Density-functional thermochemistry. IV. A new dynamical correlation functional and implications for exact-exchange mixing

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A new dynamical correlation functional is constructed subject to a small number of simple, yet key, requirements not all satisfied by existing functionals in the literature. The new functional gives good atomic correlation energies, and, in conjunction with previous gradient-corrected exchange functionals and exact-exchange mixing, excellent thermochemistry in the G2 benchmarks of Pople and co-workers. © *1996 American Institute of Physics.* [S0021-9606(96)01902-6]

I. INTRODUCTION

This is the fourth part of a systematic study of Kohn–Sham density-functional theory (DFT) on the Gaussian 2 (G2) thermochemical data set of Pople and co-workers.[1] The G2 data set is a compilation of highly accurate experimental data on atomization energies, ionization potentials, and electron and proton affinities of more than a 100 first and second-row atomic and molecular species. It serves as an excellent standard for the calibration of quantum theoretical methods, and for comparison of various methods with each other.

In the first three parts of this series, the effect of gradient corrections for exchange (Part I)[2] and dynamical correlation (Part II)[3] were investigated, and the role of exact exchange (Part III)[4] also. The optimum three-parameter synthesis of Part III gave average absolute deviations from experiment of only 2.4 kcal/mol, 0.14 eV, and 1.2 kcal/mol, respectively, for the atomization energies, ionization potentials, and proton affinities of the G2 data set. Variants known as ACM,[5] Becke3P86,[6] and Becke3LYP[6] have been incorporated into well-established Hartree–Fock programs and are now under test in a wide variety of chemical applications. Early results are very encouraging,[5,7] especially with regard to difficulties in the computation of reaction barrier heights.[5]

In the present work, the dynamical correlation part of the Kohn–Sham exchange-correlation energy is scrutinized (Sec. II), and a new functional constructed (Sec. III). This new correlation functional, combined with the gradient-corrected exchange functional of Ref. 8, is tested on the G2 thermochemical data set in Sec. IV. Its performance is rather disappointing. In Sec. V, however, the role of exact exchange in Kohn–Sham DFT is reviewed, and the new functional is correspondingly reassessed. Employing only *one* fit parameter, results superior to those of our *three*-parameter G2 fit of Part III are obtained. In the final analysis (Sec. VI) we achieve two things: a description of dynamical correlation with certain advantages over those currently available and, at the same time, a much more satisfying implementation of exact-exchange mixing than that of Part III.

II. CORRELATION FUNCTIONALS: AN ANALYSIS

The most popular dynamical correlation functionals today are those of Colle and Salvetti[9] (CS), the CS modifica-

tion by Lee, Yang, and Parr[10] (LYP), Perdew's 1986 correlation functional[11] (Pc86), Becke's 1988 correlation functional[12] (Bc88), and the Perdew–Wang correlation functional[13] of 1991 (PWc91). Though not a "popular" functional, Bc88 is included for consideration here because it largely inspires the present work. Unfortunately, every one of these functionals is deficient in at least one major respect! We elaborate on this statement in the following paragraphs.

Each of the functionals cited above is based on its own model, with its own strengths and limitations and its own degree of complexity. This variety of models is confusing and even, perhaps, unsettling. Our aim in the present work is to derive a workable correlation functional systematically, and yet as easily as possible, by imposing a minimal set of simple requirements. The approach is pragmatic and admittedly semiempirical, but straightforward and direct. Similar reasoning has generated useful exchange functionals in the past.[8,14]

Choosing "minimal" requirements is, of course, subject to debate. Which do we chose, and when do we stop? With pragmatism and simplicity as our guides, the following minimal set has been adopted for the present work:

(1) attainment of the exact uniform electron gas limit,
(2) distinct treatment of opposite-spin and parallel-spin correlations,
(3) perfectly self-interaction free (i.e., exactly zero correlation energy in any one-electron system),
(4) good fit to exact correlation energies of atomic systems.

This list could naturally be extended by including scaling conditions[15] or other conceivable constraints. These simple, physically motivated, and virtually *self-evident* requirements will, however, suffice to generate an accurate and useful correlation functional in the course of this work.

Many quantum chemists may argue, understandably, that requirement (1) is of little relevance in atomic and molecular systems. The uniform electron gas is undeniably, however, a legitimate and well-studied many-body problem. No functional failing to attain this well-understood limit is entirely satisfactory. Certainly, no such functional can be deemed a *universal* density functional. We have wavered on this issue ourselves in previous communications[12,16] (and may do so again in the future!), but are now of the opinion that the

TABLE I. Strengths and weaknesses of correlation functionals. CS: Colle–Salvetti (Ref. 9). LYP: Lee–Yang–Parr (Ref. 10). Bc88: Becke (Ref. 12). Pc86: Perdew (Ref. 11). PWc91: Perdew–Wang (Ref. 13). Bc95: Present work (Sect. III).

