

JCTC

Journal of Chemical Theory and Computation

Accurate Atomic and Molecular Calculations without Gradient Corrections: Scaled SVWNV Density Functional

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Received January 12, 2005

Abstract: The local spin density approximation (LSDA) approximation was one of the first density functional theory (DFT) methods employed to calculate atomic and molecular properties. As newer, more sophisticated methods, such as BLYP and B3LYP, were developed, the LSDA approximation has grown less popular for molecular systems. In this paper we revisit the LSDA method and investigate a simple way to improve the results that can be obtained using this approximation. By scaling the contribution of the local correlation to the SVWNV functional, improved results can be obtained for heats of formation, ionization potentials, electron affinities, bond angles, bond distances, vibrational frequencies, conformational energies, interaction energies, and barrier heights. The results of our studies show that scaling the SVWNV functional yields heats of formations with average unsigned errors up to about nine times smaller than those of the standard SVWNV functional. The decreases in the errors of other properties studied in this work were not as dramatic as those of the heat of formation but were, in most cases, significant. There is a notable time saving in this density only functional. For a 9-alanine system SVWNV is 55% faster than B3LYP and 40% faster than BLYP at a 3-21G* basis set. Based on our observations we propose an improved SVWNV density functional that is suitable for the study of molecular systems at a fraction of the cost of more sophisticated DFT methods, which also produces reasonable accuracy at small basis sets. One type of application for which the improved SVWNV functional would be extremely well suited is QM/QM methods where a fairly inexpensive method is needed for the larger part of a system that is treated at a lower level of theory.

Introduction

As the speed of modern computers increases while their cost decreases it becomes possible to consider the use of ab initio methods to calculate properties of very large molecules, such as biomolecules. These types of calculations promise to greatly increase our understanding of the structure and function of large molecular systems.¹ Although a few efforts have already been made to make such large scale calculations,^{2–6} it is not yet a common practice due to the great computational expense.¹ The first step one would take when

making ab initio calculation on very large systems would be to use a relatively inexpensive density functional theory (DFT) method,^{7,8} such as LSDA, along with a small split valence basis set with a low degree of contraction, such as 3-21G*.^{9–11} The problem with such an approach is that the LSDA method is known to give inaccurate results when used to calculate such properties as the heat of formation.^{12,13} In this study we use an empirical technique to scale the correlation (VWNV)¹⁴ part of the SVWNV functional in order to improve the overall accuracy of several atomic and molecular properties as calculated using the LSDA method. This approach was initially described by Brothers and Merz, and we have expanded on the initial observation herein.¹³

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DFT has become an extremely popular method for studying the physical properties of molecules within the past decade, and there have been many advances made in the quality of the functionals available. Most modern functionals include terms that are dependent on the gradient of the density (these are known as generalized gradient approximation, or GGA functionals),¹³ adding an extra calculation over a local only functional. The SVWNV functional is composed of a Slater exchange functional^{7,8,15} combined with a VWNV correlation functional and has no functional dependence on the density gradient; this functional is given as

$$\epsilon_{\text{SVWN5}} = \epsilon_{\text{Slater}} + \epsilon_{\text{VWN5}} \quad (1)$$

where

$$\epsilon_{\text{Slater}} = -\left(\frac{3}{4}\right)\left(\frac{6}{\pi}\right)^{1/3} (\rho_{\alpha}^{4/3} + \rho_{\beta}^{4/3}) \quad (2)$$

and

$$\begin{aligned} \epsilon_{\text{VWN5}} &= \rho \epsilon_c(x, \xi) \\ \rho &= \rho_{\alpha} + \rho_{\beta}, \quad x = \left(\frac{3}{4\pi\rho}\right)^{1/6}, \quad \xi = \frac{\rho_{\alpha} + \rho_{\beta}}{\rho} \end{aligned} \quad (3)$$

the correlation potential is given by

$$\begin{aligned} \epsilon_c(x, \xi) &= \epsilon_c^{\text{P}}(x) + \\ &\epsilon_c^{\text{A}}(x) g(\xi) \left\{ 1 + \left[\frac{4}{9(2^{1/3} - 1)} \frac{\epsilon_c^{\text{F}}(x) - \epsilon_c^{\text{P}}(x)}{\epsilon_c^{\text{A}}(x)} - 1 \right] \xi^4 \right\} \end{aligned} \quad (4)$$

