviation), spiropentane, acetonytrile (3.5 kcal/mol deviation), furane, and pyrrole

molecules (the largest deviations from the experimental ΔH_f^0-(298 K) values are noted in parentheses). We note that even the G3 ΔH_f^0(298 K) value of the COF$_2$ molecule shows a large (cf. −3.4 kcal/mol in Table 2) deviation from that of the experiment. The experimental enthalpies of formation of bicyclobutane and spiropentane are well reproduced by G3 theory, whereas our RECEP-3 parametrization cannot reproduce the experimental values. These strained cyclic hydrocarbons certainly require a different parametrization, and they should be treated separately. A similar problem was observed in our previous RECEP-2 study,[14] −5.3 and −4.3 kcal/mol deviations for bicyclobutane and spiropentane, respectively.

4. Improved Approximations to Correlation Energy

Benchmark quality ab initio atomization energies became recently available for small neutral molecules up to *trans*-butadiene and benzene;[21] this provides an opportunity to judge the quality of G3 total energies. In Table 3, we show the HF−SCF and CCSD(T) basis-set limit total energies for 17 molecules containing H, C, N, O, and F atoms. For infinite basis-set HF−SCF total energy, an A + B/C^n type extrapolation[22] formula was used, where n = 3, 4, and 5 (TQ5 extrapolation: $E_\infty = E[5] − (E[5] − E[Q])^2/(E[5] − 2E[Q] + E[T])$, using a correlation consistent basis set). For infinite basis-set CCSD-(T) valence correlation energy an A + B/n^3 type extrapolation formula[23] was used, where n = 3 and 4 (TQ extrapolation: $E_\infty = E[Q] + (E[Q] − E[T])/((^4/_3)^3 − 1)$, using a correlation consistent basis set). The core correlation was added to the valence correlation energy.[21] We note that we recalculated the CCSD(T) total energies from the published atomization energies.[21] This can led to a 1 millihartree error in the CCSD(T) energy.

There is a simple linear relationship between HF/6-311+G-(2d,p) and HF−SCF limit total energies, as can be seen in Table 3: E_0(HF−SCF limit) = 1.000 178E_0(HF/6-311+G(2d,p)) within ±5 kcal/mol error bar (the root-mean-square deviation is 2 kcal/mol, and the average absolute deviation is 1.4 kcal/mol). The largest errors were observed for O$_2$ (4.8 kcal/mol) and for benzene (−4.2 kcal/mol).

The analysis of the results in Table 3 also shows that the G3 total energy is considerably more negative than the corresponding G2 total energy. However, the CCSD(T) basis-set limit total energy is more negative than the G3 total energy. Comparison of the correlation energy defined as a difference of the G3 total energy and the HF/6-311+G(2d,p) energy with the infinite basis-set CCSD(T) correlation energy, provides that the G3 correlation energy is about the 97% of the latter one. The statistical correlation between the two correlation energies is excellent (cf. R^2 = 0.999 in Figure 4).

We note that it is possible to derive very precise correlation energies from the experimental enthalpy of formation values. Using a known molecular geometry, an extrapolated HF−SCF limit total energy can be calculated. The difference of the complete-CI energies that are estimated from the experimental enthalpy of formation and HF−SCF limit total energy could provide good quality, well-defined correlation energy. A fitting procedure for these correlation energies could provide the ultimate RECEP atomic correlation parameters. However, our preliminary study shows that the HF−SCF limit energies, which are expensive to calculate, can be substituted with lower level HF−SCF energies, and the deviation can be incorporated into the RECEP parameters as well. We are currently searching the optimal level of HF−SCF calculations for RECEP studies. These results will be published in the subsequent papers.

