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Density-functional thermochemistry. I. The effect of the exchange-only gradient correction

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Previous work by the author on diatomic molecules and by others on polyatomic systems has revealed that Kohn–Sham density-functional theory with "gradient corrected" exchange-correlation approximations gives remarkably good molecular bond and atomization energies. In the present communication, we report the results of an extensive survey of density-functional atomization energies on the 55 molecules of the Gaussian-1 thermochemical data base of Pople and co-workers [J. Chem. Phys. **90**, 5622 (1989); **93**, 2537 (1990)]. These calculations have been performed by the fully numerical molecules (NUMOL) program of Becke and Dickson [J. Chem. Phys. **92**, 3610 (1990)] and are therefore free of basis-set uncertainties. We find an average absolute error in the total atomization energies of our 55 test molecules of 3.7 kcal/mol, compared to 1.6 kcal/mol for the Gaussian-1 procedure and 1.2 kcal/mol for Gaussian-2.

I. INTRODUCTION

Since the seminal work of Hohenberg, Kohn, and Sham,[1] the density-functional theory (DFT) of electronic structure has seen significant theoretical and formal advances.[2] No longer reliant solely on the intuitive insights of its earliest incarnation, Slater's $X\alpha$ theory,[3] contemporary DFT is built soundly on a physically and mathematically rigorous foundation. At the same time, significant computational developments have stimulated a growing interest in the application of DFT methods to substantial molecular and chemical problems (see Ref. 4 for a good review).

The workhorse of density-functional quantum chemistry at present is the so-called "local spin-density" approximation (LSDA) for exchange-correlation energy. Accumulated experience over many years has revealed that the LSDA gives excellent molecular geometries, vibrational frequencies, and single-particle properties,[4] but seriously overestimates molecular bond energies.[5,6] In 1985, however, the author discovered that relatively simple corrections to the LSDA depending on spin-density *gradients* improved DFT bond energies remarkably.[7,8] Ziegler and co-workers immediately applied such "gradient corrections" to a wide variety of challenging problems in transition-metal chemistry with excellent results.[9] Thanks to subsequent improvements in their underlying theory and functional forms, exchange-correlation gradient corrections are now attracting the attention of a larger number of DFT researchers.[4]

The impressive evidence of Ziegler and co-workers notwithstanding,[9] we believe that a precise and systematic survey of the thermochemical capabilities of density-functional theory is desirable, especially with respect to accurately known experimental data. Our own previous work has focused on *fully numerical, basis-set-free* bond energy calculations on homonuclear diatomic molecules.[5-8] With the recent extension of our basis-set-free methodology to *polyatomic* molecules in general,[10-13] we can now expand our fully numerical diatomic surveys to include polyatomic tests as well. Our "numerical molecules" program system (dubbed NUMOL),[13] is uniquely suited for benchmark applications of this type, since the everpresent basis-set truncation error of conventional linear-combination-of-atomic-orbitals (LCAO) methods is eliminated.

The timing for a benchmark study of density-functional thermochemistry could not be better. Pople and coworkers[14,15] have recently published the results of extensive tests of the "Gaussian-1" (G1) *ab initio* thermochemical procedure on 55 organic and inorganic systems with accurately known experimental atomization energies. Even more recently, a revised "Gaussian-2" (G2) procedure has been calibrated on the same 55-molecule set.[16] Obviously, a direct comparison between contemporary density-functional methods and the *ab initio* G1 and G2 procedures would be of great interest. We therefore report in the present communication the results of fully numerical DFT atomization energy calculations, employing both the LSDA exchange-correlation functional itself and a gradient correction for exchange only, on the 55 first- and second-row molecules of the G1 data base.

II. BASIC THEORY

In this section, the Kohn–Sham formulation of density-functional theory is outlined briefly. Though many alternative DFT formulations are possible, Kohn–Sham theory is currently the most popular and the most powerful. The reader is referred to Ref. 2 for a detailed and comprehensive discussion.