where

$$g(\xi) = \frac{9}{8} [(1 + \xi)^{4/3} + (1 - \xi)^{4/3} - 2] \quad (5)$$

the various ϵ_c are given as

$$\begin{aligned} \epsilon_c(x) &= A \left\{ \ln \left(\frac{x^2}{X(x)} \right) + \frac{2b}{Q} \tan^{-1} \left(\frac{Q}{2x + b} \right) - \right. \\ &\left. \frac{bx_0}{X(x_0)} \left[\ln \left(\frac{(x - x_0)^2}{X(x)} \right) + \frac{2(2x_0 + b)}{Q} \tan^{-1} \left(\frac{Q}{2x + b} \right) \right] \right\} \end{aligned} \quad (6)$$

with

$$X(x) = x^2 + bx + c, \quad Q = (4c - b^2)^{1/2} \quad (7)$$

with parameters

$$\begin{aligned} A^{\text{P}} &= 0.0310907, \quad b^{\text{P}} = 3.72744, \quad c^{\text{P}} = 12.9352, \\ x_0^{\text{P}} &= -0.10498 \end{aligned}$$

$$\begin{aligned} A^{\text{F}} &= 0.0155454, \quad b^{\text{F}} = 7.06042, \quad c^{\text{F}} = 18.0578, \\ x_0^{\text{F}} &= -0.32500 \end{aligned}$$

$$\begin{aligned} A^{\text{A}} &= -0.016887, \quad b^{\text{A}} = 1.13107, \quad c^{\text{A}} = 13.0045, \\ x_0^{\text{A}} &= -0.004758 \end{aligned}$$

The parameters within this functional were determined by fitting the functional's calculated correlation energy density

to that of the homogeneous electron gas as calculated by Ceperly and Alder using quantum Monte Carlo methods.^{14,16}

In this study we restructure the SVWNV functional to include a parameter that can be varied in order to minimize the errors with respect to experimental values for the various properties we are investigating

$$\epsilon_{\text{c-SVWN5}} = \epsilon_{\text{Slater}} + c\epsilon_{\text{VWN5}} \quad (8)$$

To avoid ambiguity, this form of the functional is referred to as the c-SVWNV functional. Several other studies have been done where parameters within a functional are modified in order to reduce the errors in the values of some physical property compared to experimental data.^{13,17-21}

The atomic and molecular properties studied in this work are heat of formation, ionization potential, electron affinity, ground-state geometry, ground-state vibration frequencies, conformational energies, hydrogen bonding interaction energies, and transition state barrier heights. For the heat of formation, ionization potential, and electron affinity calculations the Gaussian G3 test set is used;^{22,23} this set includes 223 heats of formation, 88 atomic and molecular ionization potentials, and 58 atomic and molecular electron affinities. The molecules used for investigating geometric and frequency predictive accuracy were taken from the work of Johnson, Gill, and Pople.²⁴ This set includes 32 molecules for ground-state geometries and ground-state vibration frequencies. Conformational energies were calculated for ammonia (planar vs pyramidal), ethane (staggered vs eclipsed), and ethylene (orthogonal vs planar). Hydrogen bonding interaction energies for the water dimer and the transition state barrier height for the [1,5] sigmatropic shift of 1,3-pentadiene were also calculated.²⁵

The primary objective of this investigation is to study the behavior of the modified SVWNV functional used with small basis sets, and to this end we have carried out studies using the small 3-21G* and 3-21+G*²⁶ split valence basis sets. We have also carried out calculations using the much larger 6-311G**²⁷ and 6-311+G**²⁸ basis sets in order to have a set of higher quality data to which we can compare the small basis set results. To compare the results obtained using the modified c-SVWNV functionals to more widely used DFT methods, calculations were carried out using the BLYP and B3LYP functionals.²⁹⁻³²

Due to our interest in using the c-SVWNV functional for calculating heats of formation of biological molecules, we have calculated average signed and unsigned errors for the heats of formation of the systems in the set that contain only the carbon, hydrogen, oxygen, nitrogen, and sulfur atoms. We refer to this subset as the CHONS set. These are the atoms most commonly contained in proteins.

One of the goals of this study is to establish a single c-SVWNV scaling parameter that obtains reasonably accurate results for a wide variety of atomic and molecular properties. Among the scaling curves for all of the properties studied above, the one for heat of formation is by far the steepest and displays the most dramatic improvement. Because this is the case, we have determined that the average optimum heat of formation scaling parameter of 0.30 is the most appropriate universal parameter.