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TABLE 2: HF/6-311+G(2d,p) Total Energies E_T(HF−SCF), G3 Correlation Energies E_{corr}(G3) (hartree), and Deviations between RECEP Estimation and G2 or G3 Total Energies (kcal/mol) for 65 Molecules of the G2/97 Database[a]

				energy deviations E_{corr}(method) − E_{corr}(RECEP, method, charge definition, L)						
	molecule	E_T(HF−SCF)	E_{corr}(G3)	low-spin B3LYP, NPA	low-spin CI, NPA	Fit, G2, NPA, 41[b]	Fit, G3, NPA, 41	Fit, G3, NPA, 65	ΔH_f^0 (298 K) expt[c]	deviation (expt − RECEP)[d]
1	methane (CH$_4$)	−40.2102	−0.2901	−2.1	−16.3	1.3	1.4	0.9	−17.9	1.2
2	ammonia (NH$_3$)	−56.2150	−0.3251	14.2	1.8	0.0	0.0	0.0	−11.0	−0.8
3	water (H$_2$O)	−76.0527	−0.3499	19.6	−0.5	−0.9	−0.7	−0.4	−57.8	−0.7
4	hydrogenfluoride (HF)	−100.0526	−0.3574	36.7	11.3	0.4	0.3	0.3	−65.1	0.5
5	acetylene (C$_2$H$_2$)	−76.8422	−0.4601	−18.0	−39.8	1.5	1.5	1.8	54.2	1.1
6	ethylene (H$_2$C=CH$_2$)	−78.0584	−0.4979	−12.8	−36.8	3.0	2.7	2.8	12.5	3.0
7	ethane (H$_3$C−CH$_3$)	−79.2541	−0.5405	−9.8	−36.1	1.7	1.5	1.2	−20.1	1.5
8	hydrogencyanide (HCN)	−92.8979	−0.4936	−19.8	−42.1	1.9	2.1	3.0	31.5	3.2
9	formaldehyde (H$_2$C=O)	−113.9033	−0.5538	−2.8	−28.4	1.7	1.7	2.0	−26.0	2.6
10	methanol (CH$_3$−OH)	−115.0815	−0.5971	9.1	−22.6	0.8	0.9	1.9	−48.0	2.0
11	hydrazine (H$_2$N−NH$_2$)	−111.2174	−0.6097	6.0	−19.9	−0.3	−0.4	1.7	22.8	−0.4
12	hydrogenperoxide (HO−OH)	−150.8235	−0.6668	14.2	−20.9	0.2	0.0	−0.3	−32.5	−1.5
13	carbondioxide (CO$_2$)	−187.6892	−0.8225	−4.5	−37.3	−0.2	−0.3	−0.9	−94.1	0.3
14	CF$_4$	−435.7780	−1.5469	89.2	−1.0	0.6	0.7	1.1	−223.0	1.9
15	COF$_2$	−311.7100	−1.1860	41.2	−20.6	−0.3	−0.6	−0.7	−149.1	−4.1
16	N$_2$O	−183.7207	−0.8673	−46.8	−89.3	−1.5	−2.0	−2.3	19.6	−4.0
17	NF$_3$	−352.6474	−1.2967	34.5	−46.3	1.1	1.0	1.3	−31.6	1.3
18	C$_2$F$_4$(F$_2$C=CF$_2$)	−473.5672	−1.7634	65.6	−36.7	−1.8	−1.9	−2.7	−157.4	2.2
19	CF$_3$CN	−428.6011	−1.6935	30.2	−61.8	−1.3	−0.9	−0.8	−118.4	0.9
