A Simple Coupling Scheme between Hartree−Fock and Local Spin-Density Functional Theories

Sherif A. Kafafi* and El-Sayed R. H. El-Gharkawy

Center for Advanced Research in Biotechnology, University of Maryland Biotechnology Institute,
9600 Gudelsky Drive, Rockville, Maryland 20850

Received: January 7, 1998; In Final Form: March 2, 1998

A simple coupling scheme between nonlocal Hartree−Fock exchange, gradient corrected local spin-density exchange, and the Pade approximated Vosko, Wilk, and Nusair correlation functional is reported. The combination of these functionals with the electrons kinetic and Coulomb repulsion terms yields a method that scales as $\sim N^3$, where N is the number of basis functions, compared to $\sim N^7$ for Gaussian-2 (G2) ab initio theory and $\sim N^4$ and $\sim N^5$ for Becke's B3LYP and Bx88/Bc95 density functional approaches. The reported method is denoted by HFS−BVWN, which stands for Hartree−Fock−Slater−Becke−Vosko−Wilk−Nusair. The results of HFS−BVWN/6-311+g(3df, p) computations on atoms of the first two rows of the periodic table, hydrogen−argon, and selected small molecules showed that the method underestimates atomic and molecular exchange-correlation (XC) energies by ∼ 0.13% and 0.14%, respectively. We demonstrated that the application of Dewar's atom equivalent scheme to atomic energies partially compensated for the errors in XC energies. Atom equivalents for hydrogen through chlorine, excluding the noble gases, were derived. In a data set comprised of 150 atomic and molecular species, the reported method achieved average absolute errors of 1.8 kcal/mol and 0.12 and 0.13 eV for room temperature heats of formation, ionization potentials, and electron affinities, respectively. The overall average absolute error of HFS−BVWN method, 2.5 kcal/mol, is thus within 0.5 kcal/mol from the corresponding accuracies of G2 and Bx88/Bc95 theories, 2 kcal/mol, and superior to the B3LYP (3.5 kcal/mol) and BLYP (3.9 kcal/mol) methods. The HFS−BVWN/6-311+g(3df, p) level of theory is much less computer intensive than the G2, B3LYP, and Bx88/Bc95 theories and, thus, may be applicable to larger molecular systems than those attainable by the latter approaches.

I. Introduction

One of the central goals of quantum chemistry is the computation of electronic and thermodynamic properties of molecular systems with an accuracy of ±2 kcal/mol.[1−15] For highly reactive molecules, radicals, and transition states which evade experimental measurement of their thermochemical properties, quantum mechanical methods represent the only possible tools for predicting their structures and energetics.[9] Indeed, recent advances in computer technology and the concomitant development of efficient ab initio and density functional theory (DFT) computer codes led to the formulation of several methodologies capable of predicting the thermochemical properties of molecular systems with the required target accuracy.[1,2,6,8,15,16]

Gaussian-2 (G2) ab initio theory is one of the most reliable computational tools available nowadays.[1,2] It is based on computations using the 6-311+G(3df, 2p) basis sets. In addition, a correction term is added to account for the nonadditivity of diffuse sp and 2df functions. Electron correlation is partially accounted for using Moller−Plesset perturbation theory and quadratic configuration interaction. The incomplete treatment of electron correlation in G2 theory led Pople et al.[1,2] to introduce an empirical higher level correction term. G2 theory has been shown to be successful in predicting geometries, vibrational frequencies, and electronic and thermodynamic properties of numerous neutral molecules, radicals, and intermediates. The average absolute error in computed thermochemical properties from G2 theory is within 2 kcal/mol from corresponding experimental values.[1,2,15] However, its $\sim N^7$ scaling properties, where N is the number of basis functions, prohibits the application of G2 to chemical systems containing more than 8−10 atoms. A promising alternative to ab initio theories with less stringent scaling properties are DFT-based methodologies.[4−8,11,14,16]

In a series of systematic studies, Becke formulated several semiempirical DFT-based methods for predicting structures, energies, and corresponding thermochemical properties of molecular systems.[16] The most popular of these methods are Becke's three-parameter procedure, B3LYP,[16d] and its successor Bx88/Bc95.[16e] The general strategy used in formulating B3LYP and Bx88/Bc95 relies on the observation that DFT methods in which the nonlocal Hartree−Fock (HF) exchange term is replaced by any of the available gradient corrected exchange-correlation functionals cannot reproduce correctly the exchange-only limit of HF theory.[16] To remedy this problem, Becke introduced a new class of hybrid HF−DFT theories in which the exact nonlocal HF exchange is semiempirically mixed with the local Slater exchange through the adiabatic connection formula[4,16] and appropriate gradient-corrected exchange-correlation functionals.[4,16,17] To date, the large body of reported computations using various DFT-based methods support the contention that hybrid HF−DFT functionals are by far the best density functionals currently available.[4−8,11−14,16] The accuracy of predicted atomization energies is within 3−5 kcal/mol, and

---

* To whom correspondence should be addressed. Telephone: (301) 738-6133. Fax: (301) 738-6255. E-mail: Sherif@carb.nist.gov.

S1089-5639(98)00707-5 CCC: $15.00

bond lengths and angles are within a few percent of corresponding experimental values. However, B3LYP and Bx88/Bc95 scale as $\sim N^4$ and $\sim N^5$, respectively.[15] Therefore, one may ask the following: is it possible to devise an approximate DFT scheme with less stringent scaling properties while maintaining the target accuracy, ±2 kcal/mol, in computed thermochemical properties of molecules?

Largely inspired by the elegant work of Becke,[16] we report a semiempirical HF−DFT methodology which scales as $\sim N^3$ and, thus, could be applied to larger chemical systems than G2, B3LYP, and Bx88/Bc95. The reported methodology mixes the HF and gradient corrected local spin-density exchange using the adiabatic connection formula,[4,16] together with the Pade approximated Vosko, Wilk, and Nusair (VWN) correlation functional.[18] The atom equivalent scheme proposed by Dewar[19] is then used to empirically correct the computed atomic energies such that the calculated heats of formation of 118 molecules and radicals are reproduced within ±2 kcal/mol from corresponding experimental values. The data set used to validate the reported methodology includes the G2 thermochemical data which served as an excellent test for comparing the performance of various quantum chemical methods.

