Novel Density Functional Methodology for the Computation of Accurate Electronic and Thermodynamic Properties of Molecular Systems and Improved Long-Range Behavior

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A novel general purpose density functional methodology for the computation of accurate electronic and thermodynamic properties of molecules and improved long-range behavior is reported. Assuming the separability of the exchange (E_x) and correlation (E_c) contributions to the total exchange-correlation energy functional (E_{xc}), the E_x term consists of a hybrid mixture of 37.5% Hartree−Fock exchange and the appropriate local spin density exchange using the adiabatic connection formula. We demonstrated that E_x and its corresponding potential V_x [$=\mathrm{d}E_x/\mathrm{d}\rho(r)$] have the proper asymptotic limits at $r = 0$ and $r \rightarrow \infty$. E_c consists of the Vosko, Wilk, and Nusair formula for the free-electron gas correlation energy and a generalized gradient approximation term with one adjustable parameter. V_c [$=\mathrm{d}E_c/\mathrm{d}\rho(r)$] was shown to obey the $r \rightarrow \infty$ limit of the corresponding potential derived from exact atomic exchange-correlation computations; namely, V_c is proportional to r^{-4}. Most importantly, we demonstrated that, at r values where dispersion forces are operating, V_c is proportional to $1/r^n$ ($n = 4, 6, 8, ...$). The reported method was denoted by K2-BVWN because it used two adjustable parameters in its formulation. The K2-BVWN scheme scales as N^3, where N is the number of basis functions, compared to $\sim N^7$ for Gaussian-2 (G2) ab initio theory and related methods, $\sim N^5$ for Barone's mPW1,3PW, and $\sim N^4$ for Becke's three-parameter density functional approaches. The K2-BVWN/6-311g(d) model predicted the structures of numerous molecular systems with remarkable accuracy. The results of K2-BVWN/6-311+g(df), K2-BVWN/6-311+g(2df), and K2-BVWN/6-311+g(3df) computations on Li through Ar atoms showed that the calculated energies at all three levels of theory are comparable to within 0.1 kcal/mol, thus demonstrating the fast convergence of atomic energies as the size of basis sets increased. Accordingly, the thermochemical properties of molecular systems could, in principle, be calculated to increasing levels of accuracy depending on the size of the basis sets used, in accordance with the usual practice in Hartree−Fock theory. In a data set comprised of 350 atomic and molecular systems, which included the G2 data set, we demonstrated that the K2-BVWN/6-311+g(2df) level of theory is a reliable model for the computation of room-temperature heats of formation, ionization potentials, and electron and proton affinities of normal valent compounds with average errors of 1.4 kcal/mol, 0.07, 0.07, and 0.05 eV, respectively. The outliers in calculated heats of formation consisted mainly of hypervalent compounds, nonhydrides containing multiple chlorine atoms, H_2O, and HF. Enthalpies of formation of these outliers were computed using the K2-BVWN/6-311+g(3df,p) level of theory. Further refinement of calculated heats of formation of outliers was achieved through the use of atom equivalent corrections instead of increasing the size of basis sets beyond 6-311+g(3df,p). Interestingly, the only atoms that required a correction for the latter step were oxygen (0.6 kcal/mol), aluminum (0.60 kcal/mol), silicon (0.60 kcal/mol), phosphorus (0.60 kcal/mol), sulfur (0.60 kcal/mol), and chlorine (0.60 kcal/mol). Comparison of the results obtained from the K2-BVWN method and corresponding ones from G2/6-311+g(3df,2p) ab initio theory, HFS-BVWN/6-311+g(3df,p), bond additivity correction BAC-G2/6-311++g(3df,2pd), G2(MP2)/6-311+g(3df,2p), G2(MP2, SVP)/6-311+g(3df,2p), B3LYP/6-311+g(3df,2p), and mPW1,3PW/6-311++g(3df,3pd) demonstrated that G2 ab initio theory and the K2-BVWN density functional scheme have comparable average errors in computed heats of formation, ionization potentials, and electron and proton affinities of molecules and are superior to all other approaches. Furthermore, we showed that the interaction energies of nine noble gas dimers were remarkably well reproduced using K2-BVWN/3-21+g(d,p) and K2-BVWN/3-21g levels of theory. Moreover, binding energies of the hydrogen-bonded isoelectronic systems $(H_2O)_2$ and $(HF)_2$ and the interaction energy of the charge-transfer complex formed between Cl_2 and ethylene were also reliably predicted to within less than 0.5 kcal/mol from corresponding experimental values. The G2 data set complemented by the reported molecular systems investigated in this work was recommended as a critical test for evaluating novel ab initio and density functional methodologies. The K2-BVWN method has been implemented in the Gaussian series of programs.

1. Introduction

In recent years, density functional theory (DFT) based methodologies have received substantial interest in the quantum chemistry community.[1−7] Much of this interest is due to the fact that DFT methods incorporate electron correlation in their basic formalism; that is, the effective one-electron potential in Kohn−Sham self-consistent-field equations is closely related

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to the physics of electron correlation. In addition, DFT approaches can be applied to larger molecular systems than corresponding ab initio methods at a reasonable computational cost.

Unlike Hartree−Fock (HF) based methodologies,[8−13] where highly accurate values of physical observables could in principle be calculated for any system provided that powerful computers are available, the success of a DFT method in the prediction of electronic properties of atoms and molecules depends largely on the choice of the exchange-correlation energy functional (E_{xc}) used in the computations.[1−7,12−15] Despite major advances achieved in developing E_{xc} functionals,[1−7,14] there is no known systematic way to improve the accuracies of these functionals. However, the development of hybrid-exchange functionals by Becke[15] and formulation of the generalized gradient approximations (GGA)[14−16] were definitely major steps forward. These theories significantly advanced DFT methodologies from being suitable only for qualitative predictions into truly quantitative ones.

In an effort to expand the range of applicability of DFT methods, Adamo and Barone[17] demonstrated that the majority of reported DFT-based methodologies have a common difficulty in handling van der Waals and charge-transfer complexes. Starting from an analysis of the low-density and large-gradient regions, which dominate van der Waals interactions, the authors proposed an elegantly simple modification to the Perdew−Wang (PW) exchange functional,[16] which when combined with corresponding PW correlation functional improved the performance of the method, denoted by mPW1,3PW, in handling systems exhibiting noncovalent interactions, e.g., He_2 and Ne_2. Such improvement in DFT-based methodologies is expected to expand their field of application to include structural and mechanistic biochemistry where long-range interactions play important roles in the stability and reactivity of biomolecules.[18]

It is clear from the enormous amount of literature pertaining to computational DFT that, as the accuracy of developed E_{xc} functionals is improved, the complexity of corresponding methodologies increases. For example, the recently developed mPW1,3PW model of Adamo and Barone[17] scales as $\sim N,^5$ where N is the number of basis functions. Development of DFT approaches with less stringent scaling properties is currently an active area of research.[14]

Recently, we formulated an approximate coupling scheme between HF and local spin density functional theories, which was denoted by HFS-BVWN, with N^3 dependence on the size of basis functions.[19] Using standard 6-311+g(3df,p) basis sets[11] and applying Dewar's empirical atom equivalent correction,[20,21] we showed that room-temperature heats of formation, ionization potentials, and electron affinities of 150 molecular systems could be computed to within 2 kcal/mol accuracy and a maximum deviation of 8 kcal/mol. The magnitudes of atom equivalents were in the range 1−7 kcal/mol/atom for hydrogen through chlorine. Clearly, without the use of atom corrections, the average and maximum errors in computed thermochemical properties by the HFS-BVWN/6-311+g(3df,p) method are expected to be significantly higher than the above quoted deviations. In addition, similar to other DFT methods, the HFS-BVWN approach is also expected to have difficulties accounting for noncovalent interactions.[19] Therefore, one may ask the following: is it possible to develop a general purpose DFT computational scheme for the prediction of accurate structure and energetics of molecules and improved long-range behavior, which scales as N^3? In addition, can we significantly reduce or even eliminate the dependence on atom equivalent corrections in the basic formulation of such method? These are the main objectives we will attempt to achieve in this paper.

