PHYSICAL REVIEW A VOLUME 57, NUMBER 1 JANUARY 1998

Exchange-correlation density functional beyond the gradient approximation

Michael Filatov* and Walter Thiel
Organisch-Chemisches Institut, Universität Zürich, Winterthurerstrasse 190, CH-8057 Zürich, Switzerland

(Received 3 July 1997)

An exchange-correlation functional is introduced that goes beyond the conventional gradient approximation by including contributions from the Laplacian of the density. The exchange part of this functional reproduces atomic exchange energies from the optimized potential model for main group elements (H-Xe) more accurately than other established exchange functionals. By construction, the exchange functional reproduces the small-gradient expansion for the exchange energy up to the fourth order and possesses the Coulomb asymptote for the exchange potential v_x. In molecular applications, the exchange functional is combined with a modified version of a recently proposed nonlocal correlation functional based on a Coulomb hole model. Detailed results are reported for the molecules from the G2 database. In an overall assessment, the present results for the atomization energies and the molecular geometries for the G2 reference molecules seem comparable in quality to those from the B3LYP hybrid functional. Some illustrative results for transition-metal compounds are also given. [S1050-2947(98)07601-X]

PACS number(s): 31.15.Ew, 31.25.−v

I. INTRODUCTION

Density-functional theory is becoming a promising alternative to the conventional wave-function methods in computational quantum chemistry [1,2]. In the past few years there has been considerable progress within density-functional theory (DFT) primarily due to the introduction of gradient-corrected density functionals [3–24] that give an overall improvement to the exchange-correlation energies of the local-density approximation (LDA). The use of gradient-corrected functionals allows one to improve the atomization energies of the standard G2 set of molecules [25] almost by an order of magnitude compared to the LDA [26,27]. The next step has been the development of the adiabatic connection method or hybrid Hartree-Fock (HF)–DFT functionals [28–32], which include some fraction of the Hartree-Fock exchange energy. These hybrid functionals are quite accurate, but lose one of the most attractive features of pure density functionals: their locality. A possible direction for further improvement of pure density functionals is the inclusion of higher-order gradient corrections [19,33–37]. It has been demonstrated [33,35] that the Laplacian contributions are important ingredients of the gradient expansion of the exchange energy. Indeed, these terms represent the dominant corrections to the LDA in regions of nearly uniform density (e.g., near the midpoints of bonds in molecules). It has also been shown [34] that the use of Laplacian terms can help to remedy the incorrect description of the exchange-correlation contribution to the Kohn-Sham (KS) potential [38]. The exchange-correlation potential v_{xc} not only determines the shape of one-particle wave functions via the KS equations, but it is also important for the description of molecular potential-energy surfaces since the derivatives of the exchange-correlation energy E_{xc} with respect to external parameters λ (e.g., nuclear coordinates) may be obtained from a knowledge of v_{xc} [39,40]:

$$\frac{\partial E_{\mathrm{xc}}}{\partial \lambda}=\int \frac{\partial n(\mathbf{r})}{\partial \lambda}\frac{\delta E_{\mathrm{xc}}[n]}{\delta n(\mathbf{r})}\,d\mathbf{r}=\int \frac{\partial n(\mathbf{r})}{\partial \lambda}v_{\mathrm{xc}}(\mathbf{r})d\mathbf{r}. \quad (1)$$

The modern gradient-corrected functionals yield better results for the exchange-correlation energy density e_{xc} than for the potential v_{xc} [41,42]. Thus it may be anticipated that improving the latter can help to obtain better geometries from DFT calculations.

In the present paper we investigate an exchange-correlation functional that includes Laplacian contributions. The exchange part of the present functional is constructed to reproduce the small-gradient expansion up to the fourth order and to satisfy the Coulomb asymptote for both the exchange energy density e_x and the exchange potential v_x. This exchange functional is augmented by a modified version of the previously developed correlation functional [43] which has been extended to include the Laplacian of the density. The correlation functional is based on a model of the Coulomb hole distribution function and depends on both the density gradient and the Laplacian of the density. The composite exchange-correlation functional has been applied to calculate the thermochemical properties of the first-row and second-row molecules from the standard G2 data set [25]. The results are compared with those from the most accurate hybrid HF-DFT functional, i.e., B3LYP [31] (involving Becke exchange [9] and Lee-Yang-Parr correlation [10]), and from our own gradient-corrected FT97 functional [44].

II. EXCHANGE FUNCTIONAL

For an electron gas of weakly varying density, the exchange energy in the exchange-only approximation (EXOA) [35,45–47] may be expressed in terms of density derivatives via [35,48]

---

*Present address: Organic Chemistry Department, The Hebrew University of Jerusalem, Givat Ram Campus, 91904 Jerusalem, Israel.

TABLE I. Atomic exchange energies (in hartrees): Mean absolute deviations Δ_{abs}, mean signed deviations Δ, and root-mean-square errors σ (mhartree). Elements used in the parametrization are marked with asterisks.

Atom	OPM[a]	B88[b]	FT97[c]	This work
H*	−0.3125	−0.3098	−0.3120	−0.3120
He*	−1.0258	−1.0255	−1.0325	−1.0303
Li	−1.7808	−1.7752	−1.7864	−1.7851
Be*	−2.6658	−2.6578	−2.6719	−2.6707
N	−6.6044	−6.5886	−6.5871	−6.5980
Ne*	−12.1050	−12.1379	−12.1075	−12.1260
Na	−14.0131	−14.0305	−14.0021	−14.0178
Mg*	−15.9884	−16.0008	−15.9758	−15.9866
P	−22.6342	−22.6210	−22.6192	−22.6083
Ar*	−30.1748	−30.1533	−30.1711	−30.1426
K	−32.6669	−32.6490	−32.6743	−32.6434
Ca*	−35.1991	−35.1927	−35.2221	−35.1907
As	−81.4961	−81.5793	−81.5628	−81.5407
Kr*	−93.8331	−93.8706	−93.8479	−93.8404
Rb	−97.8704	−97.8944	−97.8747	−97.8660
Sr*	−101.9264	−101.9549	−101.9371	−101.9291
Sb	−163.8115	−163.8225	−163.8497	−163.8203
Xe*	−179.0638	−179.0412	−179.0573	−179.0611
Δ_{abs}		20.3	14.0	11.6
Δ		−7.2	7.3	0.2
σ		27.1	20.8	16.7

[a] Theoretical OPM data as reported in [52].

[b] Becke exchange functional [9].