Similar to the reported methodology in its N^3 scaling, Gill et al.[8d] developed a DFT-based method in which the HF exchange has been completely replaced by Becke's gradient-corrected exchange. The correlation functionals used were those due to LYP and VWN,[4b,18] and the method was abbreviated as BLYP. We will demonstrate that the DFT approach developed in this work is superior to BLYP in terms of accuracy of calculated electronic and thermodynamic properties of molecules.

The paper is structured as follows. In section II we describe the mathematical and computational aspects of the method. The application of the model to 150 atomic and molecular systems and comparisons with the G2, Bx88/Bc95, B3LYP, and BLYP methods are discussed in section III. The general conclusions drawn from the reported model are given in section IV.

II. Theoretical Model

In this section, the mathematical and computational approaches used in developing the present model are given. We did not attempt to review the vast literature on DFT because it has been elegantly and thoroughly presented in several recent reviews.[4−8,13,14,16]

In DFT, the total electronic energy, E, of an N-electron atom or molecule with electronic density ρ can be written as

$$E = E_T + E_V + E_J + E_{XC} \tag{1}$$

where, E_T is the kinetic energy of independent electrons whose density is ρ, E_V is the sum of nuclear−electron (n−e) and nuclear−nuclear (n−n) potential energies, E_J is the classical Coulomb repulsion energy between two charge distributions $\rho(r_1)$ and $\rho(r_2)$

$$E_J = 0.5\,\langle \rho(r_1) | \Delta r_{12}{}^{-1} |\, \rho(r_2) \rangle \tag{2}$$

and E_{XC} is the exchange-correlation energy which accounts for the exchange energy due to antisymmetry of the electronic wave function and dynamic correlation resulting from the motion of electrons. Therefore, given an approximate functional E_{XC} and ρ defined by a set of orthonormal spin orbitals ψ_i as

$$\rho = \sum_{i=1,N} |\psi_i|^2 \tag{3}$$

the energy expression given by eq 1 is then minimized and leads to Kohn−Sham (KS) spin orbitals ψ_i^{KS} which satisfy the one-electron KS equation. In atomic units, the KS equation takes the following form:

$$[-{}^1/_2\nabla^2 + V_{KS}]\psi_i^{KS} = E_i\psi_i^{KS} \tag{4}$$

where V_{KS} is given by

$$V_{KS} = V_{n-n} + V_{n-e} + V_{XC} \tag{5}$$

and

$$V_{XC} = \delta E_{XC}/\delta\rho \tag{6}$$

In practice, the exchange-correlation energy term in eq 1 is further decomposed into an exchange, E_X, and correlation, E_C, components:

$$E_{XC}[\rho] = E_X[\rho] + E_C[\rho] \tag{7}$$

$E_X[\rho]$ accounts for the repulsion between electrons with parallel spins, $\alpha\alpha + \beta\beta$, and $E_C[\rho]$ recovers the remaining e−e repulsion that was not accounted for in $J[\rho]$ and $E_X[\rho]$, together with a kinetic energy component resulting from the dynamic motion of the electrons.

Now, we consider the specification of functionals. For the exchange part, we employ the following adiabatic connection formula:[16]

$$E_X[\rho] = 0.20(HF_x - S_x) \tag{8}$$

where, HF_x and S_x are the nonlocal HF and local Slater exchange, respectively. Notice that eq 8 is identical to the corresponding term in the B3LYP method.[16d]

As to the correlation component, $E_C[\rho]$ in eq 7, we use the Monte Carlo simulations of Ceperley and Alder to the local spin density and empirically scale the associated Pade approximated parametrization of the free electron gas due to Vosko, Wilk, and Nusair (VWN),[18] together with a generalized gradient-correction term for exchange as given by eq 9:

$$E_C[\rho] = 0.80E_{XC}(VWN) - 0.00189\langle \rho(r)^{4/3}\, x^2(1 + 6bx \sinh^{-1} x)^{-1} \rangle$$

$$b = 0.0042 \qquad x = \rho(r)^{-4/3}|\nabla\rho| \tag{9}$$

The empirical scaling factors, 0.80 and 0.00189, appearing in eq 9 were set such that, upon solving eqs 4−6 for the hydrogen atom using the 6-311g(d, p) basis set, we get an H-atom energy ∼ 0.5 au. The constant b, whose value is 0.0042 au, was determined by Becke[16] from a fit to exact HF exchange energies of the noble gases He through Rn, and the dimensionless parameter x accounts for the nonuniformity of electronic charge density. Clearly, the reported methodology is a combination of HF, Slater, and Becke's gradient correction to exchange together with VWN correlation functionals. Accordingly, we abbreviate the method by HFS−BVWN.

For all molecules and radicals considered in this paper, full geometry optimizations with analytical derivatives using the HFS−BVWN/6-31g* method, followed by single point computations at the HFS−BVWN/6-311+g(3df, p) level of theory, were performed. For open shell systems, unrestricted wave functions were used. Geometry optimization was terminated when the largest component of the gradient was smaller than 0.0001 hartree/bohr. Thermal corrections to atomic enthalpies and molecular energies are unscaled values computed from the

HFS−BVWN/6-31g* level of theory. For all of the hypervalent species considered in this work, the unscaled zero-point energies are taken as a measure of the thermal correction.

Because unrestricted wave functions are not eigenfunctions of the total spin operator S^2, they are normally contaminated by higher spin states, e.g. a doublet radical can mix in a quadruplet or even higher spin states. This admixture of higher spin states lead to incorrect energies and unrealistic spin densities. The degree of spin contamination can be seen from the expectation value of the $\langle S^2\rangle$ [$=S(S+1)$, where S is the total spin]. Spin contamination can be eliminated by using appropriate spin projection methods or performing spin-restricted computations on open shell systems.[1−5] However, in all open shell calculations reported in this work, spin contamination from higher spin states was generally less than 0.5%. In view of this small spin mixing, no corrections to the unrestricted wave functions and energies were performed.