The paper is structured as follows. In section 2, we describe the mathematical and computational aspects of the method where we demonstrate that the exchange-correlation functional used in its formulation has the appropriate asymptotic behaviors near the nucleus of an atom and at long range. Application of the model to 350 atomic and molecular systems, which includes the G2 data set of Curtiss et al.,[13] hydrogen-bonded, and van der Waals systems is discussed in section 3. Comparisons between the reported method and G2/6-311+g(3df,2p) ab initio theory,[13] HFS-BVWN/6-311+g(3df,p),[19] bond additivity correction BAC-G2/6-311++g(3df,2pd),[22] G2(MP2)/6-311+g(3df,2p),[13] G2(MP2,SVP)/6-311+g(3df,2p),[13] B3LYP/6-311+g(3df,2p),[15] and mPW1,3PW/6-311++g(3df,3pd)[17] methods are also presented in section 3. The general conclusions drawn from the reported model are given in section 4, where we stress using the G2 data set of Curtiss et al.[13] and the additional systems investigated in this paper as a stringent test for evaluating novel ab initio and DFT methodologies.

2. Theoretical Model

In DFT,[1−7] the total electronic energy, E, of an N-electron atomic or molecular system 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 $\rho(r_2)$, and E_{xc} is the exchange-correlation energy, which accounts for the exchange energy due to the antisymmetry of the electronic wave function and dynamic correlation resulting from the motion of electrons. Therefore, given an approximate energy functional E_{xc} with ρ defined by a set of orthonormal spin orbitals ψ_i as

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

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 equations whose potential V_{KS} is given by[1−7]

$$V_{KS} = V_{n-n} + V_{n-e} + V_{xc} \tag{3}$$

and

$$V_{xc} = \delta E_{xc}/\delta\rho \tag{4}$$

The effective one-electron potential of the Kohn−Sham model has been shown to satisfy some basic requirements.[23] The most important ones include a $-1/r$ decay at large r values and finiteness at the nucleus ($r = 0$), translational and rotational invariance, and special behavior at atomic shell boundaries. Therefore, any approximation to E_{xc} and the corresponding potential derived from it, V_{xc}, should satisfy these constraints. The majority of exchange-correlation functionals reported in the literature belonging to the simple local spin density and generalized gradient approximations have been shown to obey translational and rotational invariance and the special properties at atomic shell boundaries constraints.[1−7] Accordingly, the $r = 0$ and $r \to \infty$ limits are thus key requirements, which must be satisfied when developing E_{xc} functionals that are some linear combination of existing ones.

Following the usual practice in DFT, we assume the separability of exchange and correlation components of the E_{xc} energy functional.[1-7] Therefore, $E_x[\rho]$ can be expressed using the adiabatic connection formula[15] given by eq 5

$$E_x[\rho] = (2/3)[0.375(\mathrm{HF}_x - S_x)] \tag{5}$$

where HF_x and S_x are the nonlocal Hartree−Fock and local Slater exchange, respectively. The constant value 2/3 is Slater's theoretical coefficient.[1] Obviously, the leading term in eq 5 is the local exchange, S_x, with a scaling factor equal to 0.625. The sum of the HF_x and S_x scaling coefficients equals 1, thus satisfying the basic requirement of the adiabatic connection formula.[1-3,15] $E_x[\rho]$ leads to a corresponding exchange potential $V_x = \mathrm{d}E_x/\mathrm{d}\rho(r)$. It is important at this point to discuss the benefits of mixing HF_x with the local spin density exchange, S_x.

The local spin density exchange potential decays exponentially to zero into the vacuum.[23] Therefore, at distances far from the nucleus, $r \rightarrow \infty$, the HF_x component of E_x tends to the correct $-1/2\mathrm{r}$ limit, and thus the proper $-1/\mathrm{r}$ asymptotic behavior of corresponding potential is satisfied.[15] On the other hand, at $r = 0$ the HF_x also improves the corresponding V_x such that the cusp condition is obeyed and the general behavior of V_x near the nucleus is more HF-like.[15]

The local spin density approximation (LDA) fails to describe the hydrogen atom anion, H^-, and other negative ions as bound states.[1-7,23] The main reason for the breakdown of LDA is that it lacks the $-1/r$ term in the corresponding exchange-correlation potential, which is an essential term for stabilizing the outermost electron in an anion. As discussed above, the HF_x component of E_x improved the asymptotic behavior of V_x at long-range by accounting for the missing Coulombic term. Accordingly, one would thus expects a significant improvement in the computation of electron affinities of atomic and molecular systems using the reported methodology. Taking the hydrogen atom anion as an example, which is unbound at the LDA level of theory, the reported method correctly predicts H^- to be a bound anion. Using the 6-311g* basis set, the calculated virtual orbital energy of the hydrogen atom is −0.0887 au, which is an indication that H^- is expected to be bound. In addition, the calculated electron affinity of hydrogen is positive, 0.4 eV, thus confirming the latter observation. The computed electron affinities of other molecular species using the reported method will be discussed in section 3.

Before we define the correlation energy functional, E_c, it would be instructive to discuss the basic requirements that E_c and its corresponding potential, $V_c = \mathrm{d}E_c/\mathrm{d}\rho$, must satisfy. First, we need a correlation energy functional whose derived potential decays faster than Coulombically as $r \rightarrow \infty$.[23,24] Almbladh and Pedroza[24] derived such a potential which fell off as $\sim -\alpha r^{-4}$ when $\mathrm{r} \rightarrow \infty$, where α is the polarizability of the system. This potential was derived from exact DFT computations for the helium isoelectronic series H^-, He, Li^+, and Be^{2+}, and it described the polarization of the atom by an asymptotic electron. In addition, we will also require that V_c is finite and is an attractive potential in the regions where van der Waals forces are operating; that is, V_c would have a Lennard-Jones-type dependence on r in those regions.[25]

It is important to recall at this point that correlation effects are not directly observables; that is, they are not real physical quantities where one could design an experiment to measure the magnitude of such effects. Rather, it is a measure of the errors that are inherent in the starting orbital model. Therefore, we adopt the notion advanced recently by Raghavachari and Anderson,[26] which states that "... a theory of electron correlation refers to any method for accurate treatment of interelectronic interactions starting from a suitable wave function". Accordingly, we use the solutions of Kohn−Sham one-electron equations with $E_{xc} = E_x$ as our starting approximate model, which slightly underestimates atomic and molecular exchange energies. Accordingly, E_c is then expected to consist of the appropriate Coulomb, exchange, and dynamical correlations needed to yield reliable structures and energies of molecules and accurate values of physical observables.

TABLE 1: Computed Total Energies (au) of Hydrogen through Argon Atoms Using K2-BVWN/6-311+G(df), K2-BVWN/6-311+G(2df), and K2-BVWN/6-311+G(3df) Levels of Theory[a]

	total energy, au		
atom	K2-BVWN/ 6-311+g(df)	K2-BVWN/ 6-311+g(2df)	K2-BVWN/ 6-311+g(3df)
H	−0.497313	−0.497313	−0.497313 (−0.49981)
He	−2.896132	−2.896132	−2.896132 (−2.861680)
Li	−7.449223	−7.449223	−7.449223 (−7.432726)
Be	−14.598979	−14.598979	−14.598979 (−14.573020)
B	−24.552437	−24.552565	−24.552592 (−24.529052)
C	−37.705350	−37.705490	−37.705517 (−37.690251)
N	−54.403647	−54.403647	−54.403647 (−54.400911)
O	−74.837979	−74.838151	−74.838181 (−74.809369)
F	−99.451317	−99.451501	−99.451530 (−99.40928)
Ne	−128.590180	−128.590180	−128.590180 (−128.54701)
Na	−161.853239	−161.853239	−161.853239 (−161.85889)
Mg	−199.593305	−199.593305	−199.593305 (−199.61458)
Al	−241.818680	−241.818934	−241.818952 (−241.87665)
Si	−288.756668	−288.756944	−288.756958 (−288.85426)
P	−340.572169	−340.572169	−340.572169 (−340.71866)
S	−397.347640	−397.347852	−397.347889 (−397.50475)
Cl	−459.303551	−459.303739	−459.303793 (−459.48187)
Ar	−526.609436	−526.609436	−526.609436 (−526.81734)

[a] The corresponding Hartree−Fock limit atomic energies are given in parentheses.