20	propyne (C$_3$H$_4$)	−115.8984	−0.7106	−25.0	−58.7	2.3	2.3	2.4	44.2	2.2
21	allene (C$_3$H$_4$)	−115.8970	−0.7103	−26.1	−59.1	2.3	2.1	2.0	45.5	2.4
22	cyclopropene (C$_3$H$_4$)	−115.8553	−0.7152	−29.0	−62.8	−1.8	−1.4	−0.9	66.2	−3.2
23	propylene (C$_3$H$_6$)	−117.1082	−0.7503	−21.1	−57.1	2.3	2.2	2.2	4.8	2.3
24	cyclopropane (C$_3$H$_6$)	−117.0916	−0.7539	−23.0	−59.0	−0.2	0.2	0.1	12.7	−0.6
25	propane (C$_3$H$_8$)	−118.2994	−0.7932	−18.7	−56.9	0.7	0.5	0.2	−25.0	0.5
26	*trans*-butadiene	−154.9667	−0.9611	−33.4	−79.2	2.2	1.9	2.4	26.3	2.1
27	dimethylacetylene (2-butyne)	−154.9525	−0.9618	−32.7	−78.4	2.6	2.3	2.5	34.8	2.1
28	methylenecyclopropane (C$_4$H$_6$)	−154.9303	−0.9657	−35.6	−81.4	−0.6	−0.5	−0.2	47.9	1.3
29	bicyclobutane	−154.9120	−0.9718	−39.6	−85.4	−5.3	−4.5	−4.1	51.9	−6.7
30	cyclobutane (C$_4$H$_8$)	−156.1390	−1.0076	−33.2	−81.2	−2.2	−2.0	−1.8	6.8	−1.8
31	isobutene (C$_4$H$_8$)	−156.1577	−1.0045	−30.6	−78.5	0.5	0.5	0.4	−4.0	0.4
32	*trans*-butane (C$_4$H$_{10}$)	−157.3446	−1.0463	−27.8	−78.1	−0.6	−0.9	−1.0	−30.0	−0.6
33	isobutane (C$_4$H$_{10}$)	−157.3451	−1.0484	−28.8	−79.1	−1.9	−2.0	−2.2	−32.1	−1.9
34	spiropentane (C$_5$H$_8$)	−193.9673	−1.2223	−46.7	−104.5	−4.3	−3.9	−3.5	44.3	−3.9
35	benzene (C$_6$H$_6$)	−230.7633	−1.3851	−58.8	−124.1	1.1	0.4	1.6	19.7	1.0
36	difluoromethane (H$_2$CF$_2$)	−237.9779	−0.9165	44.4	−10.3	1.7	1.4	1.5	−107.7	2.2
37	trifluoromethane (HCF$_3$)	−336.8798	−1.2319	65.2	−8.1	0.8	0.9	0.6	−166.6	1.1
38	methylamine (H$_3$C−NH$_2$)	−95.2473	−0.5744	2.0	−23.0	−1.2	−1.4	0.3	−5.5	−0.7
39	acetonitrile (CH$_3$−CN)	−131.9605	−0.7428	−26.9	−59.3	3.2	3.3	3.3	18.0	3.5
40	nitromethane (CH$_3$−NO$_2$)	−243.7359	−1.1784	−28.2	−86.0	−0.6	−0.4	−0.6	−17.8	−0.6
41	methylnitrite (CH$_3$−O−N=O)	−243.7366	−1.1735	−26.3	−84.5	0.7	1.0	1.2	−15.9	1.0
42	HCOOH (formic acid)	−188.8266	−0.8632	5.6	−34.1	−0.4	0.0	−0.3	−90.5	−0.2