All of the optimization, diagonalization, numerical integration routines, and DFT exchange-correlation functionals used in connection with HFS−BVWN method are contained in the GAUSSIAN94 program.[15] All calculations were done on an SGI Indigo-2 XZ work station with 128-MB of memory and 5-GB hard drive.

III. Results and Discussion

This section is divided into three parts. In subsection A, we demonstrate that the HFS−BVWN/6-311+g(3df, p) level of theory underestimates atomic and molecular exchange-correlation energies. To overcome the latter problem we empirically correct the calculated atomic energies using Dewar's atom equivalent scheme.[9,10] The corrected energies of hydrogen through chlorine are then used in connection with the results of computations to calculate the heats of formation of selected molecules and radicals, subsection B, as well as ionization potentials and electron affinities of selected atomic and molecular species, subsection C. Comparisons between the reported methodology and the G2, Bx88/Bc95, B3LYP, and BLYP approaches pertaining to the accuracies of computed thermochemical properties are discussed in subsections B and C.

The computed atomic energies, corrected atomic energies, total molecular energies, thermal corrections to atomic and molecular energies, room-temperature heats of formation, atomic and molecular ionization potentials, and electron affinities of selected chemical systems using the HFS−BVWN/6-311+g(3df, p) method are listed in Tables 1−5, respectively.

A. Derivation of Atom Equivalents for H through Cl. The calculated atomic energies of H through Ar using the HFS−BVWN/6-311+g(3df, p) method are listed in Table 1. With the exception of hydrogen, these energies are on the average 0.13% higher than corresponding correlated HF values of Veillard and Clementi.[20] That is, the latter values are closer from an energy standpoint to the nonrelativistic exact values. The reported method is thus expected to underestimate molecular XC energies by more than 0.13% due to the presence of bonds, a factor not present in atomic systems. As shown in Table 1, the computed total energies of some simple molecules by HFS−BVWN/6-311+g(3df, p) are on the average 0.14% higher than corresponding correlated HF values of Ermler and Kern.[21] Therefore, for a given molecule, its XC energy is at least underestimated by 0.01% relative to the corresponding energies of constituent atoms. How can we compensate for the latter error in computed molecular XC energies?

TABLE 1: Computed HFS−BVWN/6-311+g(3df, p) Total Energies (au) and Corresponding Correlated Hartree−Fock (HF) Values for Atoms of the First Two Rows of the Periodic Table and Selected Molecules

species	HFS−BVWN[a]	HF[b]
H	−0.500 966	−0.5
He	−2.900 913	−2.9042
Li	−7.465 959	−7.4781
Be	−14.624 569	−14.6673
B	−24.594 798	−24.6539
C	−37.769 113	−37.8451
N	−54.493 976	−54.5895
O	−74.952 080	−75.0673
F	−99.594 426	−99.7313
Ne	−128.768 092	−128.937
Na	−162.069 116	−162.241
Mg	−199.844 536	−200.038
Al	−242.111 164	−242.331
Si	−289.092 837	−289.343
P	−340.954 772	−341.234
S	−397.773 690	−398.093
Cl	−459.775 521	−460.142
Ar	−527.130 780	−527.542
CH_4	−40.437 336	−40.510
NH_3	−56.465 937	−56.559
H_2O	−76.318 969	−76.431
HF	−100.317 117	−100.447
CO	−113.120 708	−113.316
N_2	−109.339 618	−109.534
H_2O_2	−151.327 706	−151.549

[a] Present work. [b] See refs 20 and 21.

TABLE 2: Empirically Corrected HFS−BVWN/6-311+g(3df, p) Atomic Energies (au) of Hydrogen through Chlorine

atom	HFS−BVWN	corr values	diff
H	−0.500 966	−0.500 49	−0.000 48
Li	−7.465 959	−7.461 18	−0.004 78
Be	−14.624 569	−14.636 48	0.011 9
B	−24.594 798	−24.598 76	0.003 96
C	−37.769 113	−37.765 32	−0.003 79
N	−54.493 976	−54.490 53	−0.003 45
O	−74.952 080	−74.950 08	−0.002 0
F	−99.594 426	−99.594 11	−0.000 316
Na	−162.069 116	−162.061 57	−0.007 55
Mg	−199.844 536	−199.844 54	0.000 0
Al	−242.111 164	−242.104 68	−0.006 48
Si	−289.092 837	−289.088 88	−0.003 96
P	−340.954 772	−340.950 98	−0.003 79
S	−397.773 690	−397.770 51	−0.003 18
Cl	−459.775 521	−459.774 04	−0.001 48

Approximately 18 years ago, Dewar proposed a general scheme for reducing the errors in computed thermochemical properties of molecules based on the atoms.[19] The advantage of Dewar's atom equivalent scheme (AES) over corresponding approaches based on bond and group equivalents is its simplicity and generality.[10,19,22] The thermochemical properties of molecules, radicals, transition states, intermediates, etc., could be estimated by the AES. For example, recently Mole et al.[10] applied the AES in connection with B3LYP/6-311g(d, p), BLYP/6-311g(d, p), B3PW91/6-311g(d, p), BPW91/6-311g(d, p), B3P86/6-311 g(d, p), and LSDA/6-311g(d, p) methodologies to calculate the heats of formation of 23 stable hydrocarbons. The results of this extensive study demonstrated that the B3LYP/6-311g(d, p) method together with the AES produced the best heats of formation for the 23 hydrocarbons. The atom equivalents of carbon and hydrogen derived from the results of B3LYP/6-311g(d, p) computations were then used without any further adjustment to compute enthalpies of formation for some radicals with an overall average deviation of ±2 kcal/mol.[10] However, Mole et al.[10] completely omitted the thermal corrections to molecular energies in their computations of the heats