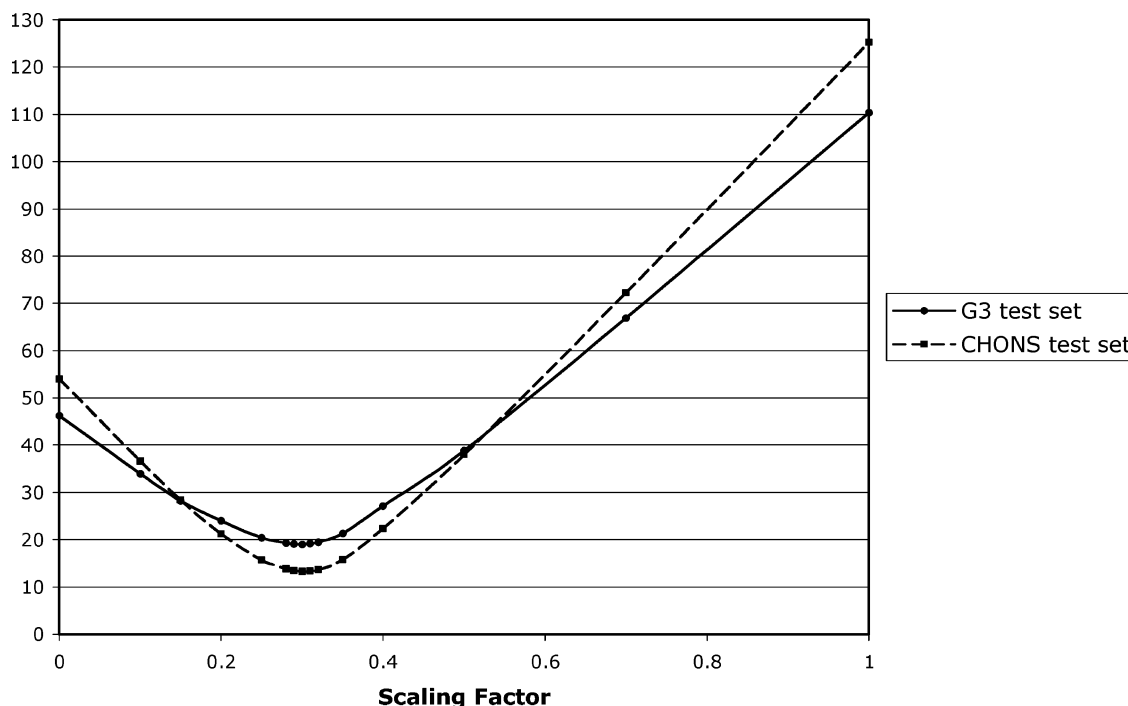


Figure 1. Average unsigned deviations of c-SVWNV with 3-21G* when VWNV part is scaled (errors in kcal/mol).

Methods

All of the calculations carried out in this study were performed using Gaussian 98.³³ Heats of formation were calculated using the method specified in “Thermochemistry in Gaussian” white paper available at http://www.Gaussian.com/g_whitepap/thermo.htm.³⁴ Experimental heats of formation, ionization potentials, and electron affinities were obtained from the G2/97 and G3 test set papers.^{22,23} Experimental bond lengths, bond angles, and vibration frequencies were obtained from Johnson, Gill, and Pople.²⁴

Values for ionization potential and electron affinity were calculated adiabatically. Hydrogen bonding calculations for the water dimer were carried out using counterpoise corrections.³⁵

Previous studies have used molecular geometries obtained at high levels of theory for the calculation of molecular properties at lower levels of theory.^{23,36} In this study molecular geometries for all calculated properties were optimized using the basis set and density functional that was being evaluated. Because information based on high levels of theory is not available for large biomolecules, we feel that this is the most appropriate way to conduct our study.

Results and Discussion

Heats of Formation. The optimization of the c-SVWNV correlation scaling factor for the 222 molecular species found within the G3 test set improves the average unsigned error from 110.4 kcal/mol to 19.0 kcal/mol for the 3-21G* basis set and from 109.0 kcal/mol to 11.9 kcal/mol for the 3-21+G* basis set with scaling factors of 0.30 and 0.29, respectively (see Figure 1). The molecule PF₅ was omitted in all calculations of average heats of formation because of its unusually large deviation from experimental values for all combinations of basis sets and functionals.

Table 1. Average Signed and Unsigned Deviations of Calculated Heats of Formation from Experiment for the G3 Test Set^a

functional	3-21G*	3-21+G*	6-311G**	6-311+G**
Average Unsigned Deviation				
Slater	46.2	43.6	45.2	47.0
SVWNV	110.4	109.0	115.2	112.1
BLYP	14.6	25.3	16.0	15.0
B3LYP	21.7	31.5	16.1	17.8
c-SVWNV	19.0	11.9	21.4	19.6
Average Signed Deviation				
Slater	-36.7	-40.4	-36.7	-40.4
SVWNV	110.3	109.0	115.2	112.1
BLYP	-12.4	-24.8	-13.0	-12.6
B3LYP	-21.2	-31.2	-16.0	-17.7
c-SVWNV	7.5	2.7	7.5	6.8
scaling factor	0.30	0.29	0.29	0.31

^a Deviations in kcal/mol. Deviation = experiment - theory.