43	HCOOCH$_3$ (methyl formate)	−227.8588	−1.1148	−6.6	−58.0	−1.2	−1.2	−1.0	−85.0	0.6
44	CH$_3$CONH$_2$ (acetamide)	−208.0454	−1.0906	−5.6	−50.8	−1.7	−1.3	−1.1	−57.0	−2.2
45	C$_2$H$_4$NH (aziridine)	−133.0800	−0.7887	−16.7	−52.5	−3.0	−2.6	−0.8	30.2	−2.0
46	NCCN (cyanogen)	−184.6243	−0.9598	−60.6	−103.4	−1.4	−1.8	−1.0	73.3	−1.3
47	(CH$_3$)$_2$NH (dimethylamine)	−134.2834	−0.8265	−10.9	−48.8	−1.6	−1.8	0.0	−4.4	−0.9
48	CH$_3$CH$_2$NH$_2$ (trans ethylamine)	−134.2953	−0.8271	−6.6	−43.7	−2.0	−2.2	−0.6	−11.3	−0.6
49	CH$_2$CO (ketene)	−151.7713	−0.7661	−18.4	−50.0	1.9	2.1	0.3	−11.4	1.1
50	C$_2$H$_4$O (oxirane)	−152.9137	−0.8125	−9.8	−50.9	−2.4	−2.2	−0.6	−12.6	−0.6
51	CH$_3$CHO (acetaldehyde)	−152.9638	−0.8045	−10.0	−46.5	2.2	2.5	1.9	−39.7	2.0
52	HCOCOH (glyoxal)	−226.6589	−1.0713	−12.1	−60.4	2.2	2.7	2.5	−50.7	3.3
53	CH$_3$CH$_2$OH (ethanol)	−154.1321	−0.8494	0.3	−42.8	0.3	0.2	0.9	−56.2	1.0
54	CH$_3$OCH$_3$ (dimethyl ether)	−154.1148	−0.8480	−2.9	−46.3	0.3	0.0	1.6	−44.0	2.0
55	CH$_2$=CHF (vinyl fluoride)	−176.9412	−0.8139	9.2	−34.8	2.0	1.7	1.7	−33.2	2.9
56	CH$_2$=CHCN (acrylonitrile)	−169.8097	−0.9547	−40.7	−83.3	2.5	2.2	2.9	43.2	1.3
57	CH$_3$COCH$_3$ (acetone)	−192.0208	−1.0567	−18.1	−65.6	1.7	2.4	1.0	−51.9	1.1
58	CH$_3$COOH (acetic acid)	−227.8859	−1.1137	−1.3	−51.9	0.4	1.0	−0.2	−103.4	−0.3
59	CH$_3$COF (acetyl fluoride)	−251.8768	−1.1212	11.9	−43.7	0.9	1.1	−0.2	−105.7	−0.1
60	(CH$_3$)$_2$CHOH (2-propanol)	−193.1819	−1.1041	−10.3	−64.5	−1.8	−1.9	−1.7	−65.2	−1.2
61	C$_2$H$_5$OCH$_3$ (methyl ethyl ether)	−193.1655	−1.1006	−12.0	−66.8	−0.5	−1.0	0.4	−51.7	1.5
62	(CH$_3$)$_3$N (trimethylamine)	−173.3212	−1.0821	−24.9	−75.4	−4.3	−4.7	−2.7	−5.7	−2.5
63	C$_4$H$_4$O (furan)	−228.6888	−1.2387	−40.7	−98.0	−4.6	−4.3	−3.8	−8.3	−4.3
64	C$_4$H$_5$N (pyrrole)	−208.8676	−1.2167	−45.4	−101.1	−5.5	−5.2	−3.2	25.9	−4.4
65	C$_5$H$_5$N (pyridine)	−246.7597	−1.4184	−58.0	−122.2	−0.3	−0.8	1.2	33.6	1.0