Given an arbitrary N-electron atom or molecule with total electronic density ρ, let us imagine a corresponding *reference* system of ultimate simplicity—a system of *N independent noninteracting* electrons in a noninteracting one-body potential $V_{\rm KS}$ yielding the *same density* ρ. Then, we express the total electronic energy as follows:

$$E_{\rm total} = T_0 + \int \rho V_{\rm nuc}\, d^3\mathbf{r} + \frac{1}{2}\int\int \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{r_{12}} \times d^3\mathbf{r}_1\, d^3\mathbf{r}_2 + E_{\rm XC}, \qquad (1)$$

where T_0 is the kinetic energy of the noninteracting reference system, the second and third terms are the nuclear interaction energy and the classical electrostatic self-interaction energy, respectively, and the last term E_{XC} is the density-functional exchange-correlation energy. The noninteracting reference orbitals ψ_i satisfy, by definition, the following independent-particle Schrödinger equation:

$$-\tfrac{1}{2}\nabla^2\psi_i + V_{KS}\psi_i = E_i\psi_i \qquad (2)$$

with the local, one-body Kohn–Sham potential V_{KS} fixed by our original assumption that the noninteracting density

$$\rho = \sum_i^N |\psi_i|^2 \qquad (3)$$

equals the density of the fully interacting system. Equation (1), in fact, *defines* the exchange-correlation energy E_{XC}. Consequently, E_{XC} contains a great deal of information, including all the effects of two-body exchange and dynamical correlations, and a kinetic energy component as well.

Nevertheless, it can be shown[1] that E_{XC} depends uniquely on the total electronic density ρ and that the Kohn–Sham potential is given by

$$V_{KS} = V_{\text{nuc}} + V_{\text{el}} + V_{XC}, \qquad (4)$$

where

$$V_{\text{el}}(\mathbf{r}_1) = \int \frac{\rho(\mathbf{r}_2)}{r_{12}}\, d^3\mathbf{r}_2 \qquad (5)$$

and

$$V_{XC} = \frac{\delta E_{XC}}{\delta\rho} \qquad (6)$$

with Eq. (6) representing the functional derivative of E_{XC} with respect to ρ. These equations are generalized easily to spin unrestricted cases also (i.e., $\rho_\alpha \neq \rho_\beta$, where α and β denote up and down electron spins) if two Kohn–Sham potentials V_{KS}^σ are admitted, one for each spin σ, with V_{XC}^σ the functional derivative of E_{XC} with respect to the *spin* density ρ_σ.

Moreover, E_{XC} is rigorously related[17,18] to a two-electron exchange-correlation "hole" function $h_{XC}(\mathbf{1},\mathbf{2})$ by the following two-electron integration:

$$E_{XC} = \frac{1}{2}\int\int \frac{\rho(\mathbf{1})h_{XC}(\mathbf{1},\mathbf{2})}{r_{12}}\, d^3\mathbf{r}_1\, d^3\mathbf{r}_2, \qquad (7)$$

where h_{XC} is determined by quantum mechanical pair probabilities and an integration over interelectronic coupling strength. Unfortunately, first-principles evaluation of exchange-correlation holes is intractable in all but very trivial systems. Therefore, despite the rigor of this general formalism, its practical value is not immediately obvious.

It is known, however, that exchange-correlation holes satisfy a variety of simple yet restrictive *global constraints* on such properties as normalization, limiting behavior for small and large r_{12}, cusp conditions, scaling conditions, etc. Notice, also, that the $\mathbf{r}_2$ integration in Eq. (7) samples only the *spherical average* of $h_{XC}(\mathbf{1},\mathbf{2})$ about the reference point $\mathbf{r}_1$ and hence the details of its angular dependence are unimportant. Thus, global constraints can be used as guides to construct spherically symmetric hole-function *models* and associated energy approximations. To the extent that known constraints contain the essential physics of exchange and correlation phenomena, hole-function models within the Kohn–Sham formalism provide a simple and convenient alternative to traditional *ab initio* technology.