Table 1 gives the average signed and unsigned errors for the c-SVWNV, SVWNV, Slater exchange only, BLYP, and B3LYP functionals along with the 3-21G*, 3-21+G*, 6-311G**, and 6-311+G** basis sets. The functional that includes exact exchange, B3LYP, and the Slater and BLYP functionals display underbinding behavior with all basis sets used in this study. The SVWNV functional exhibits significant overbinding, while the c-SVWNV functional slightly overbinds. It is clear that in terms of heat of formation unsigned errors the c-SVWNV functional is very competitive with the more advanced BLYP and B3LYP functionals. The c-SVWNV functional along with the 3-21+G* basis set does especially well in describing heats of formation compared to all other functional/basis set combinations.

Table 2 gives the average signed and unsigned heat of formation errors for the 152 molecules within the G3 set

Table 2. Average Signed and Unsigned Deviations of Calculated Heats of Formation from Experiment for the CHONS Test Set^a

functional	3-21G*	3-21+G*	6-311G**	6-311+G**
Average Unsigned Deviation				
Slater	53.9	54.3	52.4	57.4
SVWNV	125.2	127.5	133.7	137.3
BLYP	16.4	28.0	16.8	15.3
B3LYP	24.5	33.8	15.9	17.7
c-SVWNV	13.3	9.1	17.8	16.8
Average Signed Deviation				
Slater	-53.0	-54.0	-50.1	-55.6
SVWNV	125.2	127.5	133.7	137.3
BLYP	-16.2	-28.0	-14.2	-12.8
B3LYP	-24.5	-33.8	-15.9	-17.7
c-SVWNV	0.1	0.2	4.8	3.3
scaling factor	0.30	0.30	0.30	0.31

^a Deviations in kcal/mol. Deviation = experiment - theory.**Table 3.** Average Signed and Unsigned Deviations of Calculated Ionization Potentials from Experiment^a

functional	3-21G*	3-21+G*	6-311G**	6-311+G**
Average Unsigned Deviation				
Slater	35.9	26.3	30.5	28.6
SVWNV	7.5	6.6	5.1	5.2
BLYP	10.3	5.1	6.5	5.4
B3LYP	5.9	6.0	3.8	3.8
c-SVWNV	7.3	5.1	4.8	4.7
Average Signed Deviation				
Slater	35.9	26.1	30.5	28.6
SVWNV	3.2	-4.7	-0.7	-2.1
BLYP	9.0	0.3	5.0	3.3
B3LYP	2.4	-5.3	-0.5	-1.7
c-SVWNV	1.6	-0.7	0.9	0.0
scaling factor	1.05	0.87	0.95	0.93

^a Deviations in kcal/mol. Deviation = experiment - theory.

containing only the C, H, O, N, and S atoms. The results obtained for the CHONS subset yield unsigned errors that are larger than those calculated using the entire G3 set for all of the functionals with the exceptions of c-SVWNV, B3LYP/6-311G**, and B3LYP/6-311+G**. The improvements in the unsigned errors for both of the B3LYP functionals are very small (0.2 kcal/mol for 6-311G** and 0.1 kcal/mol for 6-311+G**) compared to the c-SVWNV functional, which displays dramatic improvements for all basis sets when only the CHONS molecules were considered. It is also interesting that with the CHONS test set, the c-SVWNV functional used along with the 3-21G* and 3-21+G* basis set yields average signed errors of -0.1 and -0.2 kcal/mol, respectively. The calculated signed errors for the 6-311G** and 6-311+G** basis sets are also better than those obtained with the BLYP and B3LYP methods. Although the c-SVWNV functional was fitted to the set, the ability of a local only functional to perform at such a high level is not to be overlooked.

Ionization Potentials and Electron Affinities. Table 3 gives the average signed and unsigned ionization potential errors for the 88 atoms and molecules contained within the G3 set. The c-SVWNV scaling factors for all of the basis

Table 4. Average Signed and Unsigned Deviations of Calculated Electron Affinities from Experiment^a

functional	3-21G*	3-21+G*	6-311G**	6-311+G**
Average Unsigned Deviation				
Slater	56.5	16.3	34.6	19.7
SVWNV	25.6	8.8	8.8	5.7
BLYP	31.8	5.8	13.7	3.1
B3LYP	26.2	7.3	10.9	3.4
c-SVWNV	14.6	4.8	7.2	2.6
Average Signed Deviation				
Slater	56.5	16.1	34.6	19.7
SVWNV	25.6	-8.5	6.5	-5.5
BLYP	31.7	-4.1	12.9	-0.3
B3LYP	25.9	-6.6	9.1	-2.3
c-SVWNV	13.1	-2.7	0.9	-0.4
scaling factor	1.40 ^b	0.75	1.20	0.80

^a Deviations in kcal/mol. Deviation = experiment - theory. ^b No true minimum reached.

sets are all very close to one, thus, the effects of the scaling are not nearly as pronounced as in the case of the heat of formation calculations. The c-SVWNV functional outperforms or matches the BLYP functional and obtains errors within 1.5 kcal/mol of the B3LYP results for all basis sets.