From the above discussion, we propose the following correlation energy functional, $E_c[\rho]$, given by eq 6:

$$E_c[\rho] = E_c(\mathrm{VWN}) - 0.04053\langle \rho(r)^{4/3} \rangle - \mathrm{GGA} \tag{6}$$

where, $E_c(\mathrm{VWN})$ is the Pade approximated formula of the free-electron gas correlation energy due to Vosko, Wilk, and Nusair[27] and GGA is the generalized gradient approximation expression given by eq 7.

$$\mathrm{GGA} = 0.001575\langle \rho(r)^{4/3} x^2 (1 + 0.0252 x \sinh^{-1} x)^{-1} \rangle \tag{7}$$

The variable x is in eq 7 is equal to $[(\delta\rho(r)/\delta r)/\rho(r)^{4/3}]$ and the value 0.0252 (=0.0042 × 6) is Becke's constant.[15] The factor 0.001 575 in eq 7 is not an empirical parameter. Sham[28] derived this constant by wave-vector analysis and obtained $7/432\pi(3\pi^2)^{1/3} = 0.001667$. The latter result was also arrived at by Langreth and Perdew[29] and Gross and Dreizler.[30] Recently, Lee and Zhou[31] obtained a slightly lower value of $0.001\,429 = 1/72\pi(3\pi^2)^{1/3}$ from a Taylor series expansion of the GGA expression. The value appearing in eq 7 is simply the average of Sham[28] and Lee and Zhou[31] constants. On the other hand, the factor 0.040 53 of eq 6 was set such that upon solving the Kohn−Sham self-consistent-field equations for the atoms Li through Ar using 6-311+g(3df) basis sets, the calculated atomic energies compared favorably with corresponding HF limit values of Veillard and Clementi.[32] As shown in Table 1, the atomic energies computed by the reported method reproduced corresponding HF limit values to within ±0.04%. In addition, the second term in eq 6 makes the overall exchange-correlation functional satisfy the high-density Lieb−Oxford bound[1−3,17] given by eq 8.

$$E_x > E_{xc} > -1.679\,\langle \rho(r)^{4/3} \rangle \tag{8}$$

Let us examine the behavior of E_c and its corresponding potential, V_c, as $r \to \infty$. The potential derived from the first two terms in eq 6 has been shown to decay exponentially to 0 with the charge density into the vacuum[23,24] and thus have the appropriate faster than Coulombic decay discussed above. On the other hand, the GGA potential of eq 7 decreases asymptotically as kr^{-2}, where $k \approx -\mathrm{IP}^{-1/2}$ and IP is the ionization potential of the atom.[23] Recall that the polarizability of an atom α is related to the inverse of its ionization potential;[25] thus, we see that the GGA potential falls off as $\sim -\alpha^{1/2} r^{-2}$. Therefore, at sufficiently large values of r, where charge density overlap is 0, E_c becomes the van der Waals dispersion energy or simply the long-range correlation energy.[1−7] Accordingly, it is straightforward to verify that the corresponding correlation potential is given by the following approximate expression:

$$V_c \approx -\alpha^{1/2}(r^{-4} + r^{-6} + r^{-8} + ...) \tag{9}$$

From eq 9, it is clear that the inverse fourth power dependence satisfies the Almbladh and Pedroza[24] asymptotic relation for the correlation potential in atoms to within a constant factor. The sixth and eighth inverse power terms in eq 9 resemble the induced dipole−dipole interactions and induced dipole−quadrupole interactions, respectively, characteristic of van der Waals dispersion potentials.[25] The negative sign in eq 9 implies that these interactions are always attractive because the multipole moments are aligned antiparallel to one another. Furthermore, the strength of the dispersion interaction depends on the polarizability of interacting atoms and/or molecules.[25f] This dependence on polarizability means that nonpolar atoms such as hydrogen, carbon, and the noble gases are expected to have stronger dispersion interactions than polar ones such as nitrogen, oxygen, and fluorine. In general, the series given by eq 9 is convergent because the higher terms in r tend rapidly toward 0. Therefore, it is clear from eq 9 that the long-range behavior of the correlation potential satisfies the basic requirements of the corresponding exact expression for the dispersion potential.[25]

From the above discussion and referring to eqs 5−7, the total exchange-correlation potential $V_{xc}(r)$ has the net asymptotic behavior given by eq 10.

$$V_{xc}(r) \approx -r^{-1} - \alpha^{1/2}(r^{-4} + r^{-6} + ...) \approx -r^{-1} \text{ as } r \to \infty \tag{10}$$

Because we imposed the condition that the correlation potential should decay faster than $-1/r$, it is clear from eq 10 that for a given atomic or molecular system the Coulombic potential of Kohn−Sham theory is preserved as $r \to \infty$. As discussed above, the first two terms in E_c, eq 6, decay exponentially as r increases. The GGA term falls off as r^{-2} and, at long range, turns to an r^{-n} (n is an even integer) behavior. As will be shown in the next section, the asymptotic behavior of V_{xc} will have important implications when the reported method is applied to hydrogen-bonded and van der Waals systems.

To summarize, the reported methodology used two adjustable parameters. The first parameter fixed the percentage of $\mathrm{HF_x}$ in the adiabatic connection formula (ACF), which, as we discussed above, improved the $r = 0$ and $r \to \infty$ limits of the exchange energy functional and its corresponding potential. However, the calculated hybrid $\mathrm{HF_x}$ and S_x exchange energies of atoms and molecules using the ACF are expected to be numerically less negative than the corresponding values obtained from $\mathrm{HF_x}$-only computations.[15] This led to the introduction of a second adjustable coefficient, which was used in conjunction with the correlation component of E_{xc}. The purpose of the second parameter was to guarantee that the HF limit atomic energies of Li through Ar have been reached and that the overall exchange-correlation functional obeyed the Lieb−Oxford bound at the high-density limit. Accordingly, the method will be denoted by K2-BVWN.

One of the critiques of DFT-based methods that is commonly cited in the literature is the so-called lack of “high-level” computations.[12] This means that one cannot perform a series of calculations using increasingly larger basis sets to demonstrate convergence of the energies and/or derived values of physical observables. The results of K2-BVWN/6-311+g(df), K2-BVWN/6-311+g(2df), and K2-BVWN/6-311+g(3df) computations on Li through Ar atoms shown in Table 1 address the above critique. It is clear that the calculated atomic energies of Li−Ar at all three levels of theory are comparable to within less than 0.1 kcal/mol. In fact, for Li, Be, N, Ne, Na, Mg, P, and Ar, the results of computations for each atom are identical at all three levels of theory. This is an intriguing result because it demonstrates the fast convergence of atomic energies as the size of basis sets increased. On the other hand, the situation in molecules is different due to the presence of bonds. However, one could demonstrate that, for compounds comprised of atoms in their normal valence states, convergence of molecular energies could be achieved quickly as the size of basis sets used in the computation increased. In addition, in section 3 we will show that convergence of the total energies of hypervalent compounds as a function of basis set size is slightly slower than those of normal valent molecules. Therefore, one could, in principle, calculate the electronic and thermodynamic properties of molecules to any desired accuracy depending on the size of the basis set used in the computation, in accordance with the usual practice in HF theory.[8−13]

From Table 1, we also notice that the calculated total energy of atomic hydrogen using the 6−311g(d) basis set is 0.497 313 au, instead of the correct HF value of 0.499 81 au.[11] This results in a 1.566 kcal/mol self-interaction energy term for one electron systems.[1−3] Since the calculated atomic energies of lithium through argon shown in Table 1 are within ±0.04% from the corresponding HF limit values, to a good approximation we set the hydrogen atom energy equal to 0.499 81 au.

As a result of the large data set presented in this paper, we will comment on the quality of structures obtained from the K2-BVWN method.[11c] We found the K2-BVWN/6-311g(d) model generally reliable for optimizing the geometries of molecular systems. This level of theory predicted bond lengths and angles of numerous molecules and radicals remarkably well. The average deviations in bond lengths and angles were 0.01 Å and less than 3°, respectively. The largest deviation in bond length was found for the O−O distance in F_2O_2 (0.2 Å shorter than the corresponding experimental value[10a]). Expanding the basis set size used in the geometry optimization of F_2O_2 to 6-311+g(3df) improved the O−O bond length to within the average error. A similar situation will arise when dealing with $(H_2O)_2$ and $(HF)_2$, which we discuss in the next section.

The optimum geometries of all molecules and radicals, except the noble gas dimers and hydrogen-bonded systems, considered in this paper were calculated from full geometry optimizations with analytical derivatives using the B3LYP/6-31g* method.[15,19] These were followed by single-point computations using the K2-BVWN/6-311+g(2df) and K2-BVWN/6-311+g(3df,p) levels of theory for normal-valent and hypervalent compounds, respectively. The optimum B3LYP/6-31g* geometries of the molecules and corresponding thermal corrections belonging to the G2 data set were obtained from Curtiss et al.[13] The reason for using B3LYP/6-31g* geometries is simply because of the large data set reported in the literature using this method. 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 molecular enthalpies obtained from B3LYP/6-31g* calculations were scaled by the factor 0.95.[12,13] For all of the hypervalent compounds considered in this work, the unscaled zero-point energies were taken as a measure of corresponding thermal corrections.[12,19]

The minimum-energy geometries of nine noble gas dimers were calculated using the K2-BVWN/3-21+g(d,p) and K2-BVWN/3-21g levels of theory. On the other hand, the geometries of charge-transfer systems $(H_2O)_2$, $(HF)_2$, and $Cl_2\cdots C_2H_4$ were optimized using the 6-311g(d) and 6-311+g(3df,p) basis sets.