The simplest and most popular exchange-correlation approximation, the "local spin-density" approximation (LSDA) has the form

$$E_{XC}^{\text{LSDA}} = \int e_{XC}[\rho_\alpha(\mathbf{r}),\rho_\beta(\mathbf{r})]\, d^3\mathbf{r}, \qquad (8)$$

where the integrand e_{XC} is the exchange-correlation energy density of a *uniform electron gas* with spin densities $\rho_\alpha(\mathbf{r})$ and $\rho_\beta(\mathbf{r})$ equal to their *local* atomic or molecular values. This approximation corresponds to replacement of the exact exchange-correlation hole at reference point $\mathbf{r}$ with a *model* hole from electron gas theory. The functional e_{XC} has been well characterized by Monte Carlo simulations[19] and we employ in the present work the associated parametrization of Vosko, Wilk, and Nusair.[20]

Of course, an atomic or molecular density is not homogeneous, even locally, and we thus seek improvements to the LSDA incorporating nonuniformity information. The simplest beyond-LSDA corrections depend on local spin-density *gradients* in addition to the density itself and will be called "gradient corrections" in this communication. These have been found particularly effective in the calculation of molecular dissociation energies (see Refs. 6–9) and, considering the well-known difficulties of *ab initio* thermochemistry, have given density-functional theory new and exciting vigor. We shall not review the extensive and growing literature of exchange-correlation gradient corrections here, but shall concentrate on a recent correction of the "exchange only" type with particularly interesting properties.

For reference points *asymptotically far* from a finite system, as in the exponential tails of atomic and molecular charge distributions, the exchange-correlation energy integral assumes the limiting form

$$E_{XC}(r\to\infty) = -\frac{1}{2}\int \frac{\rho}{r}\, d^3\mathbf{r} \qquad (9)$$

which is a simple consequence of the well-known hole normalization constraint

$$\int h_{XC}(\mathbf{1},\mathbf{2})\, d^3\mathbf{r}_2 = -1 \qquad (10)$$

valid at any reference point **1**. Equation (9) follows immediately from Eqs. (7) and (10) under consideration that the exchange-correlation hole remains "attached" to a finite system for reference points approaching infinity. It is a major and well-known failure of the LSDA that this correct asymptotic behavior is not reproduced. Given, therefore, that molecular bond formation essentially involves the overlap of atomic exponential tails, we begin to understand why the LSDA describes bond dissociation energies poorly.

On the other hand, the following *gradient-corrected* exchange-correlation functional correctly reproduces, by design,[6,21] the exact asymptotic limit of Eq. (9):

$$E_{\rm XC} = E_{\rm XC}^{\rm LSDA} - b \sum_{\sigma} \int \rho_{\sigma}^{4/3} \frac{x_{\sigma}^2}{(1 + 6bx_{\sigma} \sinh^{-1} x_{\sigma})} d^3{\rm r}, \tag{11}$$

where x_σ is a dimensionless nonuniformity parameter defined by

$$x_\sigma = \frac{|\nabla \rho_\sigma|}{\rho_\sigma^{4/3}} \tag{12}$$

and b is a constant of value 0.0042 a.u. as determined by a fit to exact Hartree–Fock exchange energies of the noble gas atoms He through Rn.[21] The reader may easily verify that, on substitution of an exponential tail density into the above expression, one obtains precisely Eq. (9) in the $r \to \infty$ limit.