TABLE 3: Theoretical and Experimental Gas-Phase Heats of Formation ($\Delta H_{f;298}$ (kcal/mol) of Selected Molecules and Radicals

species	tot. energy (au)	thermal corr (au)	ΔH_f theo	ΔH_f exptls[a]
H	−0.500 49	0.002 36		52.1
Li	−7.461 18	0.002 36		38.1
Be	−14.636 48	0.00236		77.5
B	−24.598 76	0.002 36		134.5
C	−37.765 32	0.002 36		171.3
N	−54.490 53	0.002 36		113
O	−74.950 08	0.002 36		59.6
F	−99.594 11	0.002 36		18.7
Na	−162.061 57	0.002 36		25.6
Mg	−199.844 54	0.002 36		35.3
Al	−242.104 68	0.002 36		78.2
Si	−289.088 88	0.002 36		108
P	−340.950 98	0.002 36		75.6
S	−397.77051	0.002 36		66.2
Cl	−459.774 04	0.002 36		29
Al_2	−484.270 557	0.003 463	117.2	116.4 ± 0.8
AlF	−341.958 081	0.0042 26	−63.1	−63.5 ± 0.8
BeF	−114.446 676	0.0051 92	−39.1	−40.6 ± 2
BeH	−15.217 500	0.006 693	80.3	82
BeO	−89.750 612	0.005 849	34.9	32.6 ± 3
BeS	−412.524 171	0.004 695	70.2	70.6
BH	−25.227 334	0.007 597	106.5	105.8 ± 2
$BHCl_2$	−945.141 152	0.018 508	−59.6	−59.3 ± 1
BHF_2	−224.935 560	0.021 322	−175.2	−175.4 ± 0.8
C_2H	−76.455 398	0.015 596	133.8	135 ± 1
C_2H_2	−77.177 080	0.029 507	54.4	54.5 ± 0.25
$C_2H_2Cl_2$	−996.907 463	0.038 528	0.3	1 ± 0.2
C_2H_3	−77.748 244	0.039 122	66.7	68.4
C_2H_3Cl	−537.672 018	0.046 392	4.8	5 ± 0.5
C_2H_3F	−177.543 597	0.047 628	−37.0	−33.5 ± 0.4
C_2H_4	−78.431 770	0.053 272	11.3	12.5 ± 0.2
C_2H_5	−78.999 460	0.062 319	25.4	26
C_2H_6	−79.668 111	0.077 089	−20.2	−20.1
$C_3H_3N_3$	−279.844 246	0.069 669	51.2	54 ± 0.2
C_3H_5	−117.025 493	0.081 209	43.5	39.1 ± 1.5
C_3H_6	−117.657 828	0.083 418	12.8	12.7 ± 0.2
$C_3H_6O_3$	−342.999 09	0.104 028	−108.0	−111.4 ± 0.1
C_3H_8	−118.900 991	0.108 625	−22.1	−25.0 ± 0.1
$C_4H_4N_2$	−263.812 086	0.081 209	46.5	46.8 ± 0.3
C_4H_8	−156.891 247	0.113 298	9.5	6.8 ± 0.2
C_5H_5N	−247.795 924	0.093 270	32.1	33
$C_6H_4O_2$	−380.762 296	0.091 582	−28.2	−29 ± 1
C_6H_5	−231.090 737	0.091 980	77.0	78.6 ± 2
$C_6H_5CH_2$	−270.360 625	0.120 604	50.0	47.8 ± 1.5
$C_6H_5CH_3$	−271.012 849	0.134 514	14.2	12.0 ± 0.1
C_6H_5CHO	−344.912 194	0.116 759	−8.9	−9 ± 0.5
C_6H_5Cl	−691.014 743	0.096 714	13.5	13.0 ± 0.2
C_6H_5F	−330.888 331	0.097 728	−29.8	−27.7 ± 0.3
$C_6H_5NH_2$	−287.041 7288	0.123 164	21.0	20.8 ± 0.2
C_6H_5OH	−306.891 173	0.110 286	−22.3	−23.0 ± 0.2
C_6H_5SH	−629.636 592	0.105 870	28.7	26.9 ± 0.2
C_6H_6	−231.776 458	0.103 821	18.9	19.8 ± 0.1
CF_4	−436.904 742	0.021 349	−226.7	−223.4 ± 0.1
CH_2NH_2	−95.031 317	0.053 878	32.2	35.7 ± 2
CH_2OH	−114.874 563	0.040 784	−7.3	−6.2 ± 1.5
CH_2(sing.)	−39.053 937	0.019 424	102.7	101.6
CH_2(trip.)	−39.077 373	0.020 271	88.6	92.6
CH_3	−39.761 180	0.032 150	31.6	32.8
CH_3F	−139.536 308	0.042 416	−58.3	−59
CH_3OH	−115.532 918	0.053 544	−47.7	−48.2 ± 0.1
CH_3SH	−438.291 423	0.049 981	−4.5	−5.5 ± 0.1
CH_4	−40.437 336	0.046 965	−18.7	−17.8 ± 0.1
Cl_2	−919.639 615	0.003 801	0.0	0
ClF	−559.467 221	0.004 232	−14.8	−12.0 ± 0.1
ClO	−534.831 342	0.004 328	21.1	23.8
CN	−92.541 167	0.007 346	106.9	104 ± 2
CO	−113.127 008	0.007 457	−25.7	−26.4
CO_2	−188.293 293	0.014 940	−98.5	−94.1
CS	−435.804 599	0.005 461	69.3	68.5
CS_2	−833.755 081	0.010 031	24.0	28 ± 0.2
F_2	−199.248 036	0.004 905	0.0	0
H_2	−1.175 511	0.012 268	−0.6	0
H_2CO	−114.314 853	0.029 108	−28.1	−26.0 ± 0.2
H_2CS	−437.054 133	0.027 824	28.6	26.2 ± 2
H_2O	−76.318 969	0.023 285	−56.9	−57.8
H_2O_2	−151.327 706	0.028 876	−32.1	−32.6
H_2S	−399.062 303	0.017 699	−5.4	−4.9
H_2S_2	−796.924 149	0.021 588	4.4	4
HCl	−460.443 607	0.008 900	−22.4	−22.1
HCN	−93.253 582	0.019 199	32.0	32.3
HCO	−113.667 301	0.015 930	5.4	8.9 ± 1.2
HCS	−436.400 132	0.014 729	66.1	< or = 73
HF	−100.317 117	0.011 074	−64.8	−65.1
HO_2	−150.685 926	0.016 890	−1.6	2.5 ± 0.6
HOCl	−535.483 744	0.014 500	−17.3	−19
HOF	−175.296 242	0.016 404	−21.6	−23 ± 1
Li_2	−14.961 684	0.003 519	50.8	51.6 ± 0.7
LiCl	−467.414 98	0.003 908	−46.2	−47 ± 3
LiF	−107.276 473	0.004 449	−82.2	−81
LiOH	−83.249 560	0.015 728	−56.7	−58.8
MgH_2	−201.012 985	0.012 335	37.7	39.7
MgS	−597.693 126	0.003 751	51.9	52
N_2	−109.339 618	0.008 164	3.2	0
N_2F_2	−308.574 484	0.015 358	12.9	19 ± 1
N_2H_2	−110.453 730	0.030 923	47.7	51
Na_2	−324.146 636	0.003 565	35.7	34.0 ± 0.3
NaCl	−621.990 728	0.003 512	−43.5	−43.0
NaF	−261.839 401	0.003 829	−71.5	−70.3
NaH	−162.640 069	0.005 080	29.0	29.6
NaOH	−237.810 485	0.012 680	−46.4	−46.4
NH_2	−55.785 142	0.021 330	41.9	42.3
NH_3	−56.465 937	0.036 580	−11.1	−11.0
NO	−129.686 66	0.007 001	19.6	21.8
O_2	−150.101 512	0.006 186	−6.2	0
O_3(sing.)	−225.081 067	0.010 348	36.0	34
OF_2	−274.290 644	0.008 648	2.4	5.9 ± 0.4
OH	−75.622 729	0.010 311	7.2	9.3 ± 0.3
P_2	−682.083 791	0.004 348	36.9	34.3 ± 0.5
P_2H_4	−684.492 662	0.039 512	6.1	5.0
PF	−440.723 285	0.004 376	−17.7	−12.5 ± 5
PF_2	−540.505 551	0.007 983	−116.3	−115 ± 0.5
PF_3	−640.303 345	0.008 470	−226.0	−229 ± 1
PH_2	−342.202 328	0.016 084	28.3	33.3
PH_3	−342.839 214	0.026 623	0.0	1.3 ± 0.4
PN	−395.668 664	0.005 522	46.6	45.6
PO	−416.129 792	0.005 181	−8.0	−8 ± 3
POF_3	−715.458 482	0.014 261	−294.1	−300 ± 2
PS	−738.887 980	0.004 133	37.0	36 ± 1
S_2	−795.709 506	0.004 151	26.3	30.7 ± 0.1
SF	−497.502 742	0.004 345	−1.8	1
SF_2	−597.237 779	0.007 886	−70.6	−71 ± 4
SF_6	−996.077 157	0.020 425	−284.8	−291.7 ± 0.2
SH	−398.412 579	0.008 445	31.8	33.3 ± 1.2
Si_2	−578.296 135	0.003 927	141.2	141 ± 3
Si_2H_6	−582.025 603	0.053 528	20.2	19
SiH_2(sing.)	−290.334 414	0.014 577	63.4	67.8
SiH_2(trip.)	−290.306 639	0.014 981	81.1	88.8
SiH_3	−290.955 306	0.023 949	44.4	48.5 ± 1.5
SiH_4	−291.605 754	0.033 886	7.2	8
SiO	−364.338 644	0.005 292	−20.1	−24 ± 2
SO	−472.925 561	0.005 090	−2.6	1.2 ± 0.3
SO_2	−548.075 153	0.007 221	−68.3	−70.9 ± 0.1
SO_3	−623.157 589	0.009 340	−91.9	−94.6 ± 0.2