The unrestricted wave functions are not eigenfunctions of the total spin operator S^2. They are normally contaminated by higher spin states. This admixture of higher spin states leads to incorrect energies and spin densities. In all open-shell calculations reported in this work, spin contamination from higher spin states was generally less than 0.2%. Accordingly, no corrections to unrestricted wave functions and energies were performed.

3. Results and Discussion

This section is divided into three parts. In section A, we establish the K2-BVWN/6-311+g(2df) level of theory, with no diffuse or polarization functions on the hydrogen atoms, as a reliable model for calculating room-temperature heats of formation of normal-valent compounds. We demonstrate that the outliers resulting from the latter computations are the hypervalent compounds, nonhydrides containing multiple chlorine atoms, water, and hydrogen fluoride. These systems were studied using the K2-BVWN/6-311+g(3df,p) level of theory. Ionization potentials, proton and electron affinities of selected compounds of the G2 data set were computed using the K2-BVWN/6-311+g(2df) model (section B). Section C is devoted to a discussion of noncovalent interactions in model systems. In particular, we demonstrate that the optimum geometries and interaction energies of nine noble gas dimers and three charge-transfer complexes are remarkably well predicted by K2-BVWN.

A. Heats of Formation of Molecules and Radicals. The room tempearture heats of formation were calculated using the following approximate formula:[19]

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

Where, $\Delta H_{\mathrm{f},298}(\mathrm{AB})$ is the calculated heat of formation at 298 K for the molecule AB, $\Sigma_{i=1,n}(\Delta H_{\mathrm{if},298})$ is the sum of room-temperature heats of formation of the individual atoms in the molecule, $\Sigma_{i=1,n}(E_{i,0} + e_i)$ 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.

Using the K2-BVWN/6-311+g(2df) level of theory as a starting model for molecular systems, we list in Table 2 its application to calculate room-temperature heats of formation of a large data set.[13,33] Our objective is to reveal which molecules are difficult to handle at this level of theory and thus need a larger basis set, 6-311+g(3df,p), for the accurate computation of corresponding enthalpies of formation.

As shown in Table 2, the K2-BVWN/6-311+g(2df) level of theory is reliable for calculating the enthalpies of formation of normal-valent compounds with an average error of 1.4 kcal/mol. It is interesting to notice that the general performance of the K2-BVWN/6-311+g(2df) model for calculating heats of formation of normal-valent compounds is comparable to G2/6-311+g(3df,2p) theory,[13] yet at a much smaller computational cost. In addition, the basis sets used in connection with K2-BVWN are significantly smaller than those employed in G2 and related methods.

Enthalpies of formation of compounds containing Li, Be, B, Na, Mg, and Al atoms (Table 2) are well reproduced to within 1 kcal/mol from corresponding experimental values.[13,33] In addition, heats of formation of open- and closed-shell aliphatic and aromatic hydrocarbons are also well predicted by the reported method with an accuracy of ±1 kcal/mol.[13,33] Furthermore, enthalpies of formation of aliphatic and aromatic hydrocarbons containing heteroatoms (nitrogen, oxygen, and sulfur) are also reliably computed using the K2-BVWN/6-311+g(2df) level of theory. In particular, it is interesting to notice that the reported model is more accurate than the G2/6-311+g(3df,2p) method for unsaturated hydrocarbons.[13]

Moreover, contrary to the general belief that strained hydrocarbons need additional p-functions on the hydrogen atoms to correctly reproduce their heats of formation and other properties,[8−10] the K2-BVWN/6-311+g(2df) model, which does not use any p-functions on H-atoms, seems quite reliable for strained compounds. Therefore, the potential energy surfaces of gas-phase reactions between hydrocarbons and/or heterocyclic compounds can be reliably explored using the K2-BVWN methodology. The application of K2-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.

Out of all of the normal-valent compounds investigated using the K2-BVWN/6-311+g(2df) model, notice the last 10 compounds listed in Table 2. These molecules are mainly nonhydrides containing multiple halogen atoms, water, and hydrogen fluoride. The heats of formation of these compounds were calculated using 6-311+g(3df,p) basis sets. The use of expanded basis sets for these outliers improved corresponding enthalpies by ∼2 and 4 kcal/mol for water and hydrogen fluoride relative to the K2-BVWN/6-311+g(2df) level of theory.

The second set of outliers listed in Table 2 are the hypervalent compounds. For these species, the 6-311+g(3df,p) basis sets must be used for computing their heats of formation. As shown in Table 2, even at the K2-BVWN/6-311+g(3df,p) level of theory the enthaplies of SO_3, PCl_5, $POCl_3$ and POF_3 are in error by 5−6 kcal/mol. To reduce the latter errors, one could add a second set of f-functions on the heavy nonhydrogen atoms and perform single-point computations using the K2-BVWN/6-311+g(3d2f,p) level of theory on these species. However, instead of increasing the size of basis sets, we can use the atom equivalent scheme to improve the computed enthalpies of these outliers.[19−21] To this end, it is straightforward to verify that by assigning a consistent 0.6 kcal/mol atom corrections to oxygen, silicon, phosphorus, sulfur, and chlorine we can significantly improve the accuracy of calculated enthalpies of formation of outliers.

TABLE 2: Theoretical and Experimental Gas-Phase Heats of Formation (ΔH_f; 298 kcal/mol) of Selected Molecules and Radicals (1 au = 627.51 kcal/mol)