[c] Own gradient-corrected exchange functional [44].

$$E_x[n_\alpha, n_\beta] = \sum_{\sigma=\alpha,\beta} \int e_x^{\mathrm{LDA}}(n_\sigma)[1 + C_{x2}\xi_\sigma + C_{x4}(\chi_\sigma^2 + C_{\chi\xi}^x \chi_\sigma \xi_\sigma + C_{\xi^2}^x \xi_\sigma^2) + \cdots]d\mathbf{r}, \tag{2}$$

where

$$e_x^{\mathrm{LDA}}(n_\sigma) = C_x n_\sigma^{4/3}, \quad C_x = -\frac{3}{4}\left(\frac{6}{\pi}\right)^{1/3} \tag{3}$$

is the exchange energy density of a uniform electron gas and

$$\xi_\sigma = \left(\frac{\nabla n_\sigma}{n_\sigma^{4/3}}\right)^2, \tag{4}$$

$$\chi_\sigma = \frac{\nabla^2 n_\sigma}{n_\sigma^{5/3}} \tag{5}$$

are the reduced density gradient and the reduced Laplacian of the density, respectively. For finite systems with exponentially decaying densities, higher-order gradient corrections to the LDA exchange energy diverge exponentially. To amend this drawback of the gradient expansion approximation the concept of the generalized gradient approximation (GGA) has been proposed [4,6,14,42]. Within the GGA the exchange energy for a nonuniform system is represented by

$$E_x^{\mathrm{GGA}}[n_\alpha, n_\beta] = \sum_{\sigma=\alpha,\beta} \int e_x^{\mathrm{LDA}}(n_\sigma) f_x^{\mathrm{GGA}}(\xi_\sigma) d\mathbf{r}. \tag{6}$$

The idea of the GGA may be interpreted [49,50] as an attempt to simulate the result of resummation of the whole gradient expansion (2). The enhancement factor f_x^{GGA} in Eq. (6) is usually constructed so that the final expression reproduces the expansion (2) up to the second term for small density gradients and obeys a number of reasonable criteria established for the exchange energy in the EXOA. For example, the widely used exchange functional due to Becke [9], which may be represented as

$$f_x^B(x_\sigma) = 1 - \frac{1}{C_x}\frac{\beta x_\sigma^2}{1 + 6\beta x_\sigma \sinh^{-1} x_\sigma}, \quad x_\sigma = \xi_\sigma^{1/2}, \tag{7}$$

reproduces the Coulomb asymptote (8) for the exchange energy density e_x in finite systems:

$$e_x(\mathbf{r})|_{r\to\infty} = -\frac{n_\sigma(\mathbf{r})}{2r}. \tag{8}$$

Expression (7) also formally reproduces the expansion (2) for small density gradients and guarantees that the exchange energy density is well behaved in the regions of large density gradients.

It is known that the exchange potential

$$v_{x,\sigma}(\mathbf{r}) = \frac{\delta e_{x,\sigma}[n_\sigma(\mathbf{r})]}{\delta n_\sigma(\mathbf{r})}, \quad \sigma = \alpha, \beta, \tag{9}$$

has to fulfill an asymptotic relation similar to Eq. (8) [41,42,46,49,51]. It has been noted [42,51] that the correct $r\to\infty$ limit for the exchange potential in spherically symmetric systems is given by

$$v_{x,\sigma}(\mathbf{r})|_{r\to\infty} = -\frac{1}{r} + \frac{C}{2}, \tag{10}$$

where C is a positive constant. This results from averaging over the discontinuity in the exact Kohn-Sham potential as the electron number passes through an integer [51]. For the exact exchange-correlation functional, C is given by the difference of the ionization potential and the electron affinity of a many-electron system [42,51]. None of the widely used GGAs for the exchange obey this constraint (10). It has been demonstrated [41,49] that, with simple algebraic representations of the enhancement factor f_x^{GGA} in Eq. (6), it is impossible to obey both constraints (8) and (10) simultaneously. Therefore, it would seem necessary to go beyond the gradient approximation to improve this deficiency. The GGA concept allows for such an extension [33], which may be represented as

$$E_x[n_\alpha, \eta_\beta] = \sum_{\sigma=\alpha,\beta} \int e_x^{\mathrm{LDA}}(n_\sigma) f_x(\xi_\sigma, \chi_\sigma) d\mathbf{r}. \tag{11}$$

The enhancement factor f_x in Eq. (11) may be constructed from the following criteria, similar to those underlying the

TABLE II. Atomic correlation energies (in hartrees): Mean absolute deviations Δ_{abs}, mean signed deviations Δ, and root-mean-square errors σ (mhartree). All energies are calculated with Clementi-Roetti densities [53].

Atom (term)	Calculated					Exp.[e]
	This work	P86[a]	LYP[b]	GGA91[c]	FT97[d]	
He(^1S)	−0.046 60	−0.043 89	−0.043 78	−0.045 90	−0.046 23	−0.042 02
Li(^2S)	−0.055 83	−0.052 68	−0.053 34	−0.057 53	−0.051 97	−0.045 33
Be(^1S)	−0.091 94	−0.093 51	−0.094 56	−0.094 28	−0.089 70	−0.094 36
B(^2P)	−0.124 23	−0.128 57	−0.128 15	−0.127 79	−0.119 47	−0.124 84
C(^3P)	−0.155 33	−0.163 47	−0.161 17	−0.162 94	−0.151 18	−0.156 36
N(^4S)	−0.189 08	−0.197 96	−0.192 69	−0.199 36	−0.186 30	−0.188 34
O(^3P)	−0.256 65	−0.265 92	−0.264 82	−0.262 54	−0.251 32	−0.257 98
F(^2P)	−0.311 55	−0.328 62	−0.326 06	−0.323 00	−0.312 20	−0.324 78
Ne(^1S)	−0.366 20	−0.389 12	−0.383 48	−0.382 43	−0.371 07	−0.391 20
Na(^2S)	−0.391 06	−0.414 05	−0.408 34	−0.406 50	−0.387 30	−0.396 48
Mg(^1S)	−0.441 36	−0.464 66	−0.459 45	−0.450 23	−0.432 04	−0.439 43
Al(^2P)	−0.476 57	−0.507 99	−0.496 43	−0.490 45	−0.463 77	−0.470 58
Si(^3P)	−0.512 66	−0.552 54	−0.532 10	−0.533 54	−0.499 42	−0.505 67
P(^4S)	−0.550 50	−0.597 09	−0.566 39	−0.577 75	−0.539 57	−0.540 93
S(^3P)	−0.614 72	−0.667 29	−0.633 86	−0.641 02	−0.611 83	−0.606 23
Cl(^2P)	−0.672 81	−0.736 48	−0.694 70	−0.707 27	−0.679 36	−0.668 28
Ar(^1S)	−0.727 88	−0.802 09	−0.750 78	−0.770 72	−0.744 39	−0.726 10
Δ_{abs}	6.1	25.5	13.3	16.2	7.8	
Δ	0.4	25.2	12.4	15.0	−2.5	
σ	8.6	36.1	16.9	21.6	9.3	

[a] Perdew correlation functional [7].

[b] Lee-Yang-Parr correlation functional [10].

[c] Perdew-Wang correlation functional [14].

[d] Own gradient-corrected correlation functional [43].