1.8 kcal/mol av error

[a] See ref 23.

of formation of hydrocarbons. This is the most serious approximation made in their study, which we have overcome in deriving the atom equivalents for hydrogen through chlorine using HFS−BVWN/6-311g(3df, p) method, Tables 2 and 3.

Application of Dewar's AES in connection with the results of HFS−BVWN/6-311+g(3df, p) computations on 118 molecules and radicals gave the corrected atomic energies for hydrogen through chlorine, excluding the noble gases, listed in Table 2. The adjusted atomic energies will be used below in connection with molecular energies and thermal corrections to estimate the heats of formation of selected molecules and radicals, Table 3. Notice that, in deriving the atom equivalents for H−Cl, we did not omit the thermal corrections to molecular energies.

B. Heats of Formation of Molecules and Radicals. The room-temperature heats of formation for 118 molecules and radicals calculated from the results of HFS−BVWN/6-311+g-(3df, p) computations and the derived atom equivalents are given in Table 3.[23] The enthalpies of formation were calculated using the following approximate formula:

$$\Delta H_{\mathrm{f},\,298}(\mathrm{AB}) = \textstyle\sum_{i=1,n}(\Delta H_{\mathrm{if},\,298}) - \{[\sum_{i=1,n}(E_{i,0} + e_i)] - (E_{\mathrm{AB},\,0} + e_{\mathrm{AB}})\}$$

where, $\Delta H_{\mathrm{f},\,298}(\mathrm{AB})$ is the calculated heat of formation at 298 K for the molecule AB, $\sum_{i=1,n}(\Delta H_{\mathrm{if},\,298})$ is the sum of room temperature heats of formation of the individual atoms in the molecule, $\sum_{i=1,n}(E_{i,0} + e_i)$ is the sum of calculated atomic energies at 0 K and corresponding thermal corrections, $E_{\mathrm{AB},\,0}$ is the calculated total molecular energy at 0 K, and e_{AB} is the corresponding calculated thermal correction of the molecule AB.