species	total energy (au)	thermal correction (au)	ΔH_f (kcal/mol)		species	total energy (au)	thermal correction (au)	ΔH_f (kcal/mol)	
			theory	exptl[a]				theory	exptl[a]
K2-BVWN/6-311+g(2df)									
H	−0.499 81	0.00236		52.1	$C_4H_4N_2$	−263.395 820	0.0781	44.4	46.8 ± 0.2
Li	−7.449 223	0.00236		38.1	C_4H_6 (*trans*-butadiene)	−155.432 134	0.0880	26.7	26.3 ± 0.2
Be	−14.598 979	0.00236		77.5	C_4H_6 (methylene cyclopropane)	−155.401 940	0.0876	45.4	47.9 ± 0.4
B	−24.552 437	0.00236		136.5	C_4H_6 (bicyclobutane)	−155.386 744	0.0860	54.0	51.9 ± 0.2
C	−37.705 350	0.00236		171.3	C_4H_6 (cyclobutene)	−155.411 005	0.0862	39.0	37.4 ± 0.4
N	−54.403 647	0.00236		113	C_4H_8 (cyclobutane)	−156.645 946	0.1095	7.1	6.8 ± 0.2
O	−74.837 979	0.00236		59.6	C_4H_8 (isobutene)	−156.662 262	0.1097	−3.0	−4.0 ± 0.2
F	−99.451 317	0.00236		18.7	C_4H_{10} (*trans*-butane)	−157.888 210	0.1330	−29.2	−30.0 ± 0.2
Na	−161.853 239	0.00236		25.6	C_4H_{10} (isobutane)	−157.889 159	0.1325	−30.1	−32.1 ± 0.2
Mg	−199.593 305	0.00236		35.3	C_5H_5N	−247.404 124	0.0900	31.1	33
Al	−241.818 680	0.00236		78.2	C_5H_8 (spiropentane)	−194.568 344	0.1164	45.0	44.3 ± 0.2
Si	−288.756 668	0.00236		108	C_5H_{10}	−195.848 025	0.1380	−16.1	−18.3 ± 0.2
P	−340.572 169	0.00236		75.6	C_6H_5	−230.721 160	0.0883	78.7	78
S	−397.347 640	0.00236		66.2	C_6H_6	−231.408 522	0.1016	19.9	19.7 ± 0.2
Cl	−459.303 551	0.00236		29	$C_6H_5CH_3$	−270.583 642	0.1282	12.6	12.0 ± 0.1
LiH	−8.043 454	0.0062	31.9	33.3	$C_6H_5CH_2$	−269.933 243	0.1146	48.0	47.8 ± 1.5
BH	−25.186 922	0.0072	105.6	105.8 ± 2	C_6H_5CHO	−344.370 628	0.1112	−8.9	−9 ± 0.5
BHF_2	−224.607 849	0.0210	−176.5	−175.4 ± 0.8	C_6H_5Cl	−690.176 228	0.0928	13.9	13.0 ± 0.2
$BHCl_2$	−944.157 169	0.0181	−60.4	−59.3 ± 1	C_6H_5F	−330.376 193	0.0938	−28.5	−27.7 ± 0.3
CH	−38.340 156	0.0095	141.7	142.5	$C_6H_2F_4$	−627.258 951	0.0760	−157.6	−154.6 ± 0.81
CH_2 ($^3B_1$)	−39.010 479	0.0203	92.1	93.7 ± 0.6	$C_6H_5NH_2$	−286.586 499	0.1178	20.0	20.8 ± 0.2
CH_2 ($^1A_1$)	−38.992 316	0.0198	103.2	102.8	C_6H_5NO	−360.295 085	0.0995	46.8	48.0 ± 1
CH_3	−39.697 089	0.0320	32.8	35.0 ± 0.1	$C_6H_5NO_2$	−435.287 311	0.1071	12.9	16.4 ± 0.2
CH_4	−40.374 776	0.0465	−19.1	−17.9 ± 0.1	C_6H_5OH	−306.407 312	0.1055	−20.4	−23 ± 0.2
NH	−55.039599	0.0105	83.3	85.2 ± 0.4	C_6H_5O	−305.764 294	0.0931	11.1	13.0 ± 1.0
NH_2	−55.696 422	0.0221	42.7	45.1 ± 0.3	C_6H_5SH	−628.844 134	0.1015	29.3	26.9 ± 0.2
NH_3	−56.376 343	0.0368	−10.5	−11.0 ± 0.1	C_6H_5S	−628.214 657	0.0891	52.4	54
OH	−75.506 368	0.0114	10.1	9.4 ± 0.1	CH_2F_2	−238.303 760	0.0362	−108.6	−107.7 ± 0.2
SiH_2 ($^1A_1$)	−290.001 381	0.0151	63.4	65.2 ± 0.7	CHF_3	−337.286 686	0.0296	−165.9	−166.6 ± 0.8
SiH_2 ($^3B_1$)	−289.968 801	0.0155	84.1	86.2 ± 1.0	CH_2Cl_2	−957.897 321	0.0331	−20.3	−22.8 ± 0.3
SiH_3	−290.619 767	0.0244	45.5	47.9 ± 0.6	CH_3NH_2	−95.535 705	0.0660	−6.3	−5.5 ± 0.1
SiH_4	−291.271 075	0.0340	7.1	8.2 ± 0.5	CH_3CN	−132.295 425	0.0482	17.3	18.0 ± 0.2
PH_3	−342.459 966	0.0272	−0.7	1.3 ± 0.4	CH_3NO_2	−244.247 070	0.0541	−20.7	−17.8 ± 0.2
P_2H_4	−683.736 427	0.0390	3.1	5.0	CH_3ONO	−244.240 205	0.0532	−17.0	−15.9 ± 0.2
SH_2	−398.635 457	0.0170	−4.2	−4.9 ± 0.2	CH_3SiH_3	−330.457 894	0.0635	−5.7	−7.0 ± 1.0
HCl	−459.969 051	0.0085	−20.5	−22.1 ± 0.0	HCOOH	−189.176 795	0.0372	−88.8	−90.5 ± 0.1
Li_2	−14.933 759	0.0044	53.2	51.6 ± 0.8	$HCOOCH_3$	−228.337 654	0.0660	−85.7	−85.0 ± 0.2
LiF	−107.117 204	0.0043	−79.4	−80.1	CH_3CONH_2 (acetamide)	−208.534 675	0.0768	−57.5	−57.0 ± 0.2
C_2H_2	−77.053 442	0.0283	55.1	54.5 ± 0.1	C_2H_4NH (aziridine)	−133.460 225	0.0720	29.8	30.2 ± 0.2
C_2H_4	−78.307 759	0.0529	11.9	12.5 ± 0.1	NCCN	−185.017 378	0.0210	74.2	73.3 ± 0.2
C_2H_6	−79.544 561	0.0757	−21.4	−20.1 ± 0.1	C_2H_6NH (dimethylamine)	−134.699 993	0.0942	−5.7	−4.4 ± 0.2
HCN	−93.106 373	0.0195	32.0	31.5 ± 1.0	$C_2H_5NH_2$	−134.710 387	0.0943	−12.2	−11.3 ± 0.2
HCO	−113.490 109	0.0166	8.5	10.0 ± 0.2	C_2H_2O (ketene)	−152.101 234	0.0350	−14.3	−11.4 ± 0.2
H_2CO	−114.139 659	0.0299	−26.5	−26.0 ± 0.1	C_2H_4O (oxirane)	−153.284 014	0.060	−12.3	−12.6 ± 0.1
CH_3OH	−115.356 234	0.0510	−48.2	−48.0 ± 0.1	CH_3CHO	−153.327 103	0.0585	−40.3	−39.7 ± 0.1
N_2H_4	−111.506 339	0.0561	21.6	22.8 ± 0.2	CHOCHO (glyoxal)	−227.096 030	0.0420	−50.0	−50.7 ± 0.2
N_2	−109.168 762	0.0082	1.4	0.0	C_2H_5OH	−154.533 305	0.0820	−53.9	−56.2 ± 0.1
NO	−129.487 069	0.0078	20.5	21.6 ± 0.0	$(CH_3)_2O$	−154.519 279	0.0823	−44.9	−44.0 ± 0.1
O_2	−149.873 888	0.0074	−3.3	0.0	C_2H_4S (thioxirane)	−475.749 084	0.0574	20.7	19.6 ± 0.3
F_2	−198.961 647	0.0059	1.1	0.0	C_2H_5SH	−476.977 139	0.0777	−8.7	−11.1 ± 0.1
CO_2	−188.003 031	0.015	−94.7	−94.1 ± 0.0	$(CH_3)_2S$	−476.976 231	0.0787	−7.5	−8.9 ± 0.2
Na_2	−323.734 199	0.0043	33.5	34.0 ± 0.3	C_2H_3F	−177.275 249	0.0469	−35.3	−33.2 ± 0.4
P_2	−681.328 129	0.0052	36.1	34.3	C_2H_5Cl	−538.312 081	0.0690	−25.9	−26.8 ± 0.3
S_2	−794.859 748	0.0051	29.4	30.7 ± 0.1	C_2H_3Cl	−537.076 776	0.0457	6.1	8.9 ± 0.3
Cl_2	−918.697 145	0.0047	1.5	0.0	CH_2CHCN (acrylonitrile)	−170.233 578	0.0542	44.8	43.2 ± 0.4
PO	−415.636 948	0.0056	−6.7	−8	$(CH_3)_2CO$	−192.510 286	0.0867	−51.6	−51.9 ± 0.2
SO	−472.384 405	0.006	1.9	1.2 ± 0.3	CH_3COOH	−228.361 044	0.0652	−101.0	−103.4 ± 0.4
ClO	−534.245 091	0.0051	23.9	24.2 ± 0.5	CH_3CFO	−252.323 520	0.0527	−105.5	−105.7 ± 0.8
ClF	−558.850 789	0.0052	−12.2	−13.2	CH_3COCl	−612.113 937	0.0512	−57.3	−58.0 ± 0.8
H_2S_2	−796.074 056	0.0206	5.6	4	C_3H_7Cl	−577.483 989	0.0976	−29.9	−31.5 ± 0.3
Si_2H_6	−581.359 039	0.0531	18.7	19.1	$(CH_3)_2CHOH$	−193.710 059	0.1082	−62.5	−65.2 ± 0.1
CH_3Cl	−499.136 452	0.0403	−19.7	−19.6 ± 0.2	$C_2H_5OCH_3$	−193.696 187	0.1107	−52.2	−51.7 ± 0.2
CH_3SH	−437.804 391	0.0489	−4.3	−5.5 ± 0.1	$(CH_3)_3N$	−173.866 763	0.1222	−6.9	−5.7 ± 0.2
BF_3	−323.649 898	0.0164	−269.6	−271.4 ± 0.4	$(CH_3)_2CH$	−118.052 377	0.0910	18.8	21.5 ± 0.4
BCl_3	−1402.972 163	0.0126	−94.0	−96.3 ± 0.2	C_4H_4O (furan)	−229.240 287	0.0723	−7.3	−8.3 ± 0.2
C_3H_4 (propyne)	−116.237 666	0.0585	44.3	44.2 ± 0.2	C_4H_4S (thiophene)	−551.695 542	0.0685	31.0	27.5 ± 0.2
C_3H_4 (allene)	−116.239 637	0.0585	43.1	45.5 ± 0.3	C_4H_4NH (pyrrole)	−209.431 791	0.0842	25.1	25.9 ± 0.1
C_3H_4 (cylcopropene)	−116.200 950	0.0583	67.2	66.2 ± 0.6	C_2H_5	−78.874 427	0.0620	26.3	28.9 ± 0.4
C_3H_6 (propene)	−117.485 388	0.0814	4.3	4.8 ± 0.2	SH	−397.986 671	0.0092	33.7	34.2 ± 0.4
C_3H_6 (cylcopropane)	−117.472 475	0.0823	12.9	12.7 ± 0.1	H_2	−1.174 115	0.0128	−0.2	0.0
C_3H_8 (propane)	−118.716 439	0.1043	−25.4	−25.0 ± 0.1	C_2H	−76.328 344	0.0150	137.5	135.1 ± 0.7
$C_3H_6O_3$	−342.476 682	0.0997	−109.4	−111.4 ± 0.1	C_2H_3	−77.622 695	0.0386	68.6	71.6