Minimal requirement (see the text)	CS	LYP	Bc88	Pc86	PWc91	Bc95
(1)	No	No	No	Yes	Yes	Yes
(2)	No	No	Yes	Yes	Yes	Yes
(3)	Yes	Yes	Yes	No	No	Yes
(4)	Yes	Yes	Yes	Yes	Yes	Yes

uniform electron gas is a logical and appealing starting point. Correlation energy is unfortunately not governed by simple dimensionality and scaling rules as is exchange. In the absence of a well-defined starting point, therefore, it could be argued that we are lost in an infinite-dimensional empirical parameter space.

The uniform electron gas *does* reflect much of the relevant physics of dynamical correlations in finite systems. Interelectronic cusp conditions, hole normalization conditions, and correlation length scales (except in exponential tails) are transferable to finite systems in the so-called "local spin-density approximation" (LSDA) and its adaptation to nonuniform systems,[13] the "generalized gradient approximation" (GGA). In the present work, therefore, we accept constraint (1) as a minimal, self-evident requirement for a good correlation functional. In this respect, three of the popular functionals listed above fall short: CS, LYP, and Bc88.

Requirement (2) has been stressed in previous work[12] and is surely important. Opposite-spin and parallel-spin correlations are mathematically (i.e., short-range r_{12} behavior) and physically distinct. Any functional blind to this fact is missing essential physics. The helium atom has zero parallel-spin correlation energy. About 21% of the correlation energy of the neon atom, however, arises from parallel-spin correlations.[17] Their relative importance increases even further with increasing atomic number. Correlation functionals calibrated only on the helium atom (e.g., CS and LYP) cannot be expected to properly capture parallel-spin physics. In fact, the CS and LYP functionals incorrectly give zero correlation energy in *any* ferromagnetic system (i.e., all spins aligned).

Minimal requirement (3) is beyond dispute, and is particularly relevant in chemistry given the ubiquitous presence of hydrogen. Both the Pc86 and the PWc91 functionals give small but nonzero correlation energy for the hydrogen atom (2 and 6 mH, respectively). These errors are uncomfortably large if the goal of density-functional thermochemistry is precision of the order a few kcal/mol or a few mH.

Minimal requirement (4) may appear obvious, but contains a subtle warning. Dynamical correlation is an implicitly *short-range* phenomenon. As such, dynamical correlation functionals should be calibrated only on atomic, and never molecular, systems. The traditional quantum chemical definition of "correlation" (i.e., with respect to the Hartree–Fock energy as reference) includes a *long-range*, nondy-namical component in molecular bonds which cancels the *long-range* nature of Hartree–Fock exchange. Traditional correlation energies of molecules, therefore, cannot be compared to *local* DFT "correlation" energies. The same is true for exchange! Local DFT exchange and correlation parts are not, except in atomic systems, separately equivalent to their traditional counterparts. These ideas arise again in Sec. V, and are further discussed in Refs. 4 and 18.

In Table I, the strengths and weaknesses of the five previously cited functionals are summarized. None of them satisfies all of the "minimal, self-evident requirements" adopted in this discussion. We feel, therefore, that the dynamical correlation problem in DFT needs further work. A new dynamical correlation functional (Bc95) is introduced in the following section which, *by construction*, satisfies all four of our minimal requirements.

III. A NEW DYNAMICAL CORRELATION FUNCTIONAL

Adopting the uniform electron gas (UEG) as our starting point, we extract its opposite-spin and parallel-spin correlation energy components using the analysis of Stoll, Pavlidou, and Preuss:[19]

$$E_{C\text{opp}}^{\text{UEG}}(\rho_\alpha,\rho_\beta)=E_C^{\text{LSDA}}(\rho_\alpha,\rho_\beta)-E_C^{\text{LSDA}}(\rho_\alpha,0)$$
$$-E_C^{\text{LSDA}}(\rho_\beta,0), \quad (1)$$

$$E_{C\sigma\sigma}^{\text{UEG}}(\rho_\sigma)=E_C^{\text{LSDA}}(\rho_\sigma,0), \quad (2)$$

where $E_C^{\text{LSDA}}(\rho_\alpha,\rho_\beta)$ is the local spin-density approximation. We employ the recent parametrization of Perdew and Wang[20] for the electron gas correlation energy.