As shown in Table 3, the average absolute error in calculated enthalpies of formation is 1.8 kcal/mol and the maximum deviation is 7 kcal/mol for the hypervalent species SF_6. The corresponding average errors in the G2, Bx88/BC95, B3LYP, and BLYP theories are 1.2, 2.0, 2.4, and 3.94 kcal/mol, respectively.[1,2,8d,16d,e] Notice that the hydrogen atom basis set used in this work contains only one set of p-functions as opposed to two sets on hydrogen in the G2 and BLYP computations. The addition of a second set of p-functions on the hydrogen to give the HFS−BVWN/6-311+g(3df, 2p) level of theory may lower the average error in computed heats of formation of molecules and radicals containing H atoms.

The enthalpies of formation of the compounds containing the Li, Be, B, Na, Mg, and Al atoms, Table 3, are well reproduced within 1 kcal/mol except BeO (2.3 kcal/mol too high). However, notice that the experimental enthalpy of formation of BeO has an uncertainty of ±3 kcal/mol. In addition, the heats of formation of open and closed shell aliphatic and aromatic hydrocarbons are well reproduced by the reported method within 2 kcal/mol from corresponding experimental values. Furthermore, enthalpies of formation of aliphatic and aromatic hydrocarbons containing heteroatoms (nitrogen, oxygen, and sulfur) are also well predicted by the reported method. Therefore, the potential energy surfaces of gas-phase reactions between hydrocarbons and/or heterocyclic compounds can be reliably explored using the HFS−BVWN methodology. The application of HFS−BVWN in the area pertaining to predicting structure and energetics of transition states as well as reaction mechanisms is underway and will be reported in a future publication.

The heats of formation of the hypervalent species SO_2 and SO_3 listed in Table 3 are reasonably well predicted by the reported method. The enthalpies of formation of POF_3 and SF_6 are underestimated by 6 and 7 kcal/mol, respectively. Irikura[26] reported G2 and G2(MP2) computations on SF_6. Surprisingly, the heat of formation of SF_6 computed by the G2(MP2) method is in much better agreement with corresponding experimental value than the more computer intensive G2 method. However, both G2 and G2(MP2) perform poorly on POF_3, ∼ 10 kcal/mol error in computed enthalpy of formation. Additional studies need to be carried out to improve the performance of the HFS−BVWN method for hypervalent compounds.

TABLE 4: Computed Atomic and Molecular Ionization Potentials (eV) Using the HFS−BVWN/6-311+g(3df, p) Method and Corresponding Experimental Values

		ionization potential	
species	tot. energy (au)	DFT	exptl[a]
H^+	0.0	13.62	13.598
He^+	−1.988 715	24.82	24.587
Li^+	−7.260 655	5.46	5.392
Be^+	−14.292 855	9.35	9.322
B^+	−24.274 556	8.82	8.298
C^+	−37.342 545	11.50	11.260
N^+	−53.949 451	14.72	14.534
O^+	−74.439 986	13.88	13.618
F^+	−98.945 325	17.65	17.422
Ne^+	−127.968 544	21.76	21.565
Na^+	−161.871 707	5.17	5.139
Mg^+	−199.564 646	7.62	7.646
Al^+	−241.888 512	5.88	5.986
Si^+	−288.791 899	8.08	8.1517
P^+	−340.569 132	10.39	10.486
S^+	−397.390 508	10.34	10.360
Cl^+	−459.297 761	12.96	12.967
Ar^+	−526.551 312	15.77	15.76
C_2H_2	−76.764 021	11.24	11.4
C_2H_4	−78.050 958	10.36	10.51
CH_4	−39.971 594	12.67	12.62
Cl_2	−919.222 311	11.36	11.5
CO	−112.609 988	14.07	14.01
H_2O	−75.854 048	12.65	12.62
HCl	−459.976 257	12.72	12.75
HF	−99.724 050	16.14	16.04
NH_3	−56.091 592	10.19	10.18
O_2	−149.641 900	12.51	12.07
SiH_4	−291.178 570	11.62	11.65
PH_3	−342.480 273	9.77	9.87
P_2	−681.689 058	10.74	10.53
S_2	−795.359 030	9.54	9.36
ClF	−559.006 296	12.54	12.66
		0.12 eV av error	

[a] See ref 23a,b.

C. Ionization Potentials and Electron Affinities. For ionization potentials (IPs), Table 4, the average absolute deviation is 0.12 eV, compared with 0.195 eV for BLYP, 0.14 eV for B3LYP, 0.12 eV for Bx88/Bc95, and 0.05 eV for G2. The largest deviations are observed for the IP of boron atom (0.52 eV too high) and triplet O_2 (0.44 eV too high). The ionization energies listed in Table 4 can be calculated from the simple formula $\mathrm{IP} = [\Delta H_{\mathrm{f;298}}(\mathrm{ion}) - \Delta H_{\mathrm{f;298}}(\mathrm{neutral})]$. Because we are using the same thermal correction for both the neutral molecule and its corresponding positive ion, the latter equation simplifies to $\mathrm{IP} = [E_{\mathrm{total}}(\mathrm{ion}) - E_{\mathrm{total}}(\mathrm{neutral})]$.

The calculated electron affinities, Table 5, have an average deviation of 0.13 eV, excluding hydrogen, compared with 0.08 eV for G2 [2] and 0.14 eV for BLYP.[24a] The largest errors are seen for the atomic electron affinities of hydrogen (0.6 eV too low) and carbon (0.33 eV too high). Similar to ionization potentials, the electron affinities (EAs) were computed from the equation, $\mathrm{EA} = [E_{\mathrm{total}}(\mathrm{neutral}) - E_{\mathrm{total}}(\mathrm{ion})]$ and relevant data from Tables 3 and 5. Ziegler and Gutsev[25] reported an extensive DFT study using different functionals on a subset of the G2 data set. The average error in computed electron affinities in the latter study was 0.2 eV. Despite the success of the HFS−BVWN/6-311+g(3df, p) and related DFT approaches in estimating atomic and molecular electron affinities, Becke[16]