[a] The corresponding $E_{corr}(N_A,Z_A)$ RECEP atomic correlation parameters are listed in Table 1. The simple sum of the HF−SCF total and the G3 correlation energy yields the G3 total energy E_T(G3) = E_T(HF−SCF) + E_{corr}(G3) for the ground electronic state (see eq 1), thus the energy differences directly provide the deviation compared to the G3 energy (E_{corr}(G3) − E_{corr}(RECEP) = E_T(G3) − E_T(RECEP), where E_T(RECEP) = E_T(HF−SCF) + E_{corr}(RECEP) in accordance with eq 4). The geometries were optimized at the MP2(FU)/6-31G(d) level. [b] G2 values from ref 14. [c] See ref 6 for experimental references. [d] Calculated from E_T(RECEP-fit, G3, NPA, 65) values.

TABLE 3: Set of 17 Molecules with Known HF−SCF, G2, G3, and CCSD(T) Total Energies[a] as well as G3 and CCSD(T) Limit Correlation Energies (hartree)

		HF/6-311+G(2d,p)	HF−SCF/limit	G2	G3	CCSD(T) limit + core correlation	correlation energy G3	correlation energy limit
1	H_2	−1.1325	−1.1337	−1.1758	−1.1768	−1.1746	−0.0443	−0.0409
2	CH	−38.2754	−38.2799	−38.4188	−38.4645	−38.4719	−0.1891	−0.1920
3	CH_3	−39.5705	−39.5767	−39.7727	−39.8210	−39.8286	−0.2504	−0.2519
4	CH_4	−40.2102	−40.2172	−40.4535	−40.5003	−40.5080	−0.2901	−0.2908
5	NH_3	−56.2150	−56.2251	−56.4917	−56.5401	−56.5573	−0.3251	−0.3323
6	H_2O	−76.0527	−76.0677	−76.3526	−76.4026	−76.4317	−0.3499	−0.3640
7	HF	−100.0526	−100.0714	−100.3589	−100.4100	−100.4528	−0.3574	−0.3814
8	C_2H_2	−76.8422	−76.8554	−77.2120	−77.3023	−77.3220	−0.4601	−0.4666
9	C_2H_4	−78.0584	−78.0709	−78.4648	−78.5563	−78.5751	−0.4979	−0.5042
10	CO	−112.7699	−112.7912	−113.1825	−113.2723	−113.3119	−0.5024	−0.5207
11	N_2	−108.9680	−108.9928	−109.3982	−109.4896	−109.5280	−0.5217	−0.5352
12	H_2CO	−113.9033	−113.9235	−114.3650	−114.4571	−114.4951	−0.5538	−0.5717
13	O_2	−149.6337	−149.6680	−150.1523	−150.2523	−150.3120	−0.6186	−0.6440
14	F_2	−198.7380	−198.7744	−199.3265	−199.4287	−199.5150	−0.6907	−0.7406
15	CO_2	−187.6892	−187.7253	−188.3727	−188.5117	−188.5798	−0.8224	−0.8545
16	*trans*-butadiene[b]	−154.9667	−154.9929	−155.7460	−155.9278	−155.9666	−0.9611	−0.9737
17	benzene[b]	−230.7633	−230.8013	−231.8767	−232.1484	−232.2103	−1.3850	−1.4090

[a] For the HF−SCF limit, the TQ5 extrapolation and for CCSD(T) limit, the Q5 extrapolations were used (cf. text, the values were derived from the non relativistic values by J. M. L. Martin in ref 21). [b] A simplified W1 extrapolation scheme was used, cf. ref 21.
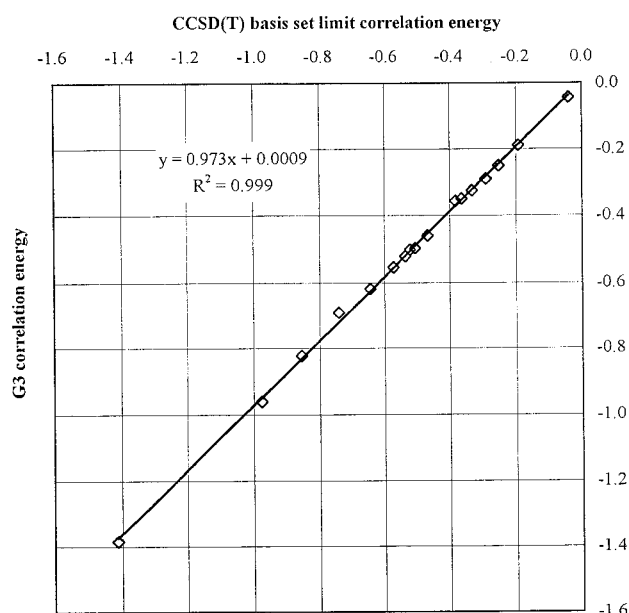