Equation (2) for parallel spins does not, of course, vanish in one-electron systems. Thus the requirement of perfect self-interaction correctness is at this stage violated. Our correlation model[12] of 1988, however, suggests a simple remedy. There, the parallel-spin correlation energy is written in the form

$$E_C^{\sigma\sigma}=-0.01\int \rho_\sigma D_\sigma z_{\sigma\sigma}^4\left[1-\frac{2}{z_{\sigma\sigma}}\ln\left(1+\frac{z_{\sigma\sigma}}{2}\right)\right]d^3\mathbf{r}, \quad (3)$$

where $z_{\sigma\sigma}$ is related to the range of the $\sigma\sigma$ correlations, and the factor D_σ is given by

$$D_\sigma=\tau_\sigma-\frac{1}{4}\frac{(\boldsymbol{\nabla}\rho_\sigma)^2}{\rho_\sigma} \quad \text{and} \quad \tau_\sigma=\sum_i |\boldsymbol{\nabla}\Psi_{i\sigma}|^2. \quad (4)$$

D_σ originates from the second-order Taylor expansion of the exact Kohn–Sham *non*interacting $\sigma\sigma$ pair density (see Ref. 12 for full details). It *vanishes identically in any one-electron system*. In any system of *more* than one electron, D_σ has positive nonzero value always. Note, also, that Eq. (4) is appropriate for systems of zero *current* density only, and takes a modified form otherwise.[21]

Given that D_σ vanishes identically in one-electron systems, and given its appearance as a prefactor in Eq. (3), an obvious self-interaction correction for Eq. (2) suggests itself. Multiply by D_σ, and divide by its uniform gas limit,

$$D_\sigma^{\text{UEG}} = \frac{3}{5}(6\pi^2)^{2/3}\rho_\sigma^{5/3} \tag{5}$$

to obtain,

$$E_C^{\sigma\sigma} = \frac{D_\sigma}{D_\sigma^{\text{UEG}}} E_{C\sigma\sigma}^{\text{UEG}}. \tag{6}$$

Equation (1) for opposite spins and the self-interaction corrected Eq. (6) for parallel spins still overestimate correlation energies of finite systems. Atoms helium and neon, for example, take respective correlation energies of 58 and 623 mH (absolute), significantly larger than the exact values of 42 and 390. Our 1988 correlation model[12] predicts, through the effect of its correlation range parameters z_{opp} and $z_{\sigma\sigma}$, that inhomogeneity (i.e., nonzero density gradient) *reduces* correlation energy. To reproduce this effect in the present work, we introduce gradient-dependent cutoff factors of simplest conceivable form. Defining the dimensionless or "reduced" spin-density gradient χ_σ as follows:

$$\chi_\sigma = \frac{|\nabla\rho_\sigma|}{\rho_\sigma^{4/3}}, \tag{7}$$

we write for the opposite-spins correlation energy the expression,

$$E_C^{\text{opp}} = [1 + c_{\text{opp}}(\chi_\alpha^2 + \chi_\beta^2)]^{-1} E_{C\text{opp}}^{\text{UEG}} \tag{8}$$

and for parallel spins,

$$E_C^{\sigma\sigma} = [1 + c_{\sigma\sigma}\chi_\sigma^2]^{-2} \frac{D_\sigma}{D_\sigma^{\text{UEG}}} E_{C\sigma\sigma}^{\text{UEG}}. \tag{9}$$

Of course, the total correlation energy is given by

$$E_C = E_C^{\text{opp}} + E_C^{\alpha\alpha} + E_C^{\beta\beta}. \tag{10}$$

Our cutoff factors are simple rational functions, with two stipulations. First, the spin dependence in Eq. (8), though not unique, is the simplest and computationally most convenient choice (since χ_α and χ_β are needed for the exchange energy anyway). Second, the cutoff factor in Eq. (9) is *squared* for sufficient attenuation in atomic and molecular tails. Otherwise, the asymptotic correlation energy density reduces to the LSDA times a constant.

The cutoff parameters c_{opp} and $c_{\sigma\sigma}$ have been fit to the correlation energies of the helium (c_{opp}) and the neon ($c_{\sigma\sigma}$) atoms. The resulting values are

$$c_{\text{opp}} = 0.0031, \quad c_{\sigma\sigma} = 0.038. \tag{11}$$

TABLE II. Atomic correlation energies (a.u.). Exact: from Ref. 22. Bc95: Present work. PWc91: Perdew–Wang, Ref. 13.