[e] Experimental estimates of correlation energies [55].

Becke functional [9]: The gradient expansion up to the fourth order should be reproduced (at least formally); the asymptotic constraints (8) and (10) should be satisfied; and the resulting functional should be well behaved in the regions of large density gradient and Laplacian. Because the Laplacian of the density diverges like r^{-1} near the atomic nucleus and hence fourth-order terms in Eq. (2) diverge too, the enhancement factor in Eq. (11) should eliminate this divergence. Moreover, the r^{-1} divergence near the nucleus should be distinguished from the exponential divergence at large distances from the nuclei caused by the exponential falloff of the density. With this in mind, we have studied the following approximate expression for the exchange energy density:

$$e_x[n_\sigma]=e_x^{\text{LDA}}[n_\sigma]\times\left\{\frac{1+af_1(\xi_\sigma)\xi_\sigma+bf_2(\xi_\sigma,\chi_\sigma)(\xi_\sigma-\chi_\sigma)^2}{1+36C_x^2b\xi_\sigma}\right\}^{1/2}, \tag{12}$$

where the constant C_x and the dimensionless variables ξ_σ and χ_σ are given in Eqs. (3), (4), and (5), respectively. The coefficients a and b in Eq. (12) are chosen such that the coefficients C_{x2} and C_{x4} in Eq. (2) are exactly reproduced when expanding Eq. (12) around $\xi_\sigma=\chi_\sigma=0$ with $f_1=f_2=1$:

$$a=2C_{x2}+72C_{x4}C_x^2=0.005\,280\,14\ldots, \tag{13}$$

$$b=2C_{x4}=0.000\,039\,045\,39\ldots \tag{14}$$

The numerical values for a and b follow from those for C_{x2} and C_{x4}, which are exactly known from linear response [33,35,48]. The other coefficients $(C^x_{\chi\xi},C^x_{\xi^2})$, which may be obtained from nonlinear response [33,35], are not reproduced by Eq. (12). It has been demonstrated [33], however, that for weakly inhomogeneous systems, the contributions from these nonlinear terms are small and mostly compensate each other.

Equation (12) possesses a functional derivative with respect to the density

$$v_x[n_\sigma]=\frac{\partial e_x[n_\sigma]}{\partial n_\sigma}-\nabla\cdot\frac{\partial e_x[n_\sigma]}{\partial(\nabla n_\sigma)}+\nabla^2\frac{\partial e_x[n_\sigma]}{\partial(\nabla^2 n_\sigma)}, \tag{15}$$

which for spherically symmetric systems with an exponentially decaying density

$$n_\sigma(\mathbf{r})|_{r\to\infty}\propto e^{-\lambda r} \tag{16}$$

TABLE III. Atomization energies D_0 (in kcal/mol). All calculations employ the TZ2P basis [56,57] for the first-row elements and the McLean-Chandler [58] VTZ basis augmented with two polarization functions from 6-31G $(2df,p)$ [59] for the second-row elements. This basis is not available for Li, Be, and Na [56]; hence the molecules LiH, BeH, Li_2, LiF, Na_2, and NaCl from the original $G2$ set [25] are not included.

Molecule	This work	B3LYP[a]	Expt.[b]	Molecule	This work	B3LYP	Expt.
H_2	106.9	104.0	103.3	$SiH_{2(^1A_1)}$	143.0	145.3	144.4
CH	81.4	80.8	79.9	$SiH_{2(^3B_2)}$	124.2	124.8	123.4
$CH_{2(^3B_2)}$	182.7	181.4	179.6	SiH_3	206.3	209.5	214.0
$CH_{2(^1A_1)}$	169.2	169.5	170.6	SiH_4	297.3	303.5	302.8
CH_3	291.7	291.9	289.2	PH_2	148.0	149.4	144.7
CH_4	393.9	393.3	392.5	PH_3	226.6	228.9	227.4
NH	81.5	82.5	79.0	SH_2	171.7	171.7	173.2
NH_2	170.9	174.5	170.0	ClH	101.8	100.6	102.2
NH_3	273.3	278.0	276.7	Si_2	77.4	67.8	74.0
OH	99.5	102.0	101.3	P_2	115.1	110.9	116.1
OH_2	212.6	216.1	219.3	S_2	104.7	98.0	100.7
FH	131.8	132.3	135.2	Cl_2	57.0	51.9	57.2
C_2H_2	385.5	384.2	388.9	SiO	180.6	183.1	190.5
C_2H_4	532.9	530.5	531.9	SC	168.0	161.4	169.5
C_2H_6	666.2	664.7	666.3	SO	124.0	119.7	123.5
CN	180.5	174.5	176.6	ClO	67.0	60.8	63.3
HCN	300.4	300.6	301.8	ClF	61.4	56.4	60.3
CO	250.5	250.2	256.2	Si_2H_6	490.1	497.8	500.1
HCO	272.5	270.2	270.3	CH_3Cl	372.4	368.5	371.0
H_2CO	356.2	354.8	357.2	CH_3SH	443.7	441.3	445.1
CH_3OH	476.6	477.9	480.8	HOCl	153.7	151.9	156.3
N_2	222.7	222.4	225.1	SO_2	241.4	234.0	254.0
N_2H_4	401.3	407.5	405.4				
NO	153.2	149.2	150.1				
O_2	128.0	119.1	118.0				
H_2O_2	248.2	248.3	252.3				
F_2	44.2	35.0	36.9				
CO_2	378.7	376.9	381.9				

[a] B3LYP exchange-correlation functional [31] as implemented in CADPAC6 [61].

[b] Experimental data from [25] and [59].

asymptotically behaves as

$$v_x(\mathbf{r})|_{r\to\infty} = \frac{\lambda}{6} - \frac{1}{r} + O(r^{-2}). \tag{17}$$

This reproduces the exact asymptotic behavior (10) of the exchange potential (up to an additive constant). The exchange energy density, obtained via Eq. (12), behaves asymptotically as

$$e_x(\mathbf{r})|_{r\to\infty} = -\frac{n_\sigma(\mathbf{r})}{3r}. \tag{18}$$

This dependence is Coulombic, but the asymptotic values for e_x are too small by a factor of $\frac{2}{3}$ [see Eq. (8)]. The exact asymptote for e_x could be restored by another choice of the prefactor in the denominator of Eq. (12), but this would introduce a corresponding discrepancy into the r dependence for v_x and make the resulting potential too deep. We prefer the actual choice (12) because we focus on improvements in the exchange potential in order to obtain better energy derivatives and molecular geometries [see Eq. (1)]. As for the total exchange energies, we optimize our functional (12) against theoretical reference data for atoms to ensure that the exchange energies will be reasonable.