Note that the correction of Eq. (11) is an "exchange only" correction in its dimensionality (or equivalently, its scaling properties[22]) and its trivial spin dependence (i.e., a sum of two distinct terms, one for each spin). It is the only reported exchange-correlation correction of the *gradient* type which reproduces the exact asymptotic limit of Eq. (9). Also, the fact that Eq. (11) contains only a single free parameter b highly recommends this particular functional over several other functionals, containing two or more parameters, suggested in the literature.[23]

Dynamical correlation corrections are considerably more complicated in their scaling properties and their spin dependence and are not considered in the present work. Fortunately, previous work on diatomic systems has indicated that their influence on thermochemical calculations is relatively small compared to the exchange correction[6] and may therefore be neglected in a first approximation. Let us also point out that in previous work we have often espoused[7,8,13] the use of the correlation self-interaction correction of Stoll, Pavlidou, and Preuss[24] (SPP). On the basis of unpublished work by us and our collaborators, it appears that the SPP correction, when combined with gradient corrections for exchange, yields much too long molecular bond *lengths* despite its excellent bond energies. We therefore emphasize that the present work employs the "full" LSDA for dynamical correlation with no corrections whatsoever.

For the benefit of interested readers, we list, in Tables I and II, density-functional exchange and correlation energies of the present model for all first- and second-row atoms from H through Ar. These data are obtained from spherically symmetrized atomic Hartree–Fock spin densities and have been compiled previously in Refs. 18 (correlation) and 21 (exchange). The quality of the gradient-corrected exchange energies of Table I is excellent, whereas the LSDA correlation energies in Table II tend to overestimate the exact results by a factor of roughly 2. The physical origin of this well-known discrepancy has been elucidated by Stoll and co-workers[24] and arises from the fact that the uniform-gas correlation hole compensates, in part, for long-range *oscillations* in the uniform-gas *exchange* hole. Separation of the total LSDA exchange-correlation energy into an "exchange" and a "correlation" piece thus introduces an artifact into each component which renders comparisons such as those of Table II somewhat ambiguous. We should not, therefore, be overly alarmed by the apparent discrepancies in Table II, but should view the functional of Eq. (11) as a *total* exchange-correlation model.

TABLE I. Atomic exchange energies (a.u.).

Atom	Exact[a]	LSDA[b]	GC[c]
H	− 0.313	− 0.268	− 0.310
He	− 1.026	− 0.884	− 1.025
Li	− 1.781	− 1.538	− 1.775
Be	− 2.667	− 2.312	− 2.658
B	− 3.744	− 3.272	− 3.728
C	− 5.045	− 4.459	− 5.032
N	− 6.596	− 5.893	− 6.589
O	− 8.174	− 7.342	− 8.169
F	− 10.00	− 9.052	− 10.02
Ne	− 12.11	− 11.03	− 12.14
Na	− 14.02	− 12.79	− 14.03
Mg	− 15.99	− 14.61	− 16.00
Al	− 18.07	− 16.53	− 18.06
Si	− 20.28	− 18.59	− 20.27
P	− 22.64	− 20.79	− 22.62
S	− 25.00	− 23.00	− 24.98
Cl	− 27.51	− 25.35	− 27.49
Ar	− 30.19	− 27.86	− 30.15

[a] Exact—exact Hartree-Fock (from Ref. 21).
[b] LSDA—local spin-density approximation.
[c] GC—with gradient correction of Eq. (11).

III. THE PRESENT CALCULATIONS

The present calculations actually serve a double purpose. As implied by its title and as described in Sec. I, this paper is concerned primarily with the systematic testing of density-functional thermochemistry on the 55 molecules of the Gaussian-1 data base.[14,15] The G1 data base has been carefully selected by its authors to include only molecules with experimental total atomization energies *known to within 1 kcal/mol.* It is therefore of obvious and great value for the testing of quantum thermochemical methods.

Also, however, these calculations constitute the first ex-

TABLE II. Atomic correlation energies (a.u.).