Table 4 gives the average signed and unsigned electron affinity error for the 58 atoms and molecules in the G3 set. The c-SVWNV functional outperforms both the BLYP and B3LYP functionals in terms of unsigned electron affinity errors for all basis sets. The scaling factor associated with the 3-21G* basis set is not at a minimum; we limited the upper limit to which this parameter could be varied to 1.40 in the case of electron affinity calculations. It should be noted that the standard SVWN functional does better than BLYP and B3LYP with the 3-21G* and 6-311G** basis sets. All of the results obtained using the 3-21G* basis set are very poor compared with the other three basis sets considered in this study.

It is also interesting, but not surprising, that the presence of diffuse functions has a great effect on the quality of the electron affinity and ionization potential calculations. The basis sets with diffuse functions yield much lower values for the average signed errors compared to the basis functions with no diffuse functions.

As expected, the local exchange only Slater functional performs very poorly for both ionization potential and electron affinity calculations.

Ground-State Geometries. Table 5 shows the average signed and unsigned errors for the 16 bond angles (from 12 molecules) considered in this study. For the cases of the 3-21G* and the 3-21+G* basis sets, the minimum in the c-SVWNV functional occurs with a scaling factor of zero, which is merely the Slater exchange only functional. As the larger basis set calculations yield optimum scaling factors of 0.95 in both cases, the errors obtained were very close to those of the standard SVWNV functional.

The inclusion of diffuse functions within the basis sets improves the bond angles for all of the functionals except for B3LYP. With the exception of SVWNV/3-21G*, all calculations using basis sets with no diffuse functions present yield angles that are smaller than experiment. The values

Table 5. Average Signed and Unsigned Deviations of Calculated Bond Angles from Experiment^a

functional	3-21G*	3-21+G*	6-311G**	6-311+G**
Average Unsigned Error				
Slater	2.35	1.95	2.05	1.98
SVWNV	2.44	2.40	1.85	1.82
BLYP	2.35	2.08	1.92	1.90
B3LYP	1.85	2.32	1.86	1.94
c-SVWNV	2.35	1.95	1.85	1.82
Average Signed Error				
Slater	0.97	-0.71	0.68	-0.22
SVWNV	-0.39	-1.60	0.06	0.06
BLYP	1.69	-0.61	0.95	0.25
B3LYP	0.54	-1.45	0.40	-0.18
c-SVWNV	0.97	-0.71	0.09	0.09
scaling factor	0.00 ^b	0.00 ^b	0.95	0.95

^a Deviations in degrees. Deviation = experiment - theory. ^b No true minimum reached.

Table 6. Average Signed and Unsigned Deviations of Calculated Bond Distances from Experiment^a

functional	3-21G*	3-21+G*	6-311G**	6-311+G**
Average Unsigned Error				
Slater	0.050	0.051	0.029	0.030
SVWNV	0.032	0.033	0.017	0.016
BLYP	0.036	0.038	0.015	0.015
B3LYP	0.024	0.025	0.007	0.008
c-SVWNV	0.025	0.025	0.013	0.013
Average Signed Error				
Slater	-0.049	-0.051	-0.028	-0.029
SVWNV	-0.028	-0.030	-0.008	-0.009
BLYP	-0.035	-0.038	-0.014	-0.015
B3LYP	-0.021	-0.024	-0.002	-0.003
c-SVWNV	-0.018	-0.020	0.001	0.000
scaling factor	1.50 ^b	1.50 ^b	1.50 ^b	1.50 ^b

^a Deviations in angstroms. Deviation = experiment - theory. ^b No true minimum reached.

for all angles calculated with the 3-21+G* basis set are larger than experiment.

Table 6 gives the average signed and unsigned errors for the 44 bond lengths (from 32 molecules) studied in this work. The scaling of the c-SVWNV functional does not reach a true minimum for any of the basis sets, so the scaling factor was limited to a maximum value of 1.50. The effects of the scaling factor are very small in terms of the bond length errors and typically only gave improvements of a few thousandths of an angstrom.

The c-SVWNV results are comparable to those of BLYP for all basis sets and to B3LYP for the smaller 3-21G* and 3-21+G* basis sets. The B3LYP functional along with the larger 6-311G** and 6-311+G** basis sets yield the best results with errors that are about half those obtained with BLYP and c-SVWN. Interestingly, the presence of diffuse functions in the basis functions seems to have a minimal effect on the bond lengths with all of the functionals used in this study.