Figure 4. CCSD(T) basis-set limit correlation energy vs G3 correlation energy $E_{corr}(G3)$, where $E_{corr}(G3) = E_T(G3) − E_T(HF/6-311+G(2d,p))$. The CCSD(T) basis-set limit correlation energy is calculated as a difference of the infinite basis-set CCSD(T) valence correlation energy [an $A + B/n^3$ type extrapolation formula[23] was used, where $n = 3$ and 4; TQ extrapolation: $E_\infty = E[Q] + (E[Q] − E[T])/((^4/_3)^3 − 1))$ plus core correlation correction and infinite basis-set HF−SCF total energy [an $A + B/C^n$ type extrapolation[22] formula was used, where $n = 3, 4,$ and 5; TQ5 extrapolation: $E_\infty = E[5] − (E[5] − E[Q])^2/(E[5] − 2E[Q] + E[T])$, using correlation consistent basis sets].[21]

5. Conclusions

Our radically new RECEP method was parametrized to reproduce the G3 total energy using single-point HF/6-311+G-(2d,p) total energies and partial atomic charges. For this purpose, we have selected 65 molecules from the G2/97 thermochemistry database composed of the elements H, C, N, O, and F. The RECEP correlation energies calculated with the low-spin CI or B3LYP atomic correlation parameters with NPA charges do not reach the required chemical accuracy (the root-mean-square deviation of RECEP total energies from G3 total energies for the selected 65 molecules is about 29 kcal/mol).[24] To obtain better energies, we have optimized the RECEP atomic correla-

tion parameters by a simple multilinear fit to approximate the G3 total energies of the above-mentioned 65 molecules for various charge definitions (MK, ChelpG, Mulliken, and NPA). We experienced that different partial charge definitions provide only slight differences in the correlation energy. The best results were obtained with NPA charges. The overall root-mean-square deviation of fitted RECEP-3 total energies from G3 total energies for the 65 energies is 1.76 kcal/mol (the average absolute deviation is 1.43 kcal/mol).

The root-mean-square deviation of the best RECEP ΔH_f^0-(298 K) values from the experimental values is 2.17 kcal/mol (the average absolute deviation is 1.75 kcal/mol) for the set of 65 molecules. The most problematic molecules for the RECEP-3 method were bicyclobutane (−6.7 kcal/mol deviation) and acetonytrile (3.5 kcal/mol deviation). In some of the problem cases, the G3 method also has a large deviation from the experiment (e.g., −3.4 kcal/mol for the COF_2 molecule). The G3 errors make the RECEP errors somewhat larger. Our preliminary results shows that the elimination of the errors arising from the G3 method decrease the average absolute deviation of the RECEP ΔH_f^0(298 K) values from the experimental values to 1.6−1.4 kcal/mol. The strained hydrocarbons probably require a different parametrization, and they should be treated separately. Otherwise the current RECEP-3 can be used to approximate very rapidly the enthalpies of formation of the studied compounds with the above-mentioned error bars. We are currently searching the optimal level of HF−SCF calculations for RECEP studies, where the basis-set error still can be incorporated into the RECEP atomic correlation parameters as well.

Comparison of G2, G3, and CCSD(T) basis-set limit core correlated total energies has provided that the G3 energies are considerably better than the G2 energies, but does not reach the CCSD(T) basis-set limit quality. We arbitrarily defined the G3 correlation energy as a difference of the G3 total energy and the HF/6-311+G(2d,p) energy. This correlation energy shows an excellent linear correlation ($R^2 = 0.999$) with the CCSD(T) basis-set limit correlation energy.

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References and Notes

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