Atom	Exact[a]	LSDA[b]
H	0.000	− 0.022
He	− 0.042	− 0.113
Li	− 0.046	− 0.151
Be	− 0.094	− 0.225
B	− 0.125	− 0.291
C	− 0.157	− 0.360
N	− 0.189	− 0.430
O	− 0.258	− 0.539
F	− 0.322	− 0.644
Ne	− 0.390	− 0.746
Na	− 0.398	− 0.805
Mg	− 0.444	− 0.892
Al	− 0.479	− 0.966
Si	− 0.520	− 1.042
P	− 0.553	− 1.119
S	− 0.634	− 1.227
Cl	− 0.714	− 1.330
Ar	− 0.787	− 1.431

[a] Exact (from Ref. 18).
[b] LSDA—local spin-density approximation.

tensive test of our new and unique basis-set-free NUMOL program system.[10–13] Since its introduction in 1989,[13] the NUMOL program has undergone steady improvement and enhancement. Discussion of technical developments is deferred, however, to other publications. For the present purpose, it is sufficient to note that our computational method is fully numerical and completely basis-set free. All requisite procedures (numerical integration,[10] solution of Poisson's equation for the electronic Coulomb potential,[11] and solution of Schrödinger's single-particle equation for the molecular orbitals[12]) are carried out by *separation into independent single-center problems* using a "smooth" single-center partitioning scheme. The resulting atomiclike problems are handled easily using standard numerical methods in spherical polar coordinates and reassembled when necessary by cubic spline interpolation. The molecular orbitals are computed by an iterative perturbation-variation technique—first-order orbital corrections are obtained from numerical solution of an *inhomogeneous* Kohn–Sham equation and then mixed variationally with the starting orbitals. This numerical perturbation-variation cycle is then iterated as part of the normal self-consistent field (SCF) iteration procedure. Interested readers will find further details in Ref. 13.

Since our method is basis-set free, Hellmann–Feynman forces should be calculable by straightforward numerical electrostatic integration, provided, of course, that sufficient numerical precision is achieved overall. Indeed, tests of our numerically derived forces indicate that their quality is quite adequate for the purpose of geometry optimization[25] and NUMOL has recently been programmed to optimize molecular geometries using either internal or Cartesian coordinates at the LSDA theoretical level. Special features of our optimization schemes will be discussed elsewhere. Suffice it to say that all 55 molecular structures of the present survey were optimized successfully by our Cartesian algorithm and comparisons of their geometries with experiment will be provided in future publications.

Our procedure for thermochemical energy studies is extremely simple. First, molecular geometries are optimized at the LSDA level and the gradient correction of Eq. (11) then added in a "post-LSDA" manner at the optimized LSDA geometry. This is a matter of convenience, as the gradient part of the functional derivative of Eq. (6) is awkward to calculate by the finite-difference methods of NUMOL, especially in the sensitive asymptotic limit. Unpublished work by the author and a very recent report of Fan and Ziegler[26] have justified the post-LSDA approach. Second, zero-point vibrational energy corrections must be considered in order to make comparisons with experiment. These have been tabulated in the Gaussian-1 papers[14,15] and have been adopted without change in the present work. Finally, "nonspherical corrections" must be made for our reference atoms.[27] These can be quite substantial in gradient-corrected density-functional theories (e.g., of the order of 10 kcal/mol in the case of oxygen) and, therefore, our reference atomic energies have been calculated using nonspherical open-shell densities derived from nonspherical self-consistent fields by NUMOL computations on appropriately populated dimers at large internuclear separations.

Note also that many of the molecules of the G1 data base (and, of course, our reference atoms) have open-shell electronic structures. These have been treated using spin-unrestricted Kohn–Sham theory, outlined in Sec. II, which is analogous to the familiar unrestricted Hartree–Fock (UHF) procedure of *ab initio* theory.

IV. RESULTS AND CONCLUSIONS

Total atomization energies of the molecules of the G1 data base are listed in Tables III and IV for first- and second-row systems, respectively. We give results for both the local spin-density approximation itself and for the LSDA plus the gradient correction of Eq. (11) (denoted LSDA-GC in the tables). Absolute errors with respect to experiment are indicated in brackets.