Expression (12) contains two functions $f_1(\xi_\sigma)$ and $f_2(\xi_\sigma,\chi_\sigma)$, which are introduced to adjust the exchange functional to theoretical reference data and to remove undesirable divergences. The choice of these functions is restricted by the conditions

$$f_1(\xi_\sigma)|_{\xi_\sigma\to 0} = 1, \tag{19}$$

$$f_2(\xi_\sigma,\chi_\sigma)|_{\substack{\xi_\sigma\to 0\\ \chi_\sigma\to 0}} = 1, \tag{20}$$

$$f_2(\xi_\sigma,\chi_\sigma)|_{\substack{\xi_\sigma\to\infty\\ \chi_\sigma\to\infty}} = 1, \tag{21}$$

$$f_2(\xi_\sigma,\chi_\sigma)|_{\substack{\xi_\sigma\to \mathrm{const}\\ \chi_\sigma\to -\infty}} \propto r. \tag{22}$$

The first two conditions (19) and (20) guarantee that the small-gradient expansion (2) is reproduced. Equation (21) allows one to retain the Coulombic asymptote for e_x and v_x. Equation (22) ensures that e_x remains finite near the atomic

TABLE IV. Molecular geometries (in angstroms and degrees). All calculations employ the TZ2P basis [56,57] for the first-row elements and the McLean-Chandler [58] VTZ basis augmented with two polarization functions from 6-31G $(2df,p)$ [59] for the second-row elements. This basis is not available for Li, Be, and Na [56]; hence the molecules LiH, BeH, Li_2, LiF, Na_2, and NaCl from the original $G2$ set [25] are not included.

Molecule	This work	B3LYP[a]	Expt.[b]
H_2			
HH	0.736	0.740	0.741
CH			
CH	1.122	1.123	1.120
$CH_{2(^3B_2)}$			
CH	1.076	1.077	1.078
HCH	138.0	135.2	136.0
$CH_{2(^1A_1)}$			
CH	1.109	1.109	1.111
HCH	102.1	101.8	102.4
CH_3			
CH	1.076	1.078	1.079
CH_4			
CH	1.085	1.088	1.086
NH			
NH	1.043	1.040	1.045
NH_2			
NH	1.029	1.027	1.024
HNH	102.9	103.2	103.4
NH_3			
NH	1.013	1.013	1.012
HNH	105.6	107.0	106.0
OH			
OH	0.981	0.975	0.971
OH_2			
OH	0.965	0.961	0.959
HOH	104.2	105.0	103.9
FH			
FH	0.930	0.923	0.917
C_2H_2			
CC	1.206	1.196	1.203
CH	1.060	1.062	1.061
C_2H_4			
CC	1.329	1.325	1.339
CH	1.079	1.082	1.085
HCH	116.5	116.6	117.8
C_2H_6			
CC	1.517	1.529	1.526
CH	1.087	1.091	1.088
HCH	107.7	107.5	107.4
CN			
CN	1.178	1.162	1.172
HCN			
CN	1.158	1.146	1.143
CH	1.064	1.066	1.065
CO			
CO	1.138	1.125	1.128
HCO			
CO	1.186	1.173	1.175
CH	1.116	1.123	1.119
HCO	123.6	124.2	124.4
Molecule	This work	B3LYP	Expt.
H_2CO			
CO	1.211	1.200	1.208
CH	1.102	1.105	1.116
HCH	115.4	116.0	116.5
CH_3OH			
CO	1.431	1.424	1.421
CH_a	1.084	1.087	1.093
CH_b	1.091	1.094	1.093
OH	0.965	0.960	0.963
OCH_a	105.9	106.7	107.0
COH	107.4	108.7	108.0
H_aCH_b	108.4	108.4	108.5
N_2			
NN	1.103	1.091	1.098
N_2H_4			
NN	1.441	1.437	1.449[c]
NH_{av}	1.014	1.012	1.021[c]
NNH_{out}	106.0	107.4	106.0[c]
NNH_{in}	111.2	111.9	112.0[c]
$H_{out}NNH_{in}$	90.8	90.7	91.0[c]
NO			
NO	1.160	1.147	1.151
O_2			
OO	1.223	1.208	1.207
H_2O_2			
OO	1.472	1.455	1.475
OH	0.972	0.966	0.950
OOH	99.6	100.4	94.8
HOOH	112.3	112.6	120.0
F_2			
FF	1.428	1.404	1.417
CO_2			
CO	1.173	1.160	1.162
$SiH_{2(^1A_1)}$			
SiH	1.537	1.522	1.516
HSiH	90.9	91.6	92.5
$SiH_{2(^3B_2)}$			
SiH	1.498	1.485	
HSiH	118.5	118.5	
SiH_3			
SiH	1.479	1.466	
SiH_4			
SiH	1.490	1.479	1.480
PH_2			
PH	1.436	1.424	1.428[d]
HPH	90.6	91.8	91.5[d]
PH_3			
PH	1.432	1.419	1.4121[d]
HPH	92.0	93.5	93.3[d]
SH_2			
SH	1.345	1.343	1.336[3]

TABLE IV. (*Continued*).

Molecule	This work	B3LYP[a]	Expt.[b]	Molecule	This work	B3LYP	Expt.
PH	1.432	1.419	1.421[d]	ClF	1.676	1.628	1.628
HPH	9.20	93.5	93.3[d]	Si_2H_6			
SH_2				SiSi	2.344	2.360	2.327
SH	1.345	1.343	1.336[e]	SiH	1.493	1.482	1.486
HSH	91.3	92.5	9.21[e]	HSiH	108.5	108.6	107.8
ClH				CH_3Cl			
ClH	1.282	1.283	1.275	ClC	1.800	1.809	1.781
Si_2				CH	1.080	1.084	1.096
SiSi	2.272	2.169	2.246	HCH	110.6	110.9	110.0
P_2				CH_3SH			
PP	1.915	1.899	1.893	CH_a	1.083	1.087	1.091
S_2				CH_b	1.083	0.87	1.091
SS	1.931	1.925	1.889	CS	1.825	1.838	1.819
Cl_2				SH	1.344	1.343	1.336
ClCl	2.024	2.033	1.988	H_aCH_b	111.5	110.6	109.8
SiO				CSH	96.2	97.1	96.5
SiO	1.543	1.515	1.510	HOCl			
SC				OH	0.973	0.967	0.975
SC	1.547	1.536	1.535[f]	OCl	1.732	1.720	1.690
SO				HOCl	101.9	102.9	102.5
SO	1.518	1.499	1.481	SO_2			
ClO				SO	1.465	1.447	1.431
ClO	1.611	1.604	1.570	OSO	118.6	118.8	119.3
ClF							

[a] B3LYP exchange-correlation functional [31] as implemented in CADPAC6 [61].
[b] Experimental data from [59] and [62] unless noted otherwise.
[c] From [63].
[d] From [64].
[e] From [65].
[f] From [66].