Johnson, Gill, and Pople noted that density functional methods typically yield bond lengths that are too long;²⁴ our studies seem to agree with this observation, with bond lengths

Table 7. Average Signed and Unsigned Deviations of Calculated Vibrational Frequencies from Experiment^a

functional	3-21G*	3-21+G*	6-311G**	6-311+G**
Average Unsigned Error				
Slater	115	119	69	67
SVWNV	87	84	43	41
BLYP	99	92	37	34
B3LYP	105	103	83	79
c-SVWNV	84	82	40	39
Average Signed Error				
Slater	99	111	58	61
SVWNV	18	28	-19	-15
BLYP	35	41	-8	-7
B3LYP	-37	-27	-78	-76
c-SVWNV	40	47	0	3
scaling factor	0.75	0.75	0.75	0.75

^a Deviations in cm⁻¹. Deviation = experiment - theory.

being too long for all functional/basis set combinations except c-SVWNV/6-311G**. It is interesting to note that the average bond lengths computed using the 6-311G** and 6-311+G** basis sets are generally shorter than those calculated using the 3-21G* and 3-21+G* basis sets.

Ground-State Vibration Frequencies. Table 7 gives the average signed and unsigned errors for the 111 vibration frequencies (from 31 molecules) considered in this study. Although the scaling of the c-SVWNV functional yields improvements of only 2 or 3 cm⁻¹ over the standard SVWNV functional due to the shallowness of the scaling curve, it is remarkable that the scaling factor is exactly the same (0.75) for all of the basis sets studied. The best vibrational frequency results were obtained with the BLYP, c-SVWNV, and SVWNV functionals along with the 6-311G** and 6-311+G** basis sets. The B3LYP functional performs surprisingly poorly and, when combined with the larger basis sets, is outperformed by the Slater functional.

The presence of diffuse functions in the basis sets does not have a very large effect on the average vibration frequency errors. There is a very marked improvement in the quality of the frequency calculations when we go from using the 3-21G* and 3-21+G* basis sets to the larger 6-311G** and 6-311+G** basis sets.

Model Chemistry for the c-SVWNV Functional ($c = 0.30$). The average signed and unsigned errors obtained for heats of formation, ionization potentials, electron affinities, bond angles, bond distances, and vibrational frequencies using a c-SVWNV scaling parameter of 0.30 are given in Table 8. The values of the quantities listed above are reasonably good; there is a fairly large decrease in quality in the ionization potential and electron affinity results compared to the optimized parameter results, but the average deviations for diffuse function calculations are still less than 1 eV (23.06 kcal/mol).

It should be noted that the same kind of parametrization presented here could be carried out for other functionals, such as BLYP and B3LYP, with small basis sets. Such studies might improve the small basis set results of atomic and molecular properties for these functionals significantly.

Table 8. Average Signed and Unsigned Deviations from Experiment for Various Atomic and Molecular Properties with a c-SVWNV Scaling Factor of 0.30^a

	3-21G*	3-21+G*	6-311G**	6-311+G**
Average Unsigned Error				
heat of formation ^b	19.0	11.9	21.4	19.6
heat of formation (CHONS) ^b	13.3	9.1	17.8	17.5
ionization potential ^b	26.2	17.5	23.7	19.6
electron affinity ^b	47.2	11.0	25.9	13.5
bond angle ^c	2.35	2.00	2.01	1.95
bond distance ^d	0.044	0.046	0.025	0.025
vibrational frequency ^e	98	98	56	51
Average Signed Error				
heat of formation ^b	7.5	4.2	9.0	5.3
heat of formation (CHONS) ^b	0.1	0.2	4.8	2.1
ionization potential ^b	26.1	16.9	23.5	19.4
electron affinity ^b	47.2	9.9	25.8	13.4
bond angle ^c	0.54	-0.92	0.48	-0.28
bond distance ^d	-0.044	-0.045	-0.023	-0.023
vibrational frequency ^e	75	82	34	38

^a Deviation = experiment - theory. ^b kcal/mol. ^c Degrees. ^d Angstroms. ^e cm⁻¹.