A variety of meshes were employed in these computations to establish a reasonable numerical error estimate. The number of radial points on each nucleus has been varied from $5\times(Z^{2/3}+1)$ to $10\times(Z^{2/3}+1)$, where Z is the nuclear charge, and two classes of angular meshes consisting of 50/110 and 110/194 points for nuclei with $Z\leqslant 4/Z\geqslant 5$, respectively, have also been tested. As a result of our trials, we believe that the total atomization energies reported in Tables

TABLE III. Atomization energies D_0 (kcal/mol) of first-row molecules.

	Expt.[a]	LSDA[b]		LSDA-GC[c]	
LiH	56.0	58.9	(2.9)	61.7	(5.7)
BeH	46.9	57.7	(10.8)	57.9	(11.0)
CH	79.9	88.0	(8.1)	80.4	(0.5)
CH_2 (trip.)	179.6	202.7	(23.1)	184.6	(5.0)
CH_2 (sing.)	170.6	188.9	(18.3)	174.9	(4.3)
CH_3	289.2	322.0	(32.8)	295.9	(6.7)
CH_4	392.5	435.7	(43.2)	397.7	(5.2)
NH	79.0	91.0	(12.0)	86.7	(7.7)
NH_2	170.0	196.6	(26.6)	181.1	(11.1)
NH_3	276.7	316.8	(40.1)	285.1	(8.4)
OH	101.3	118.3	(17.0)	100.8	(− 0.5)
H_2O	219.3	253.8	(34.5)	222.4	(3.1)
HF	135.2	156.7	(21.5)	136.7	(1.5)
Li_2	24.0	23.1	(− 0.9)	21.1	(− 2.9)
LiF	137.6	154.2	(16.6)	138.8	(1.2)
C_2H_2	388.9	443.6	(54.7)	387.6	(− 1.3)
C_2H_4	531.9	601.8	(69.9)	532.4	(0.5)
C_2H_6	666.3	749.7	(83.4)	665.8	(− 0.5)
CN	176.6	217.1	(40.5)	182.7	(6.1)
HCN	301.8	350.8	(49.0)	306.7	(4.9)
CO	256.2	295.9	(39.7)	253.4	(− 2.8)
HCO	270.3	325.0	(54.7)	274.6	(4.3)
H_2CO	357.2	417.6	(60.4)	359.8	(2.6)
CH_3OH	480.8	555.7	(74.9)	480.9	(0.1)
N_2	225.1	264.1	(39.0)	230.6	(5.5)
N_2H_4	405.4	483.8	(78.4)	413.4	(8.0)
NO	150.1	196.2	(46.1)	154.3	(4.2)
O_2	118.0	172.4	(54.4)	124.8	(6.8)
H_2O_2	252.3	319.0	(66.7)	255.0	(2.7)
F_2	36.9	76.7	(39.8)	40.2	(3.3)
CO_2	381.9	465.9	(84.0)	381.4	(− 0.5)

[a] Expt.—from Refs. 14 and 15.
[b] LSDA—local spin-density approximation [Eq. (8)].
[c] LSDA-GC—post-LSDA gradient corrected [Eq. (11)].

III and IV have a numerical precision of better than 1 kcal/mol. All computations were carried out on an IBM RISC System/6000 model 320 workstation.

Notice, first of all, that the LSDA seriously overestimates the atomization energies of this study. The worst case is CO_2, overbound by 84 kcal/mol. Notice also that, in a relative sense, the F_2 molecule is overbound by over 100%. The average absolute error for all 55 molecules in Tables III and IV is 36.2 kcal/mol (or 1.6 eV, 151 kJ/mol). Clearly, the local spin-density approximation is inadequate for thermochemical purposes.

Addition of the gradient correction (LSDA-GC), on the other hand, improves our results dramatically. Now the largest errors are of the order of 11 kcal/mol for, interestingly enough, some of the "lightest" molecules in Table III (BeH and NH_2). This emphasizes an aspect of density-functional theory that is, at the same time, its great weakness and yet its great strength—namely, DFT does not discriminate between molecules containing light atoms and those containing heavy atoms. DFT computations can be carried out with uniform ease *anywhere in the Periodic Table* (witness, e.g., the applications collected in Ref. 4).