nucleus. Plausible rational approximations to the functions f_1 and f_2 can be constructed by considering spherically symmetric densities as given in Eq. (16). There are various reasonable choices for f_1 [see Eq. (19)], while it is more difficult to satisfy all conditions for f_2 simultaneously [see Eqs. (20)–(22)]. We have tested several combinations of approximations in both atomic and molecular calculations and obtained the best overall performance with the empirical functions

$$f_1(\xi_\sigma)=(1+a_1\xi_\sigma)^{1/2}/(1+b_1\xi_\sigma)^{3/4}, \tag{23}$$

$$f_2(\xi_\sigma,\chi_\sigma)=[1+a_2q_1(\xi_\sigma,\chi_\sigma)][1+q_2(\xi_\sigma,\chi_\sigma)]/[1+(2^{1/3}-1)q_2(\xi_\sigma,\chi_\sigma)]^3, \tag{24a}$$

$$q_1(\xi_\sigma,\chi_\sigma)=(\xi_\sigma-\chi_\sigma)^2/(1+\xi_\sigma)^2, \tag{24b}$$

$$q_2(\xi_\sigma,\chi_\sigma)=[(b_2^2+1)^{1/2}-b_2]/\{q_3(\xi_\sigma,\chi_\sigma)+[q_3(\xi_\sigma,\chi_\sigma)^2+1]^{1/2}\}, \tag{24c}$$

$$q_3(\xi_\sigma,\chi_\sigma)=\xi_\sigma^2-\chi_\sigma^2-b_2. \tag{24d}$$

With this choice, the exchange energy density e_x always remains finite near the atomic nucleus, as guaranteed by Eqs. (22) and (24). The potential v_x diverges like

$$v_x(\mathbf{r})|_{r\to 0}=\frac{C_0}{r}, \tag{25}$$

where C_0 is a small constant. This divergence is due to the contribution from the term $2(\nabla^2 n_\sigma/n_\sigma^{2/3})\partial f_x(\xi_\sigma,\chi_\sigma)/\partial\xi_\sigma$ and is inherent to all gradient-corrected functionals. For instance, the constant C_0 in Eq. (25) for our functional equals $+0.066\,104\ldots$ for a $1s$-like atomic densityand is zero for other ns-type densities. For theBecke [9] functional, $C_0=-0.039\,568\ldots(1s)$, $+0.005\,120\ldots(2s)$, $+0.003\,621\ldots(3s)$, etc.

The final expressions for our exchange functional [Eqs. (12)–(14), (23), and (24)] depend on four adjustable parameters a_1, a_2, b_1, and b_2. The values of these parameters were optimized against atomic exchange energies of closed-shell atoms marked in Table I with asterisks. The theoretical reference data were taken from optimized potential model (OPM) calculations of Engel and Vosko [52]. The densities used in the optimization were derived from the Clementi-Roetti wave functions [53] assuming that these Hartree-Fock

TABLE V. Dipole moments (in debye). All calculations employ the TZ2P basis [56,57] for the first-row elements and the McLean-Chandler [58] VTZ basis augmented with two polarization functions from 6-31G $(2df,p)$ [59] for the second-row elements.

Molecule	This work	B3LYP[a]	Expt.[b]	Molecule	This work	B3LYP	Expt.[c]
CH	1.449	1.523	1.46	$SiH_{2(^1A_1)}$	0.209	0.236	
$CH_{2(^1A_1)}$	1.850	1.926		$SiH_{2(^3B_2)}$	0.033	0.095	
$CH_{2(^3B_2)}$	0.680	0.652		PH_2	0.637	0.608	
NH	1.541	1.581	1.389	PH_3	0.706	0.666	0.58
NH_2	1.853	1.908		SH_2	1.131	1.112	0.97
NH_3	1.683	1.666	1.47	ClH	1.209	1.204	1.08
OH	1.678	1.718	1.66	SiO	2.898	3.139	3.10[d]
OH_2	1.948	1.975	1.85	SC	1.937	1.957	1.98
FH	1.826	1.885	1.82	SO	1.464	1.597	1.55[d]
CN	0.954	1.379	1.15	ClO	1.358	1.309	1.30[e]
HCN	2.937	3.028	2.98	ClF	0.960	1.005	0.88
CO	0.171	0.090	0.112	CH_3Cl	2.069	2.128	1.87
HCO	1.597	1.681		CH_3SH	1.655	1.670	1.52
H_2CO	2.351	2.421	2.33	HOCl	1.578	1.621	1.52[e]
CH_3OH	1.679	1.728	1.70	SO_2	1.657	1.753	1.63
N_2H_4	2.032	2.016	1.75				
NO	0.143	0.120	0.153				
H_2O_2	1.788	1.830	1.57[f]				

[a] B3LYP exchange-correlation functional [31] as implemented in CADPAC6 [61].

[b] Experimental data from [62] unless noted otherwise.

[c] Experimental data from [59] unless noted otherwise.

[d] Reference [73].

[e] Reference [74].

[f] Reference [75].

densities are sufficiently close [47] to the OPM densities that are not available to us. The optimized values of the adjustable parameters are $a_1=2.816\,049$, $a_2=0.879\,058$, $b_1=0.398\,773$, and $b_2=66.364\,138$.

In Table I the results of atomic calculations with the proposed functional are compared with those from the Becke exchange functional [9] and from our own gradient-corrected FT97 functional [44] using Clementi-Roetti densities [53]. In a statistical sense, the OPM exchange energies are best reproduced by the present functional because the mean absolute deviation (11.6 mhartree) and root-mean-square error (16.7 mhartree) are slightly lower than for the other functionals. In this comparison, the present functional benefits from the parametrization since the larger number of adjustable parameters allows for a more flexible fitting.

III. CORRELATION FUNCTIONAL

As the correlation counterpart of the exchange functional described in the preceding section we use a modified version of the nonlocal correlation functional developed previously [43]. This functional is based on a model of the Coulomb hole distribution function in the uniform electron gas and is constructed to satisfy known uniform and nonuniform scaling constraints derived for inhomogeneous systems [54]. The basic parameter of the model Coulomb hole is the effective hole radius r_C, which is assumed to depend on a density parameter r_s^σ (Wigner radius) and an inhomogeneity parameter y_σ:

$$r_c=f(r_s^\sigma,y_\sigma), \tag{26}$$

$$r_s^\sigma=(3/4\pi n_\sigma)^{1/3}. \tag{27}$$

Previously [43] the inhomogeneity parameter y_σ was given in terms of the density gradient (∇r_s^σ). In the present work, we also include Laplacian terms into y_σ, in analogy with the treatment of exchange [see Eq. (12)]:

$$\begin{aligned} y_\sigma&=(\nabla r_s^\sigma)^2+c_1[(\nabla r_s^\sigma)^2-\nabla^2 r_s^\sigma]^2\\ &=\frac{1}{9}\left(\frac{3}{4\pi}\right)^{2/3}\xi_\sigma+c_1\frac{1}{9}\left(\frac{3}{4\pi}\right)^{4/3}(\xi_\sigma-\chi_\sigma)^2, \end{aligned} \tag{28}$$

where c_1 is an unknown coefficient that is treated as an adjustable parameter.