TABLE 2: Continued

species	total energy (au)	thermal correction (au)	ΔH_f (kcal/mol)		species	total energy (au)	thermal correction (au)	ΔH_f (kcal/mol)	
			theory	exptl[a]				theory	exptl[a]
K2-BVWN/6-311+g(2df)									
CH_3CO	−152.677 853	0.0465	−4.6	−2.4 ± 0.3	CO	−112.951 469	0.0071	−23.8	−26.4
H_2COH	−114.694 916	0.0402	−4.2	−4.1 ± 0.8	CS	−435.318 781	0.0053	71.1	68.5
CH_3O	−114.686 801	0.0400	0.8	4.1 ± 0.9	H_2CS	−436.568 141	0.0267	29.0	26.2
C_2H_5O	−153.862 438	0.0684	−5.7	−3.7 ± 0.8	H_2O_2	−151.096 986	0.0277	−29.6	−32.5
CH_3S	−437.162 461	0.0386	27.8	29.8 ± 0.4	HOF	−175.037 587	0.0164	−19.7	−22 ± 1
C_4H_9 (*tert*-butyl radical)	−157.229 82	0.1193	11.1	12.3 ± 0.4	HOCl	−534.898 062	0.0140	−16.1	−17.8 ± 0.5
C_6H_{12}	−235.028 852	0.1650	−26.4	−29.4 ± 0.2	PF	−440.198 060	0.0044	−15.4	−12.5 ± 5
CF_4	−436.264 885	0.022	−221.0	−223.0 ± 0.4	PF_2	−539.836 685	0.00789	−113.6	−115 ± 0.5
OCS	−510.424 910	0.0126	−34.5	−33.1 ± 0.2	SF	−496.933 064	0.00434	0.5	1
CS_2	−832.844 364	0.0106	27.5	28.0 ± 0.2	SF_2	−596.523 443	0.00790	−67.3	−70 ± 4
ClNO	−588.852 443	0.0107	11.1	12.4 ± 0.1	PN	−395.204 005	0.00552	45.9	45.6
NF_3	−353.090 079	0.0158	−35.5	−31.6 ± 0.3	PO	−415.636 840	0.00518	−6.8	−8 ± 3
OF_2	−273.890 515	0.0101	4.8	5.9 ± 0.5	PS	−738.085 994	0.00413	37.1	36 ± 1
ClF_3	−757.861 918	0.0130	−40.9	−38.0 ± 0.7	MgH_2	−200.763 462	0.0123	35.8	38.2
C_2F_4	−474.155 436	0.0310	−161.8	−157.4 ± 0.7	MgS	−597.017 254	0.0038	53.0	52
CF_3CN	−429.184 088	0.0288	−116.5	−118.4 ± 0.7	SH^-	−398.073 792	0.0092	−20.9	−19.4
C_6F_6	−825.161 061	0.0621	−232.5	−229.0 ± 1	$C_6H_5^-$	−230.759 562	0.0883	54.6	55.9
CF_3	−336.610 439	0.0167	−113.9	−112.0 ± 1	$C_6H_5CH_2^-$	−269.965 567	0.1146	24.4	27
CF_2	−237.017 866	0.0107	−46.2	−43.5	$C_6H_5O^-$	−305.846 512	0.0931	−40.5	−40.6
BeF	−114.273 651	0.0052	−43.6	−40.6	$C_6H_5S^-$	−628.299 800	0.0891	−1.0	1.5 ± 2
BeO	−89.611 037	0.0058	28.5	30	CN^-	−92.543 373	0.007	13.2	14.5
BeS	−412.074 145	0.0047	63.7	63.0	CH_3COO^-	−227.802 431	0.0532	−122.2	−120.7
O_3 ($^1A_1$)	−224.739 117	0.0100	38.8	34.1 ± 0.5	CH_3O^-	−114.741 799	0.0375	−35.3	−33.2 ± 2
CN	−92.391 395	0.0070	108.5	104.9 ± 0.5	CH_3^-	−437.232 071	0.0398	−15.1	−14.3 ± 2
K2-BVWN/6-311+g(3df,p)									
SO_2	−547.424206	0.0098	−64.3	−70.3 ± 0.1	$(CH_3O)_2SO$	−701.945346	0.0890	−112.0	−115 ± 0.5
SO_3	−622.396387	0.0120	−89.0	−94.6 ± 0.2	$(CH_3)_3PO$	−535.056656	0.1180	−103.9	−104 ± 2
S_2O	−869.854121	0.0050	−10.6	−12 ± 0.2	$CHCl_3$	−1416.657911	0.0251	−21.4	−24.7 ± 0.3
PF_3	−639.496235	0.0119	−224.5	−229 ± 1	CCl_4	−1875.408059	0.0162	−16.5	−22.9 ± 0.5
PCl_3	−1718.848482	0.0094	−67.0	−69	Si_2 ($^3\Sigma_g$)	−577.624602	0.0047	146.2	141
PCl_5	−2637.568680	0.014	−80.1	−86	SiO	−363.892778	0.0050	−19.3	−24 ± 2
$POCl_3$	−1793.877273	0.012	−127.3	−133.8	NaCl	−621.308069	0.0034	−41.1	−43.6
POF_3	−714.539333	0.0141	−293.7	−300 ± 1	$AlCl_3$	−1620.208183	0.0109	−134.3	−139.7 ± 0.7
NSF	−551.520715	0.0055	−2.8	−5 ± 0.9	COF_2	−312.118516	0.0184	−148.1	−152.7 ± 0.4
NSF_3	−750.608424	0.0129	−79.8	−85 ± 0.5	C_2Cl_4	−1913.363738	0.0228	0.4	−3.0 ± 0.7
$(CH_3)_2SO$	−551.958523	0.0833	−37.0	−36.2 ± 0.2	OH_2	−76.208420	0.0233	−58.7	−57.8 ± 0.0
$(CH_3)_2SO_2$	−626.970917	0.0847	−87.5	−89 ± 0.7	HF	−100.174537	0.0107	−65.6	−65.1 ± 0.2

[a] See ref 33.

The K2-BVWN model is more reliable for predicting heats of formation of molecules and radicals than the bond additivity correction BAC-G2/6-311++g(3df,2pd),[22] G2MP2/6-311+g(3df,2p),[13] G2(MP2,SVP)/6-311+g(3df,2p),[13] HFS-BVWN/6-311+g(3df,p),[19] B3LYP/6-311+g(3df,2p)[13,15] and mPW1,3PW/6-311++g(3df,3pd).[17] The average errors in calculated heats of formation by the latter methods are 1.7, 1.9, 2, 2, 3, and 3.5 kcal/mol, respectively. In addition, because of the much less stringent scaling of K2-BVWN compared to ab initio and other DFT-based methods and the use of smaller basis sets, the reported methodology may be applicable to larger chemical systems than any of the other computational schemes.

B. Ionization Potentials and Proton and Electron Affinities. For molecular ionization potentials (IPs)[33] Table 3 the average absolute deviation is 0.07 eV, compared with 0.12 eV for HFS-BVWN, 0.14 eV for B3LYP, and 0.05 eV for G2. The largest deviations are observed for the IP of the boron atom (0.4 eV too high) and triplet O_2 (0.5 eV too high). Because we are using the same thermal correction for both a neutral molecule and its corresponding positive ion, the IP = $[E_{total}(\text{ion}) - E_{total}(\text{neutral})]$.