The average absolute error for the LSDA-GC results is 3.7 kcal/mol (or 0.16 eV, 16 kJ/mol). This is ten times smaller than the error of the LSDA and, in our opinion, very respectably small by most other standards. Our theory does not match the accuracy of the G1 and G2 procedures, with average absolute errors of 1.6 and 1.2 kcal/mol, respectively, but is not inordinately worse. In defense of the density-functional approach, however, we reiterate that DFT computations of similar quality are possible and, indeed, routine throughout the Periodic Table (see Ref. 9). Also, we point out that the procedure of the present work is considerably simpler than the G1 and the G2 procedures, which involve basis-set corrections, Møller–Plesset corrections, a quadratic configuration interaction (CI) correction, and a fitted "higher level" correction. The present NUMOL calculations need no basis-set corrections, are based on an extremely simple exchange-correlation functional, and involve no adjustments of any kind.

TABLE IV. Atomization energies D_0 (kcal/mol) of second-row molecules.

	Expt.[a]	LSDA[b]		LSDA-GC[c]	
SiH_2 (sing.)	144.4	159.1	(14.7)	150.0	(5.6)
SiH_2 (trip.)	123.4	139.7	(16.3)	128.4	(5.0)
SiH_3	214.0	233.8	(19.8)	218.8	(4.8)
SiH_4	302.8	328.0	(25.2)	308.3	(5.5)
PH_2	144.7	165.6	(20.9)	152.4	(7.7)
PH_3	227.4	255.1	(27.7)	232.1	(4.7)
H_2S	173.2	197.3	(24.1)	174.3	(1.1)
HCl	102.2	116.4	(14.2)	101.7	(− 0.5)
Na_2	16.6	19.9	(3.3)	16.3	(− 0.3)
Si_2	74.0	92.5	(18.5)	73.4	(− 0.6)
P_2	116.1	142.4	(26.3)	114.7	(− 1.4)
S_2	100.7	134.4	(33.7)	100.4	(− 0.3)
Cl_2	57.2	82.7	(25.5)	51.7	(− 5.5)
NaCl	97.5	102.8	(5.3)	91.0	(− 6.5)
SiO	190.5	222.4	(31.9)	189.1	(− 1.4)
CS	169.5	200.3	(30.8)	165.4	(− 4.1)
SO	123.5	166.2	(42.7)	126.6	(3.1)
ClO	63.3	104.1	(40.8)	64.9	(1.6)
ClF	60.3	94.2	(33.9)	59.8	(− 0.5)
Si_2H_6	500.1	549.4	(49.3)	501.3	(1.2)
CH_3Cl	371.0	424.9	(53.9)	367.4	(− 3.6)
CH_3SH	445.1	508.6	(63.5)	441.6	(− 3.5)
HOCl	156.3	203.3	(47.0)	155.6	(− 0.7)
SO_2	254.0	332.5	(78.5)	249.9	(− 4.1)

[a] Expt.—from Refs. 14 and 15.

[b] LSDA—local spin-density approximation [Eq. (8)].

[c] LSDA-GC—post-LSDA gradient corrected [Eq. (11)].

Gradient corrections for dynamical correlation have not been considered in the present work. As discussed in Sec. II, proper treatment of atomic and molecular *tail* behavior is of primary concern in describing bond dissociation, and the quality of the present and previous[6] results supports this view. Nevertheless, the fine tuning afforded by correlation corrections will be studied in future work. Several interesting and viable approaches to the density-functional theory of dynamical correlations are currently under discussion in the literature.[18,28–31] It is not yet clear, however, which of the existing functionals is preferable and we feel that further progress and consolidation is urgently required in this area.

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