The present correlation functional is defined exactly in the same manner as before [43], except that there is a different empirical ansatz for the dependence of the effective correlation length on the inhomogeneity parameter y_σ. Using our previous notation [43] this dependence is now given by

$$F_{\sigma\sigma'}(r_s^{\sigma'},y_{\sigma'})=\frac{1+(c_2y_{\sigma'})^2}{(1+c_3y_{\sigma'}/r_s^{\sigma'})^{1/2}}\exp[-(c_2y_{\sigma'})^2], \tag{29}$$

$$F_{\sigma\sigma}(r_s^{\sigma},y_{\sigma})=\frac{1+(c_4 y_{\sigma})^2}{[1+(4.979\,634-c_3)y_{\sigma}/r_s^{\vec{\sigma}}]^{1/2}}\times\exp[-(c_4 y_{\sigma})^2]. \tag{30}$$

In Eqs. (28)–(30) c_1-c_4 are adjustable parameters obtained by calibration against empirical atomic correlation energies [55]. Details of the parametrization procedure may be found in our previous paper [43]. The optimized values of the parameters are $c_1=0.099\,635$, $c_2=0.083\,726$, $c_3=0.064\,988$, and $c_4=2.807\,834$. Table II compares the atomic correlation energies calculated from the current version of the correlation functional and from other functionals with the reference values [55].

IV. RESULTS AND DISCUSSION

The present exchange-correlation functional that depends on the density and its first and second derivatives has been incorporated into the CADPAC5 code [56]. The implementation of such functionals in the Kohn-Sham self-consistent-field approach has been described in detail [40]. In analogy to our previous work with the gradient-corrected FT97 functional [44], we have evaluated the performance of the present functional for the atoms and molecules of the standard $G2$ data set [25]. The self-consistent Kohn-Sham calculations were performed with the a triple-zeta doubly polarized (TZ2P) basis set [56,57] for the first-row elements, and the McLean-Chandler valence triple-zeta (VTZ) basis [58] augmented with two polarization functions taken from the 6-31$G(2df,p)$ basis [59] for the second-row elements. Molecular geometries were optimized numerically (since an analytic gradient has not yet been implemented). Zero-point vibrational corrections were taken from the $G1$ data base [60]. Tables III, IV, and V list respectively the atomization energies, molecular geometries, and dipole moments obtained from the present exchange-correlation functional and from the B3LYP functional as implemented in CADPAC6 [61]. Table VI contains a statistical evaluation of the calculated thermochemical and structural data with regard to experiment [25,59,60,62–66], for the present functional as well as for B3LYP and FT97.

According to the statistical results in Table VI, all three functionals yield thermochemical properties with similar accuracy. The mean absolute deviation between calculated and experimental atomization energies is around 3 kcal/mol. Concerning bond lengths, the present functional approaches the accuracy of B3LYP and improves on FT97, which generally overestimates the bond lengths. With regard to bond lengths and dipole moments, the three functionals again give results of comparable quality.

Density-functional calculations are particularly useful for transition-metal compounds. In analogy to our previous work [44], we have checked the performance of the present functional in this area. Table VII collects selected results for the carbonyls $Cr(CO)_6$, $Fe(CO)_5$, and $Ni(CO)_4$; the chromyl halides CrO_2F_2 and CrO_2Cl_2, and ferrocene $Fe(C_5H_5)_2$. Without attempting to review the extensive literature on computational studies of these molecules (see, e.g., [67–69]), we only note that conventional *ab initio* methods encounter considerable problems, whereas density-functional methods are quite successful. Inspection of Table VII shows that the three functionals considered again yield results that are generally of similar accuracy. Compared to FT97, the present functional better reproduces the experimental bond lengths (often within the experimental error bars). This is especially gratifying for ferrocene, which is known to be a ''difficult'' molecule [69].

TABLE VI. Statistical evaluations: Mean absolute deviations $\Delta_{\rm abs}$, mean signed deviations Δ, and root-mean-square errors σ. All calculations employ the same basis. All calculations employ the TZ2P basis [56,57] for the first-row elements and the McLean-Chandler [58] VTZ basis augmented with two polarization functions from 6-31G $(2df,p)$ [59] for the second-row elements.

	This work	B3LYP[a]	FT97[b]
Atomization energy (kcal/mol)			
$\Delta_{\rm abs}$	3.3	3.2	3.1
Δ	-0.8	-2.0	-0.3
σ	4.3	4.4	4.1
Bond lengths (Å)			
$\Delta_{\rm abs}$	0.012	0.010	0.017
Δ	0.009	0.002	0.017
σ	0.017	0.017	0.022
Angles (deg)			
$\Delta_{\rm abs}$	1.2	1.0	1.2
Δ	-0.4	0.1	-0.5
σ	2.0	1.9	2.0
Dipole moments (D)			
$\Delta_{\rm abs}$	0.102	0.112	0.101
Δ	0.055	0.105	0.021
σ	0.129	0.137	0.125

[a] B3LYP exchange-correlation functional [31] as implemented in CADPAC6 [61].

[b] Own gradient-corrected exchange-correlation functional [44].

Numerical problems have been reported [34,37] for Kohn-Sham calculations with functionals that depend on second derivatives of the density. We have found that computations with the present functional indeed tend to be numerically more sensitive than those with gradient-corrected functionals (e.g., FT97) and that they generally require more self-consistent field iterations until convergence. However, when using the ''high-accuracy'' grid of CADPAC5 [56] with large basis sets (see above), the results are sufficiently stable against further grid extension. At this level, single-point energy calculations with the present functional require about twice as much CPU time as with gradient-corrected functionals.

In an overall assessment of the results (Tables III–VII), it should be kept in mind that both FT97 and the present functional are ''pure'' density functionals without any admixture of Hartree-Fock exchange (used in hybrid functionals such as B3LYP). It would therefore seem remarkable that FT97 and the present functional yield results of essentially B3LYP quality while being more accurate than other pure density functionals, especially for atomization energies (see Ref. [27] for the relevant data).

On the other hand, the present functional has originally been designed to improve upon gradient-corrected functionals by including second-order Laplacian terms. In this con-

TABLE VII. Results for transition-metal compounds. Bond lengths AB (in angstroms), bond angles $\angle A—B—C$ (in degrees), and bond dissociation energies ΔE (in kcal/mol). All calculations employ a $(14s11p6d)/[8s6p4d]$ all-electron basis from Wachters [70] for the metal (augmented with two additional p functions [70] and a diffuse d function [71]) and the 6-31G* basis [59] for the ligands. Experimental data are taken from [67–69,72].