Table 9. Conformational Energies^a

functional	3-21G*	3-21+G*	6-311G**	6-311+G**
Ethane (Staggered vs Eclipsed)				
Slater	2.9	2.7	2.7	2.7
SVWNV	2.9	2.8	2.8	2.8
c-SVWNV(0.3)	2.9	2.7	2.7	2.7
BLYP	2.7	2.5	2.6	2.6
B3LYP	2.7	2.6	2.7	2.7
expt ^b	2.9			
Ammonia (Pyramidal vs Planar)				
Slater	1.1	0	5.1	3.4
SVWNV	0.4	0	4.4	3.1
c-SVWNV(0.3)	0.8	0	4.9	3.3
BLYP	2.1	0.6	5.7	4.2
B3LYP	1.6	0.4	5.4	4
expt ^b	6			
Ethylene (Orthogonal vs Planar)				
Slater	64.2	62.6	62.4	61.6
SVWNV	73.4	71.9	71.5	70.8
c-SVWNV(0.3)	67	65.4	65.1	64.4
BLYP	67.9	66.8	66.2	65.6
B3LYP	66.0	65.3	64.5	64.1
expt ^b	65			

^a Conformation energies in kcal/mol. ^b Reference 41.

Conformational Energies. The conformational energies for ethane (staggered vs eclipsed), ammonia (pyramidal vs planar), and ethylene (planar vs orthogonal) are given in Table 9.

For the conformational energy of the ethane molecule the SVWN functional yields the best results for all basis sets. The c-SVWNV(0.3) functional and the Slater functional also obtain results that are the same or better than those of the BLYP and B3LYP functionals. The most accurate results were obtained using the SVWNV, c-SVWNV(0.3), and Slater functionals along with the 3-21G* basis set.

Table 10. Interaction Energies^a and Interoxygen Distances for the Water Dimer^b

functional	3-21G*	3-21+G*	6-311G**	6-311+G**
Interaction Energy				
Slater	-10.4	-11.6	-7.5	-7.9
SVWN	-10.9	-12.0	-7.9	-8.3
c-SVWNV(0.3)	-12.3	-13.2	-8.7	-9.1
BLYP	-6.6	-7.3	-4.7	-4.6
B3LYP	-7.3	-7.9	-5.1	-5.1
expt ^c	-5.4			
R(O-O)				
Slater	2.782	2.717	2.873	2.806
SVWN	2.762	2.696	2.846	2.782
c-SVWNV(0.3)	2.714	2.654	2.804	2.725
BLYP	2.869	2.846	3.03	2.97
B3LYP	2.826	2.811	2.991	2.938
expt ^c	2.946			

^a Interaction energies in kcal/mol. ^b Interoxygen distances in angstroms. ^c Reference 42.

The BLYP and B3LYP functionals outperform the Slater, SVWN, and c-SVWNV(0.3) functionals for the conformational energy of the ammonia molecule. For all functionals, calculations made with the 3-21G* and 3-21+G* basis sets yield results that are extremely low; this can be explained by the fact that, with these small basis sets, the pyramidal structure for this molecule is still very flat. The best results were obtained using the 6-311G** basis set for all functionals.

For the conformational energy of the ethylene molecule the SVWNV functional yields results that are too high, while the Slater functional yields results that are too low. The c-SVWNV(0.3), BLYP, and B3LYP functionals obtain very good results for this quantity. The addition of diffuse functions to the basis set does not seem to have a major impact on the overall quality of the calculated conformational energy of this system.

Water Dimer Interaction Energies. Table 10 gives the calculated interaction energies and interoxygen distances, R(O-O), for the water dimer. The interaction energies obtained using the BLYP and B3LYP functionals along with the larger 6-311G** and 6-311+G** basis functions were much better than those obtained with any other functional/basis set combination and were slightly too high. The SVWNV, Slater, and c-SVWNV(0.3) functionals all perform poorly compared to the BLYP and B3LYP functionals in terms of both interaction energies and interoxygen distances and always yield interaction energies that are too low. This is not a surprising result because the LSDA functionals lack the nonlocal terms necessary to describe long-range interactions. Among the local-only functionals the Slater functional yields the best results for both interaction energies and interoxygen distances for all basis sets.

It is interesting to note that when diffuse functions are added into the basis sets the interoxygen distance always decreases. This shortening of the interoxygen distance corresponds to a lowering of the interaction energy for all functional/basis set combinations except BLYP/6-311G** and B3LYP/6-311G**.

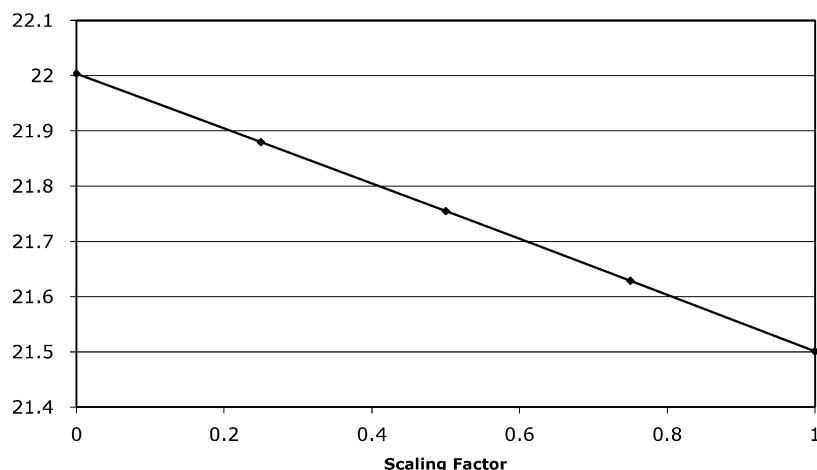


Figure 2. Barrier height of the [1,5]-sigmatropic shift for the 1,3-pentadiene molecule as a function of the c-SVWNV scaling factor (kcal/mol).