TABLE 5: Computed Atomic and Molecular Electron Affinities (eV) of Selected Chemical Systems Using the HFS−BVWN/6-311+g(3df, p) Method and Corresponding Experimental Values

species	tot. energy (au)	electron affinity	
		DFT	exptl[a]
H^-	−0.507 768	0.20	0.8
He^-	−2.110 704	−0.22	
Li^-	−7.485 343	0.66	0.618
Be^-	−14.618 077	−0.50	
B^-	−24.612 812	0.38	0.277
C^-	−37.823 883	1.59	1.263
N^-	−54.492 564	0.06	
O^-	−75.007 382	1.56	1.462
F^-	−99.720 395	3.44	3.399
Ne^-	−128.524 357	−6.63	
Na^-	−162.088 965	0.75	0.548
Mg^-	−199.838 486	−0.16	
Al^-	−242.128 655	0.65	0.441
Si^-	−289.145 662	1.55	1.385
P^-	−340.985 344	0.93	0.77
S^-	−397.851 711	2.21	2.077
Cl^-	−459.909 725	3.69	3.617
Ar^-	−527.022 261	−2.95	
CH_3	−39.756 849	−0.12	0.08
Cl_2	−919.741 179	2.76	2.4, 2.5, 3.2
CN	−92.687 781	3.99	3.82
OH	−75.685 966	1.72	1.83
SH	−398.496 526	2.28	2.314
S_2	−795.768 974	1.62	1.663
SiH_3	−291.003 966	1.32	1.406
NH_2	−55.809 281	0.66	0.74
		0.13 eV av error	

[a] See ref 23a,b.

in his publications of the B3LYP and Bx88/Bc95 methodologies omitted the computation of this electronic property. The author[16] suspected that the exchange-correlation potentials used in developing the methods may not bind negative ions.

In agreement with Becke's notion pertaining to EAs, the local spin-density exchange-correlation potential has been shown to decay exponentially into the vacuum instead of the Coulomb-like $-1/r$ behavior.[24] Therefore, an outer electron is too weakly bound and for negative ions may even be unbound. That is why the energies of the highest occupied and lowest empty molecular orbitals cannot be directly equated to the first ionization potential and electron affinity of the molecule, respectively, as in the HF theory. Accordingly, the success of the reported methodology and related DFT approaches in computing electron affinities is due to the use of large basis sets on heavy (non-hydrogen) atoms which provide sufficient stabilization to the anion.

IV. Conclusions

A simple coupling scheme between HF, gradient-corrected local spin-density exchange, and Pade approximated Vosko, Wilk, and Nusair correlation functionals has been developed. The new methodology is abbreviated by HFS−BVWN. We demonstrated that the combination of Dewar's atom equivalent scheme together with the results of HFS−BVWN/6-311+g(3df, p) computations on 150 atomic and molecular species, room-temperature heats of formation, ionization potentials, and electron affinities were reproduced with an overall absolute mean deviation of 2.5 kcal/mol, compared to 1.4 kcal/mol for G2, 2.0 kcal/mol for Bx88/Bc92, 3.5 kcal/mol for B3LYP, and 3.9 kcal/mol for BLYP.

The HFS−BVWN and BLYP methodologies have similar $\sim N^3$ scaling and, thus, are much less computer intensive than B3LYP ($\sim N^4$), Bx88/Bc95 ($\sim N^5$), and G2 ($\sim N^7$). Therefore, the HFS−BVWN method seems to be a reasonable compromise between accuracy of calculated electronic properties of molecular systems and computational cost.

The HFS−BVWN/6-311+g(3df, p) level of theory needs further improvements in the description of hypervalent compounds and molecules having triplet ground states. Future studies will also investigate the application of the reported methodology, using smaller basis sets and effective core potentials, to large chemical systems. In addition, the prediction of activation energies and reaction mechanisms is currently under investigation.

Acknowledgment. This work was supported by the U.S. Department of the Army, U.S. Army Research Office (USARO), North Carolina, under Contract No. 38522-CH to S.A.K. The authors acknowledge numerous discussions and useful critical comments made by Dr. W. Tsang at the National Institute of Standards and Technology, Dr. C. Melius at Sandia National Laboratory, and Dr. W. White at Edgewood Research Laboratory. Also, we acknowledge the suggestions made by Professor M. N. H. Moussa (Department of Chemistry, Mansoura University, Egypt) and the efforts of Mr. A. G. Kafafi (Misr University for Science and Technology) in carrying out some of the computations. E.-S.R.H.E-G. acknowledges the financial support of Mansoura University/Egyptian Embassy Educational Bureau, Washington, DC, for his research training scholarship at the Center for Advanced Research in Biotechnology.

References and Notes

(1) Pople, J. A.; Head-Gordon, M.; Fox, D. J.; Raghavachari, K.; Curtiss, L. A. *J. Chem. Phys.* **1989**, *90*, 5622.

(2) Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys.* **1991**, *94*, 7221.

(3) (a) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab initio molecular orbital theory*; John Wiley & Sons: New York, 1986. (b) Kafafi, S. A.; LaFemina, J. P.; Nauss, J. L. *J. Am. Chem. Soc.* **1990**, *112*, 8742. (c) Kafafi, S. A.; Hudgens, J. W. *J. Phys. Chem.* **1989**, *93*, 3474. (d) Magnusson, E.; Schaefer, H. F. *J. Chem. Phys.* **1985**, *83*, 5721. (e) Hudgens, J. W.; Johnson, R. D.; Tsai, B. L.; Kafafi, S. A. *J. Am. Chem. Soc.* **1990**, *112*, 5763. (f) Dearden, D. V.; Hudgens, J. W.; Johnson, R. D.; Tsai, B. P.; Kafafi, S. A. *J. Phys. Chem.* **1992**, *96*, 585. (g) Del Bene, J. E. In *Molecular Structure and Energetics: Chemical Bonding Models*; Liebman, J. F., Greenberg, A., Eds.; VCH Publishers: New York, 1986; Vol. 1, pp 319−349. (h) Clark, T. *A Handbook of Computational Chemistry*; Wiley-Interscience: New York, 1985.

(4) (a) Parr, R. G.; Yang, W. *Density-Functional Theory of Atoms and Molecules*; Oxford University Press: New York, 1989. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 3098.

(5) *Energy Density Functional Theory of Many-Electron Systems*; Kryachko, E. S., Ludena, E. V., Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1990.