Molecule	Point group	Property	This work	B3LYP[a]	FT97[b]	Expt.
$Cr(CO)_6$	O_h	CrC	1.926	1.930	1.940	1.914±0.002
		CO	1.163	1.150	1.167	1.140±0.002
		ΔE[c]	40.2	39.5	40.1	36.8±2.0
$Fe(CO)_5$	D_{3h}	FeC_{ax}	1.813	1.834	1.832	1.810±0.003
		FeC_{eq}	1.842	1.825	1.830	1.831±0.003
		$(CO)_{ax}$	1.162	1.148	1.166	1.153±0.003
		$(CO)_{eq}$	1.164	1.151	1.169	1.153±0.003
		ΔE[d]	42.3	41.0	41.5	41±2
$Ni(CO)_4$	T_d	NiC	1.841	1.848	1.842	1.838±0.002
		CO	1.160	1.146	1.163	1.141±0.002
		ΔE[e]	26.5	23.4	27.4	25±2
CrO_2F_2	C_{2v}	CrO	1.579	1.558	1.589	1.575±0.002
		CrF	1.738	1.717	1.736	1.720±0.002
		∠O—Cr—O	108.5	108.3	108.5	107.8±0.8
		∠F—Cr—F	110.3	110.2	110.7	111.9±0.9
CrO_2Cl_2	C_{2v}	CrO	1.580	1.559	1.590	1.581±0.002
		CrCl	2.138	2.135	2.136	2.126±0.002
		∠O—Cr—O	109.1	109.1	109.2	108.5±0.4
		∠Cl—Cr—Cl	111.3	111.1	110.8	113.3±0.3
$Fe(C_5H_5)_2$	D_{5h}	Fe-cp[f]	1.665	1.690	1.645	1.660±0.008
		FeC	2.061	2.082	2.054	2.058±0.005
		CC	1.428	1.429	1.446	1.431±0.005
		CH	1.082	1.083	1.093	1.122±0.020
		α[g]	0.8	0.7	1.2	4.6±2.7

[a] B3LYP exchange-correlation functional [31] as implemented in CADPAC6 [61].

[b] Own gradient-corrected exchange-correlation functional [44].

[c] Calculated with respect to singlet $Cr(CO)_5$ optimized in C_{4v} symmetry.

[d] Calculated with respect to singlet $Fe(CO)_4$ optimized in D_{2d} symmetry.

[e] Calculated with respect to singlet $Ni(CO)_3$ optimized in C_{3v} symmetry.

[f] Metal-ring distance.

[g] Angle between the C—H bond and the ring plane.

text, it should be compared with our FT97 functional [44], which has been developed using similar strategies and optimization techniques. The present functional has some slight advantages over FT97 for bond lengths, as anticipated from its focus on the exchange potential (see Secs. I and II), but there is no real progress for other properties. When considering the additional complexity and the higher computational effort, we believe that the present functional is less suitable than FT97 for actual large-scale applications.

V. CONCLUSIONS

We have investigated an exchange-correlation functional that goes beyond the conventional gradient approximation by including contributions from the Laplacian of the density. This basic idea is not new, of course, and has been explored by several groups (see, e.g., Refs. [33, 47–49] for detailed theoretical analyses). Like others [34,37], we find that the inclusion of higher-order terms into density functionals is not an easy or safe way to improve them. Our functional with second-order terms is successful in the sense that it provides results of essentially B3LYP quality (without any admixture of Hartree-Fock exchange), and it is, to our knowledge, the first functional with Laplacian terms that reaches such an accuracy. However, it does not significantly improve on our simpler gradient-corrected FT97 exchange-correlation functional [44] so that we consider FT97 to be preferable in practical applications.

ACKNOWLEDGMENTS

This work was supported by the Schweizerischer Nationalfonds.