Table 11. Barrier Height of the [1,5]-Sigmatropic Shift for the 1,3-Pentadiene Molecule^a

functional	3-21G*	3-21+G*	6-311G**	6-311+G**
Slater	22.0	23.2	22.9	22.9
SVWNV	21.5	22.6	22.2	22.2
c-SVWNV(0.3)	21.8	23.0	22.7	22.7
BLYP	30.1	31.3	31.6	31.6
B3LYP	33.4	34.4	34.9	34.8
expt ^b	35.4			

^a Barrier heights in kcal/mol. ^b References 43 and 44.

[1,5]-Sigmatropic Shift Barrier Heights. The experimental and calculated barrier heights of the [1,5]-sigmatropic shift for the 1,3-pentadiene molecule are given in Table 11. All of the density functional methods underestimated the barrier height for this reaction, and all results obtained with the Slater, SVWNV, and c-SVWNV(0.3) methods were off by more than 34%. The B3LYP functional yields the best results with the B3LYP/6-311G** combination coming within 2% of the experimental value.

Figure 2 shows the c-SVWNV/3-21G* barrier height as a function of the scaling factor, *c*. The values for the barrier height are linearly dependent on the scaling factor with the Slater functional (*c*=0) giving the best results. Similar results were obtained with the other three basis sets.

The addition of diffuse functions to the 3-21G* basis set has a significant impact on the quality of the barrier height calculations for all of the functionals and typically bring the DFT results about 1 kcal/mol closer to the experimental value. The effects of introducing diffuse functions to the 6-311G** basis set are negligible.

Conclusions

In summary, we have shown that, by scaling the VWNV part of the SVWNV functional, the quality of LSDA results can be improved significantly. The heats of formation obtained with the c-SVWNV functional were improved by factors of 5.4 (for the 6-311G** basis set) and 9.2 (for the 3-21+G* basis set) compared to the standard SVWNV functional, yielding results comparable to those obtained with BLYP and B3LYP. The electron affinity results obtained using the c-SVWNV functional are generally quite a bit better

than those of the SVWNV functional and are better than results obtained using BLYP and B3LYP for all of the basis sets studied here. The ionization potential, vibrational frequency, bond angle, and bond length results are affected very little by the optimization of the scaling parameter and are very similar to the results obtained using the SVWNV functionals. The c-SVWNV (and SVWNV) values of the four aforementioned properties are generally fairly competitive with the BLYP and B3LYP results. The results obtained using the universal scaling parameter of 0.3 are fairly good for all of the properties mentioned above although the electron affinity and ionization potential values are worse than those obtained using the standard SVWNV functional. Nonetheless, the use of the 0.3 scaling factor yields, in general, a model chemistry that is superior to standard SVWNV and is competitive with nonlocal methods such as BLYP and B3LYP at a fraction of the cost.

The conformational energies obtained with the c-SVWNV-(0.3) functional are comparable to those calculated using the BLYP and B3LYP functionals. The small basis results for the ammonia molecule are poor for all functionals. The water dimer interoxygen distances and interaction energies calculated using the c-SVWNV(0.3) functional are poor as expected. The only good results for these quantities are those obtained using the BLYP and B3LYP functionals along with the larger 6-311G** and 6-311+G** basis sets. The [1,5] sigmatropic shift barrier heights are too low except when calculated using the B3LYP functional. Despite these results, for thermochemistry the c-SVWNV(0.3) functional, combined with a 3-21G* basis set, is extremely competitive with more modern functionals, for much lower computational costs. Because of its relative accuracy and low computational cost, the c-SVWNV(0.3) method would be an excellent candidate for the “inexpensive” part of QM/QM^{37–40} calculations that use two or more levels of theory to describe a system.

Acknowledgment. We thank the NSF (MCB-0211639) for their generous support of this work.

Supporting Information Available: The deviations from experiment of the heat of formation for the optimized

c-SVWNV, BLYP, and B3LYP functionals along with 3-21G* and 3-21+G* basis sets for each of the molecules in the G3 test set. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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CT050007C