	Exact	Bc95	PWc91
H	0.000	0.000	−0.006
He	−0.042	−0.042	−0.045
Li	−0.045	−0.054	−0.057
Be	−0.094	−0.093	−0.094
B	−0.125	−0.127	−0.124
C	−0.156	−0.160	−0.158
N	−0.188	−0.192	−0.196
O	−0.258	−0.264	−0.255
F	−0.325	−0.329	−0.316
Ne	−0.390	−0.390	−0.378

Correlation energies of the first-row atoms H through Ne are presented in Table II, with comparisons to experiment[22] and to the PWc91 functional of Perdew and Wang.[13] Though relying on no empirical fit parameters, PWc91 performs excellently. Its significant nonzero correlation energy for hydrogen, however, is unacceptable by the rules of the present work. Our newly constructed "Bc95" functional, on the other hand, satisfies all four of the minimal self-evident requirements of the previous section. No effort has been made to incorporate known asymptotic scaling conditions,[15] but this may be considered in future work. Uniform asymptotic scaling of exchange-correlation energy (i.e., high-Z limit of isoelectronic series) is, in any case, dominated by exchange.

A more extensive discussion of this new correlation functional, with complete comparisons to previous functionals in the literature, will be published elsewhere.[23] Our purpose here is to assess its utility in thermochemical applications.

IV. TESTS ON THE G2 DATA SET

For the present thermochemical tests, the Bc95 correlation functional is combined with the gradient-corrected exchange functional of Ref. 8 (Bx88), characterized by exact asymptotic behavior of the exchange energy density. Since chemical bond formation involves overlapping of atomic tails, Bx88 is a logical choice of exchange partner.

Our computations are carried out, as in Parts I to III, in a post-LSDA manner using the fully numerical, basis-set-free NUMOL program.[24] All open-shell systems are spin unrestricted, and the atomic reference computations are "nonspherical." The 56 atomization energies, 42 ionization potentials, and 8 proton affinities of the G2 data set are included for consideration here. We omit the G2 electron affinity tests due to the instability of negative ions in the LSDA. Tables III, IV, and V contain our atomization energy, ionization potential, and proton affinity results, respectively.

For the G2 atomization energies, the average absolute deviation from experiment for the Bx88/Bc95 exchange-correlation combination is 8.6 kcal/mol. The *maximum* deviation is a rather large 28.6 kcal/mol. Perusal of Table III reveals, moreover, a clear *overbinding* tendency especially in nonhydride bonds. The functional Bx88/PWc91, investigated

TABLE III. Atomization energies D_0 (kcal/mol).

	Expt.[a]	Bx88/Bc95[b]	Eq. (14)[c]		Expt.[a]	Bx88/Bc95[b]	Eq. (14)[c]
H_2	103.5	102.2	101.8	$SiH_2(^1A_1)$	144.4	144.8	144.2
LiH	56.0	52.9	52.4	$SiH_2(^3B_1)$	123.4	124.0	124.6
BeH	46.9	51.3	51.5	SiH_3	214.0	211.0	212.5
CH	79.9	80.3	78.4	SiH_4	302.8	298.3	300.9
$CH_2 (^3B_1)$	179.6	180.6	180.0	PH_2	144.7	148.2	146.6
$CH_2 (^1A_1)$	170.6	169.5	167.1	PH_3	227.4	228.9	227.1
CH_3	289.2	290.1	289.2	H_2S	173.2	175.7	173.9
CH_4	392.5	393.5	392.2	HCl	102.2	103.9	102.7
NH	79.0	82.4	78.7	Na_2	16.6	15.1	14.1
NH_2	170.0	175.7	169.9	Si_2	74.0	81.4	77.2
NH_3	276.7	282.0	275.2	P_2	116.1	127.0	116.3
OH	101.3	105.4	100.9	S_2	100.7	116.9	108.2
H_2O	219.3	224.3	216.9	Cl_2	57.2	66.0	60.1
HF	135.2	139.3	133.8	NaCl	97.5	93.7	93.5
Li_2	24.0	17.5	17.4	SiO	190.5	200.3	186.4
LiF	137.6	138.7	131.3	CS	169.5	180.8	169.0
C_2H_2	388.9	397.7	388.0	SO	123.5	142.3	127.1
C_2H_4	531.9	538.8	532.5	ClO	63.3	81.9	66.4
C_2H_6	666.3	668.6	666.0	ClF	60.3	73.4	61.6
CN	176.6	195.0	174.8	Si_2H_6	500.1	492.5	496.9
HCN	301.8	316.8	301.6	CH_3Cl	371.0	376.2	372.9
CO	256.2	268.3	254.7	CH_3SH	445.1	450.9	447.2
HCO	270.3	287.5	272.5	HOCl	156.3	169.3	156.5
H_2CO	357.2	370.7	357.1	SO_2	254.0	281.7	252.8
CH_3OH	480.8	488.6	479.3				
N_2	225.1	241.6	222.9				
N_2H_4	405.4	418.0	403.7				
NO	150.1	170.5	150.6				
O_2	118.0	142.8	122.2				
H_2O_2	252.3	268.4	248.9				
F_2	36.9	53.8	35.0				
CO_2	381.9	410.6	384.8				