[1] R. G. Parr and W. Yang, *Density-Functional Oxford Theory of Atoms and Molecules* (Oxford University Press, Oxford, 1989).
[2] R. M. Dreizler and E. K. U. Gross, *Density Functional Theory: An Approach to the Quantum Many-Body Problem* (Springer-Verlag, Berlin, 1990).
[3] A. D. Becke, Int. J. Quantum Chem. **23**, 1915 (1983).
[4] A. D. Becke, J. Chem. Phys. **84**, 4524 (1986).
[5] A. D. Becke, J. Chem. Phys. **85**, 7184 (1986).
[6] J. P. Perdew and Y. Wang, Phys. Rev. B **33**, 8800 (1986).
[7] J. P. Perdew, Phys. Rev. B **33**, 8822 (1986).
[8] A. E. De Pristo and J. D. Kress, J. Chem. Phys. **86**, 1425 (1987).
[9] A. D. Becke, Phys. Rev. A **38**, 3098 (1988).
[10] C. Lee, W. Yang, and R. G. Parr, Phys. Rev. B **37**, 785 (1988).
[11] A. D. Becke and M. R. Roussel, Phys. Rev. A **39**, 3761 (1989).
[12] L. C. Wilson and M. Levy, Phys. Rev. B **41**, 12 930 (1990).
[13] J. P. Perdew, in *Electronic Structure of Solids*, edited by P. Ziesche and H. Eschrig (Akademie-Verlag, Berlin, 1991), p. 11.
[14] J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, Phys. Rev. B **46**, 6671 (1992).
[15] P. M. W. Gill and J. A. Pople, Phys. Rev. A **47**, 2383 (1993).
[16] D. J. Lacks and R. G. Gordon, Phys. Rev. A **47**, 4681 (1993).
[17] G. J. Laming, V. Termath, and N. C. Handy, J. Chem. Phys. **99**, 8765 (1993).
[18] R. van Leeuwen and E. J. Baerends, Phys. Rev. A **49**, 2421 (1994).
[19] E. I. Proynov, A. Vela, and D. R. Salahub, Chem. Phys. Lett. **230**, 419 (1994).
[20] P. A. Stewart and P. M. W. Gill, J. Chem. Soc. Faraday Trans. **91**, 4337 (1995).
[21] G. J. Laming, N. C. Handy, and W. H. Miller, J. Phys. Chem. **99**, 1880 (1995).
[22] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
[23] R. M. Koehl, G. K. Odom, and G. E. Scuseria, Mol. Phys. **87**, 835 (1996).
[24] P. M. W. Gill, Mol. Phys. **89**, 433 (1996).
[25] L. A. Curtiss, K. Raghavachari, G. W. Trucks, and J. A. Pople, J. Chem. Phys. **94**, 7221 (1991).
[26] C. W. Bauschlicher Jr., Chem. Phys. Lett. **246**, 40 (1995).
[27] L. A. Curtiss, K. Raghavachari, P. C. Redfern, and J. A. Pople, J. Chem. Phys. **106**, 1063 (1997).
[28] A. D. Becke, J. Chem. Phys. **98**, 1372 (1993).
[29] A. D. Becke, J. Chem. Phys. **98**, 5648 (1993).
[30] A. D. Becke, J. Chem. Phys. **104**, 1040 (1996).
[31] P. J. Stevens, F. J. Devlin, C. F. Chablowski, and M. J. Frisch, J. Phys. Chem. **98**, 11 623 (1994).
[32] M. J. Frisch, G. W. Trucks, M. Head-Gordon, P. M. W. Gill, M. W. Wong, J. B. Foresman, B. G. Johnson, H. B. Schlegel, M. A. Robb, E. S. Replogle, R. Gomperts, J. L. Andres, K. Raghavachari, J. S. Binkley, C. Gonzalez, R. L. Martin, D. J. Fox, D. J. De Frees, J. Baker, J. J. P. Stewart, and J. A. Pople, GAUSSIAN92/DFT, Gaussian, Inc., Pittsburgh, PA, 1993.
[33] E. Engel and S. H. Vosko, Phys. Rev. B **50**, 10 498 (1994).
[34] P. Jemmer and P. J. Knowles, Phys. Rev. A **51**, 3571 (1995).
[35] P. S. Svendsen and U. von Barth, Int. J. Quantum Chem. **56**, 351 (1995).
[36] O. Gritsenko, R. van Leeuwen, and E. J. Baerends, Int. J. Quantum Chem. **57**, 17 (1996).
[37] R. Neumann and N. C. Handy, Chem. Phys. Lett. **266**, 16 (1997).
[38] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).
[39] M. E. Mura, P. J. Knowles, and C. A. Reynolds, Chem. Phys. Lett. **262**, 533 (1996).
[40] R. Neumann, R. H. Nobes, and N. C. Handy, Mol. Phys. **87**, 1 (1996).
[41] R. van Leeuwen and E. J. Baerends, Phys. Rev. A **49**, 2421 (1994).
[42] J. P. Perdew and K. Burke, Int. J. Quantum Chem. **57**, 309 (1996).
[43] M. Filatov and W. Thiel, Int. J. Quantum Chem. **62**, 603 (1997).
[44] M. Filatov and W. Thiel, Mol. Phys. **91**, 847 (1997).
[45] R. T. Sharp and G. K. Horton, Phys. Rev. **90**, 317 (1953).
[46] J. D. Talman and W. F. Shadwick, Phys. Rev. A **14**, 36 (1976).
[47] D. C. Langreth and M. J. Mehl, Phys. Rev. B **28**, 1809 (1983).
[48] E. Engel and S. H. Vosko, Phys. Rev. B **42**, 4940 (1990); **44**, 1446 (1991).
[49] E. Engel, J. A. Chevary, L. D. Macdonald, and S. H. Vosko, Z. Phys. D **23**, 7 (1992).
[50] E. Engel and S. H. Vosko, Phys. Rev. B **47**, 13 164 (1993).
[51] J. P. Perdew, R. G. Parr, M. Levy, and J. L. Balduz Jr., Phys. Rev. Lett. **49**, 1691 (1982).
[52] E. Engel and S. H. Vosko, Phys. Rev. A **47**, 2800 (1993).
[53] E. Clementi and C. Roetti, At. Data Nucl. Data Tables **14**, 177 (1974).
[54] A. Goerling and M. Levy, Phys. Rev. A **45**, 1509 (1992).
[55] S. J. Chakravorty and E. R. Davidson, J. Phys. Chem. **100**, 6167 (1996).
[56] R. D. Amos, I. L. Alberts, J. S. Andrews, S. M. Colwell, N. C. Handy, D. Jayatilaka, P. J. Knowles, R. Kobayashi, N. Koga, K. E. Laidig, P. E. Maslen, C. W. Murray, J. E. Rice, J. Sanz, E. D. Simandiras, A. J. Stone, and M.-D. Su, CADPAC5, The Cambridge Analytic Derivatives Package, Cambridge, UK, 1992.
[57] T. H. Dunning, J. Chem. Phys. **55**, 716 (1971).
[58] A. D. McLean and G. S. Chandler, J. Chem. Phys. **72**, 5639 (1980).
[59] W. J. Hehre, L. Radom, P. von R. Schleyer, and J. A. Pople, *Ab Initio Molecular Orbital Theory* (Wiley-Interscience, New York, 1986).
[60] J. A. Pople, M. Head-Gordon, D. J. Fox, K. Raghavachari, and L. A. Curtiss, J. Chem. Phys. **90**, 5622 (1989); L. A. Curtiss, C. Jones, G. W. Trucks, K. Raghavachari, and J. A. Pople, *ibid.* **93**, 2537 (1990).
[61] R. D. Amos, I. L. Alberts, J. S. Andrews, S. M. Colwell, N. C. Handy, D. Jayatilaka, P. J. Knowles, R. Kobayashi, G. J. Laming, A. M. Lee, P. E. Maslen, C. W. Murray, P. Palmieri, J. E. Rice, E. D. Simandiras, A. J. Stone, M.-D. Su, and D. J. Tozer, CADPAC6.0, The Cambridge Analytic Derivatives Package, Cambridge, UK, 1995.
[62] B. G. Johnson, P. M. W. Gill, and J. A. Pople, J. Chem. Phys. **98**, 5612 (1993).
[63] K. Kohata, T. Fukuyama, and K. Kuchitsu, J. Phys. Chem. **86**, 602 (1982).
[64] G. Herzberg, *Molecular Spectra and Molecular Structure* (Van Nostrand Reinhold, New York, 1966), Vol. 3.
[65] T. H. Edwards, N. K. Moncur, and L. E. Snyder, J. Chem. Phys. **46**, 2139 (1967).

[66] R. Kewley, K. V. L. N. Sastry, M. Winnewisser, and W. Gordy, J. Chem. Phys. **39**, 2856 (1963).

[67] V. Jonas and W. Thiel, J. Chem. Phys. **102**, 8474 (1995), and references cited therein.

[68] M. Torrent, P. Gili, M. Duran, and M. Sola, J. Chem. Phys. **104**, 9499 (1996), and references cited therein.

[69] W. Klopper and H. P. Lüthi, Chem. Phys. Lett. **262**, 546 (1996), and references cited therein.

[70] A. J. H. Wachters, J. Chem. Phys. **52**, 1033 (1970).

[71] P. J. Hay, J. Chem. Phys. **66**, 4377 (1977).

[72] R. K. Bohn and A. Haarland, J. Organomet. Chem. **5**, 470 (1966).

[73] *Molecular Constants*, edited by K.-H. Hellwege, Landolt-Börnstein, New Series, Group II, Vol. 6 (Springer-Verlag, Berlin, 1974).

[74] *Molecular Constants*, edited by O. Madelung, Landolt-Börnstein, New Series, Group II, Vol. 19, pt. c (Springer-Verlag, Berlin, 1992).

[75] *Molecular Constants*, edited by K.-H. Hellwege, Landolt-Börnstein, New Series, Group II, Vol. 14, pt. a (Springer-Verlag, Berlin, 1982).