Proton affinities[8,9] (Table 3) were calculated taking into account differences in zero-point energies. The average error in computed proton affinities is 0.05 eV, which is identical to the corresponding mean deviation in the G2 method.[8,9]

The calculated molecular electron affinities[33] Table 4 have an average deviation of 0.07 eV, compared with 0.08 eV for G2 and 0.13 eV for HFS-BVWN. The electron affinities (EAs) were computed from the equation, EA = $[E_{total}(\text{neutral}) - E_{total}(\text{ion})]$ and relevant data from Table 2. Ziegler and Gutsev[34] 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.

To summarize, the K2-BVWN/6-311+g(2df) model predicted ionization potentials and electron and proton affinities of molecular systems with a precision comparable to G2/6311+g(3df,2p) ab initio theory.

C. Noncovalent Interactions. In this section, we apply the K2-BVWN method to selected van der Waals and charge-transfer complexes,[35] namely nine noble gas dimers, $(H_2O)_2$, $(HF)_2$, and the complex formed between Cl_2 and C_2H_4 model systems.

Recently, Adamo and Barone[17] applied several density functional methods to calculate binding energies of selected van der Waals and hydrogen-bonded complexes. These authors discovered that the spread of results obtained by different DFTs is quite significant and that the majority of the methods seriously underestimated the binding energies of these systems. In particular, van der Waals complexes such as the dimers of noble gases are predicted by the majority of reported DFT methods to have no interaction or a strongly repulsive one.[17] As discussed above, Adamo and Barone[17] proposed the appropriate modifications to the PW exchange-correlation functional such that the resulting model mPW1,3PW correctly predicted the interaction energies of He_2 and Ne_2 using quadruple-ζ basis sets supple-

TABLE 3: Computed Atomic and Molecular Ionization Potentials (eV) and Proton Affinities (kcal/mol) Using the K2-BVWN/6-311+g(2df) Method and Corresponding Experimental Values ΔH_f (H^+) = 367.2 kcal/mol

species	total energy (au)	ionization potential (eV)		species	total energy (au)	ionization potential (eV)	
		DFT	exptl[a]			DFT	exptl[a]
H^+	0.0	13.601	13.598	HS	−397.601 277	10.49	10.422
Li^+	−7.244 181	5.58	5.392	SH_2 ($^2B_1$)	−398.251 819	10.44	10.453
Be^+	−14.261 448	9.185	9.322	SH_2 ($^2A_1$)	−398.167 651	12.73	12.78
B^+	−24.232 607	8.706	8.298	Cl_2	−918.276 406	11.45	11.5
C^+	−37.280 368	11.568	11.260	CO	−112.428 971	14.22	14.01
N^+	−53.862 059	14.737	14.534	P_2	−680.929 915	10.84	10.567, 11.7
O^+	−74.321 846	14.049	13.618	S_2	−794.507 294	9.59	9.36, 9.6, 9.5
F^+	−98.800 499	17.715	17.422	ClF	−558.385 266	12.67	12.66
Na^+	−161.655 773	5.373	5.139	CS	−434.896 768	11.48	11.335; 11.39
Mg^+	−199.308 398	7.753	7.646	N_2 ($^2\Sigma_g$)	−108.584 086	15.91	15.58
Al^+	−241.595 339	6.084	5.986	N_2 ($^2\Pi_u$)	−108.554 565	16.71	16.70
Si^+	−288.455 683	8.198	8.1517	C_6H_6	−231.071 135	9.18	9.244
P^+	−340.186 869	10.485	10.486	C_6H_5	−230.415 929	8.31	8.32
S^+	−396.959 323	10.572	10.360	$C_6H_5CH_3$	−270.263 714	8.71	8.828 ± 0.001
Cl^+	−458.821 937	13.111	12.967	$C_6H_5CH_2$	−269.669 874	7.17	7.242 ± 0.006
C_2H_2	−76.638 212	11.30	11.4	C_6H_5CHO	−344.020 211	9.54	9.5 ± 0.08
C_2H_4	−77.924 527	10.43	10.51	C_6H_5Cl	−689.848 110	8.93	9.07 ± 0.02
CH_4	−39.902 528	12.85	12.62	C_5H_5N	−247.068 145	9.14	9.26 ± 0.01
OH	−75.020 957	13.21	13.10	$C_4H_4N_2$	−263.056 378	9.24	9.28 ± 0.01
H_2O	−75.734 419	12.64	12.62	C_6H_5S	−627.902 517	8.49	8.63 ± 0.1
HCl	−459.499 396	12.78	12.75	$C_6H_4O_2$	−379.801 614	9.98	10.0 ± 0.1
HF	−99.575 534	16.12	16.04	C_6H_5F	−330.042 285	9.09	9.2, 9.11
NH_3	−55.999 618	10.25	10.18	$C_6H_5NH_2$	−286.308 299	7.57	7.65, 7.72
SiH_4	−290.863 125	11.10	11.15	C_6H_5NO	−359.997 529	8.10	8.0, 8.09
PH	−340.817 487	10.23	10.149	$C_6H_5NO_2$	−434.922 826	9.92	9.94 ± 0.08
PH_2	−341.456 999	9.943	9.84	C_6H_5OH	−306.100 385	8.35	8.47 ± 0.02; 8.37
PH_3	−342.096 030	9.90	9.87	C_6H_5SH	−628.544 584	8.15	8.30 ± 0.05

species	total energy (au)	protein affinity (kcal/mol)		species	total energy (au)	protein affinity (kcal/mol)	
		DFT	exptl[a]			DFT	exptl[a]
NH_3	−56.710 536	201.0	202.5	SH_2	−398.911 866	166.5	168.5
OH	−75.734 419	142.6	141.8	C_6H_5O	−306.100 385	203.0	205.0
OH^-	−76.208 420	391.7	390.7 ± 0.1	$C_6H_5O^-$	−306.407 312	347.0	348 ± 2
OH_2	−76.469 928	163.7	165.1	$C_6H_5CH_2$	−270.263 714	199.0	198.7
SH^-	−398.635 457	352.3	350.7 ± 0.9	$C_6H_5CH_2^-$	−270.583 642	379.6	380.5 ± 1
CN^-	−93.106 373	348.4	348.2 ± 2	C_6H_5	−231.071 135	212.8	211.3
C_2H	−76.638 212	186.7	184.6[b]	$C_6H_5^-$	−231.408 522	401.9	401.7 ± 0.5
C_2H_2	−77.302 767	152.0	152.3	CH_3COO^-	−228.361 044	348.8	348.0 ± 2
C_2H_3	−77.924 527	181.5	180.5	CH_3NH_2	−95.887 360	215.0	214.9
PH_3	−342.763 088	183.1	187.6				

[a] See ref 33. [b] Based on an ionization potential value for acetylene equal to 11.4 eV.

mented by two sets of d-functions and one set of f-functions for helium and 3d−2f-1g for neon.

In section 2, we demonstrated that the correlation energy functional, E_c, used in the formulation of K2-BVWN has the appropriate dependence on r at large distances, see eq 9. Therefore, one should expect that the reported methodology to properly account for the interactions taking place between atoms at large distances, where charge density overlaps are absent.

In Table 5, we list the results of K2-BVWN/3-21+g(d,p) and K2-BVWN/3-21g optimizations on nine noble gas dimers. Both basis sets predicted comparable equilibrium distances, r_e, for all nine systems and seem to properly account for van der Waals long-range attraction between the noble gas atoms. In addition, the qualitative trends and interaction energies are well predicted by both basis sets. As shown in Table 5, the K2-BVWN/3-21g level of theory underestimated the interaction energies of noble gases by a constant factor except for the Ne···Xe, Xe···Xe, and Kr···Xe systems, which are overestimated. On the other hand, the K2-BVWN/3-21+g(d,p) model consistently overbinds the noble gas dimers, except He_2, which is underestimated. By averaging the interaction energies of inert gas dimers obtained from both levels of theory, we get a very good agreement with corresponding experimental values.[33,35] However, instead of the latter averaging procedure, we recommend using the K2-BVWN/3-21+g(d,p) level of theory in the investigation of the above van der Waals complexes and related systems because the errors in calculated binding energies are more consistent than for the K2-BVWN/3-21g method.