(6) (a) Kohn, W.; Becke, A. D.; Parr, R. G. *J. Phys. Chem.* **1996**, *100*, 12974. (b) Dickson, R. M.; Becke, A. D. *J. Chem. Phys.* **1993**, *99*, 3898. (c) Slater, J. C. *The Calculation of Molecular Orbitals*; John Wiley & Sons: New York, 1979.

(7) *Chemical Application of Density-Functional Theory*; Laird, B. B., Ross, R. B., Ziegler, T., Eds.; ACS Synposium Series 629; American Chemical Society: Washington, DC, 1996.

(8) (a) Andzelm, J.; Wimmer, E. *J. Chem. Phys.* **1992**, *96*, 1280. (b) Ziegler, T. *Chem. Rev.* **1991**, *91*, 651. (c) Gill, P. M. W.; Johnson, B. G.; Pople, J. A. *Chem. Phys. Lett.* **1992**, *197*, 499. (d) Gill, P. M. W.; Johnson, B. G.; Pople, J. A.; Frisch, M. J. *Int. J. Quantum Chem.: Quantum Chem. Symp.* **1992**, *26*, 319. (e) Ruiz, E.; Salahub, D. R.; Vela, A. *J. Am. Chem. Soc.* **1995**, *117*, 7, 1141. (f) Adamo, C.; Barone, V. *J. Chem. Phys.* **1998**, *108*, 664.

(9) (a) Houk, K. N.; Li, Y.; Evanseck, J. D. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 682. (b) Jursic, B. S. In *Recent Developments and Applications of Modern DFT*; Seminario, J. M., Ed.; Elsevier Publishers: New York, 1996; pp 709−741.

(10) Mole, S. J.; Zhou, X.; Liu, R. *J. Phys. Chem.* **1996**, *100*, 14665 and references therein.

(11) Clementi, E.; Chakravorty, S. J. *J. Chem. Phys.* **1990**, *93*, 2591.

(12) Martell, J. M.; Goddard, J. D.; Eriksson, L. A. *J. Phys. Chem. A* **1997**, *101*, 1927.

(13) *Theoretical and Computational Chemistry, Vol. 2, Modern Density Functional Theory-A Tool For Chemistry*; Seminario, J. M., Politzer, P., Eds.; Elsevier: Amsterdam, 1995.

(14) *Recent Advances in Density Functional Methods;* Chong, D. P., Ed.; World Scientific Publishing: Singapore, 1995.

(15) (a) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; Peterson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *GAUSSIAN 94*, revision B.3; Gaussian Inc.: Pittsburgh, PA, 1995. (b) *Exploring Chemistry with Electronic Structure Methods*, 2nd ed.; Forseman, J. B., Frisch, A., Eds.; Gaussian Inc.: Pittsburgh, PA, 1996.

(16) (a) Becke, A. D. *J. Chem. Phys.* **1992**, *96*, 2155. (b) Becke, A. D. *J. Chem. Phys.* **1993**, *97*, 9173. (c) Becke, A. D. *J. Chem. Phys*. **1993**, *98*, 1372. (d) Becke, A. D. *J. Chem. Phys*. **1993**, *98*, 5648. (e) Becke, A. D. *J. Chem. Phys.* **1995**, *104*, 1040. (f) Becke, A. D. In *Modern Electronic Structure Theory*; Yarkony, D. R., Ed.; World Scientific: New York, 1995.

(17) (a) Perdew, J. P.; Wang, Y. *Phys. Rev. B* **1992**, *45*, 13244. (b) Perdew, J. P.; Zunger, A. *Phys. Rev. B* **1981**, *23*, 5084.

(18) Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200.

(19) (a) Dewar, M. J. S. *J. Phys. Chem.* **1985**, *89*, 2145. (b) Dewar, M. J. S.; Storch, D. M. *J. Am. Chem. Soc.* **1985**, *107*, 3898.

(20) Veillard, E.; Clementi, E. *J. Chem. Phys.* **1968**, *49*, 2415.

(21) Ermler, W. C.; Kern, C. W. *J. Chem. Phys.* **1974**, *61*, 3860.

(22) (a) Wiberg, K. B.; Hadad, C. M.; Rablen, P. R.; Cioslowski, J. *J. Am. Chem. Soc.* **1992**, *114*, 8644. (b) Wiberg, K. B.; Rablen, P. R.; Marquez, M. *J. Am. Chem. Soc.* **1992**, *114*, 8654. (c) Benson, S. W. *Can. J. Chem.* **1983**, *61*, 881. (d) Cohen, N.; Benson, S. W. *Chem. Rev.* **1993**, *93*, 2419. (e) Reed, A. E.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1990**, *112*, 1434. (f) Ibrahim, M. R.; Schleyer, P. v. P. *J. Comput. Chem.* **1985**, *6*, 157. (f) Wiberg, K. B. *J. Comput. Chem.* **1984**, *5*, 197. (g) Miller, J. A.; Melius C. F. *Combust. Flame* **1992**, *91*, 21. (h) Allinger, N. L.; Schmitz, L. R.; Motoc, I.; Bender, C.; Labanowski, J. K. *J. Am. Chem. Soc.* **1992**, *114*, 2880.

(23) (a) *NIST Chemistry WebBook*; NIST Standard Reference Database Number 69; ionization potential data compiled by Lias, S. G.; Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T.; Holmes, J. L.; Levin, R. D.; Liebman, J. F.; Kafafi, S. A.; NIST: Washington, DC, 1997. (b) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*, 1. (c) McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *110*, 7339.

(24) (a) Baerends, E. J.; Gritsenko, O. V.; van Leeuwen, R. In *Chemical Application of Density-Functional Theory*; Laird, B. B., Ross, R. B., Ziegler, T., Eds.; ACS Symposium Series 629; American Chemical Society: Washington, DC, 1996; p 20. (c) Wang, Y.; Parr, R. G. *Phys. Rev. A* **1993**, *47*, 1591.

(25) Ziegler, T.; Gutsev, G. L. *J. Comput. Chem.* **1992**, *13*, 70.

(26) Irikura, K. K. *J. Chem. Phys.* **1995**, *102*, 5357.