Now we examine the water dimer. Geometry optimizations on $(H_2O)_2$ were done using 6-311g(d) and 6-311+g(3df,p) basis sets. The resulting optimum geometries of water dimer obtained from both basis sets differed in only one aspect. The 6-311+g(3df,p) basis set gave a more reliable O···O distance, 2.92 Å, than did 6-311g(d), 2.83 Å. (The experimental O···O bond length is 2.95 Å).[10a,35] The calculated binding energy of $(H_2O)_2$ using the K2-BVWN/6-311+g(3df,p) level of theory is 4.94 kcal/mol, in excellent agreement with corresponding experimental value of 5.44 ± 0.7 kcal/mol,[35] correlated HF compuations, 4.7 kcal/mol,[17] and the mPW1PW/6-311++g(3df,3pd) value of 4.5 kcal/mol.[17]

We treated hydrogen fluoride dimer in a manner similar to its isoelectronic counterpart $(H_2O)_2$ described above. The F···F distance calculated using the 6-311+g(3df,p) basis set is 2.73 Å, which agrees reasonably well with corresponding experimental value of 2.79 ± 0.05 Å.[10a,33] The calculated heat of formation of hydrogen fluoride dimer is −134.0 kcal/mol using the unscaled thermal correction 0.0257 au. The corresponding experimental value is −136.87 kcal/mol.[33] However, the

TABLE 4: Computed Atomic and Molecular Electron Affinities (eV) of Selected Chemical Systems Using K2-BVWN/6-311+g(2df) Method and Corresponding Experimental Values

species	total energy (au)	electron affinity (eV)	
		DFT	exptl[a]
C^-	−37.759 516	1.47	1.263
O^-	−74.896 738	1.59	1.462
F^-	−99.578 633	3.46	3.399
Si^-	−288.810 303	1.45	1.385
P^-	−340.608 460	0.99	0.77
S^-	−397.430 465	2.25	2.077
Cl^-	−459.441 481	3.75	3.617
CH	−38.391 595	1.40	1.24
CH_2	−39.037 650	0.74	0.65
CH_3	−39.700 202	0.085	0.08
OH	−75.570 241	1.74	1.83
SH	−398.073 792	2.37	2.314
SiH_3	−290.673 263	1.456	1.406
NH	−55.054 310	0.40	0.38
NH_2	−55.721 005	0.67	0.74
SiH_2 ($^2B_1$)	−290.045 964	1.21	1.123
PH	−341.235 121	1.14	1.028
PH_2	−341.869 818	1.29	1.26, 1.271
Cl_2	−918.801 049	2.83	2.4, 2.5, 3.2
CN	−92.543 373	4.14	3.862
S_2	−794.924 292	1.756	1.663
O_2	−149.892 515	0.51	0.44
PO	−415.684 04	1.28	1.092
C_6H_6	−231.361 552	−1.28	−1.1, −1.2
C_6H_5	−230.759 562	1.045	1.096
C_6H_5S	−628.299 800	2.32	2.26 ± 0.1
$C_6H_5CH_3$	−270.539 859	−1.19	−1.16, −1.06
$C_6H_5CH_2$	−269.965 567	0.88	0.90
$C_6H_4O_2$	−380.247 775	2.16	1.99 ± 0.048
C_6H_5CHO	−344.387 729	0.46	0.39, 0.43
C_6H_5OH	−306.365 048	−1.15	−1.1[b]
C_6H_5O	−305.846 512	2.24	2.253 ± 0.006
$C_6H_5NO_2$	−435.330 535	1.18	1.18 ± 0.05, 1.01 ± 0.1
CH_3O	−114.741 799	1.50	1.57 ± 0.022
CH_3S	−437.232 071	1.89	1.871 ± 0.012

[a] See ref 33. [b] Estimated value.

TABLE 5: Computed Interaction Energies (eV) of Noble Gas Dimers Using the K2-BVWN/3-21+g(d,p) and K2-BVWN/3-21g (in Parentheses) Levels of Theory and Corresponding Experimental Values (1 au = 27.21161 eV)

species	total energy (au)	r_e (Å)	interaction energy (eV)	
			theor	exptl[a]
He	−2.870077			
He···He	−5.740159	3.7688	−0.000136 (−0.000144)	−0.0009
Ne	−127.909907			
Ne···Ne	−255.820498	2.923	−0.0186 (−0.00161)	−0.0035
He···Ne	−130.780991	2.662	−0.0274 (−0.000762)	−0.0012
Ar	−524.137185			
Ar···Ar	−1048.275826	3.8555	−0.0396 (−0.00547)	−0.012
Kr	−2738.339659			
Kr···Kr	−5476.679558	4.0422	−0.0653 (−0.0049)	−0.0174
Kr···Ne	−2866.250963	3.3725	−0.0380 (−0.0120)	−0.0065
Xe	−7197.598140			
Xe···Xe	−14395.200527	4.9846	−0.116 (−0.115)	−0.0243
Ne···Xe	−7325.510645	3.8463	−0.0707 (−0.0724)	−0.0065
Kr···Xe	−9935.940041	4.5167	−0.0610 (−0.060)	−0.018

calculated enthalpy of formation of $(HF)_2$ is improved by 1 kcal/mol if we scale the above thermal correction of $(HF)_2$ by 0.95. The computed binding energy of $(HF)_2$ is 4.87 kcal/mol, which compares remarkably well with the accepted experimental value of 4.56 ± 0.3 kcal/mol[10a,33d,35] and corresponding ab initio computations of Sosa et al.[33d] of 4.8 kcal/mol.

The charge-transfer complex formed between Cl_2 and C_2H_4 has been suggested by Adamo and Barone[17] as an important system for testing the reliability of novel DFT approaches. The majority of reported DFT methods, including the recent mPW1,-PW model, underestimated the $Cl\cdots C_2H_4$ distance by 0.4−0.8 Å (the experimental bond length is 3.13 Å).[17,36] By optimizing the geometry of the complex using K2-BVWN/6-311g(d) level of theory, we get a $Cl\cdots C_2H_4$ bond length of 2.923 Å, that is, ~0.2 Å shorter than the experimentally determined distance. Increasing the size of basis sets to 6-311+g(3df,p) significantly improved the latter bond length to within less than 0.03 Å from the corresponding experimental value. On the other hand, the computed interaction energy of Cl_2 and C_2H_4 by the K2-BVWN/6-311+g(3df,p) method is −2.3 kcal/mol, in excellent agreement with corresponding average experimental value of −2.2 kcal/mol[17,36] and the mPW1PW/6-311++g(3df,3pd) value of −1.4 kcal/mol.[17]

4. Conclusions

A novel DFT methodology for the computation of accurate electronic and thermodynamic properties of molecular systems and improved long-range behavior has been developed. The exchange-correlation energy functional, E_{xc}, was approximated by a linear combination of an adiabatic connection formula, a Pade approximated VWN correlation functional, and a GGA term. The exchange-correlation potential, V_{xc}, derived from E_{xc} has been shown to have the proper $r = 0$ and $r \rightarrow \infty$ limits of Kohn−Sham theory and the appropriate faster than Coulombic dependence at long range. The method was denoted by K2-BVWN because it used two adjustable parameters in its formulation. The K2-BVWN scheme scaled 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 related methods and $\sim N^5$ for the majority of reported DFT-based methodologies.

The calculated atomic energies of Li through Ar were shown to converge rapidly as a function of basis set sizes. Thus, the value of a physical observable derived from the total energy of the system could be computed to any degree of accuracy depending on the size of basis functions used, in accordance with corresponding well-founded concepts in computational HF theory. The K2-BVWN/6-311+g(2df) model, with no diffuse or polarization functions on the hydrogen atoms, has been established as a reliable level of theory for computing the electronic and thermodynamic properties of normal-valent compounds with a precision comparable to that of G2/6-311+g-(3df,2p) theory. For hypervalent compounds and well-defined normal-valent compound cases, the K2-BVWN/6-311+g(3df,p) model was found more appropriate than K2-BVWN/6-311+g-(2df) for the proper description of these systems. The general performance of K2-BVWN closely paralleled the G2 method in the computation of room-temperature heats of formation, ionization potentials, and electron and proton affinities of molecular systems.

The capability of the K2-BVWN model in accounting for weak noncovalent interactions taking place in van der Waals and charge-transfer systems has been demonstrated for noble gas dimers and charge-transfer model systems.

The expanded G2 data set of Curtiss et al.[13] complemented by the molecular systems reported in this study are expected to provide a stringent test for evaluating novel ab initio and DFT-based methodologies.

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