[a]Expt: from Ref. 1.
[b]Bx88/Bc95: Present work, no exact-exchange mixing.
[c]Equation (14): Present work, with exact-exchange mixing parameter $a_0=0.28$.

in Part II, has somewhat smaller errors of 5.7 (average absolute) and 18.4 (maximum) kcal/mol. For the Bx88/Bc95 ionization potentials and proton affinities, deviations from experiment are listed in Table VI.

It would appear, on the basis of the atomization energy data, that the Bx88/Bc95 exchange-correlation combination is inferior to Bx88/PWc91 in thermochemical applications. It is possible, however, that our recent studies of the role of *exact exchange* in DFT thermochemistry[4,18,25] may render this conclusion premature. In the following section, we review our exact-exchange mixing theory of Ref. 4 (Part III) and reconsider the performance of the PWc91 and the Bc95 correlation functionals in this expanded context.

V. EXACT-EXCHANGE MIXING

The role of exact exchange in DFT reveals itself in the "adiabatic connection" or "coupling-strength integration" formula for the Kohn–Sham exchange-correlation energy.[26] Expressible in many forms, we write this tremendously important formula as follows:

$$E_{XC} = \frac{1}{2} \int \int \frac{\rho(\mathbf{r}_1)}{r_{12}} \left[\int_0^1 h_{XC}^\lambda(\mathbf{r}_1,\mathbf{r}_2) d\lambda \right] d^3\mathbf{r}_1 \ d^3\mathbf{r}_2. \quad (12)$$

This simplified form is for spin unpolarized systems (see Refs. 12 and 18 for spin-dependent details in polarized systems). An exchange-correlation "hole" function h_{XC}^λ, depending on a coupling-strength parameter λ, appears prominently in the integrand. The hole function is related to the pair density P_2^λ by

$$h_{XC}^\lambda(\mathbf{r}_1,\mathbf{r}_2) = \frac{P_2^\lambda(\mathbf{r}_1,\mathbf{r}_2)}{\rho(\mathbf{r}_1)} - \rho(\mathbf{r}_2) \quad (13)$$

which, except for the λ parameter, is a well-known definition.[27] In Kohn–Sham DFT, the λ parameter "turns on" the interelectronic $1/r_{12}$ repulsion between electrons. At the same time, the external one-body potential is suitably adjusted to *hold the density of the system fixed*. Thus $\lambda=1$ corresponds to the real, fully interacting system. $\lambda=0$ corresponds to a system of *noninteracting* electrons in an effective one-body potential V_{KS} having the *same density* as the real system (the Kohn–Sham noninteracting reference state). A

TABLE IV. Ionization potentials (eV).

	Expt.[a]	Bx88/Bc95[b]	Eq. (14)[c]		Expt.[a]	Bx88/Bc95[b]	Eq. (14)[c]
H	13.60	13.54	13.55	HCl	12.75	12.65	12.66
He	24.59	24.75	24.69	C_2H_2	11.40	11.27	11.19
Li	5.39	5.47	5.45	C_2H_4	10.51	10.45	10.32
Be	9.32	8.91	8.91	CO	14.01	13.87	14.03
B	8.30	8.48	8.44	$N_2(^2\Sigma_g)$	15.58	15.28	15.73
C	11.26	11.38	11.34	$N_2(^2\Pi_u)$	16.70	16.57	16.59
N	14.54	14.62	14.58	O_2	12.07	12.14	12.30
O	13.61	13.95	13.71	P_2	10.53	10.30	10.33
F	17.42	17.66	17.42	S_2	9.36	9.25	9.43
Ne	21.56	21.74	21.51	Cl_2	11.50	11.03	11.25
Na	5.14	5.20	5.15	ClF	12.66	12.28	12.47
Mg	7.65	7.51	7.47	CS	11.33	11.21	11.27
Al	5.98	5.87	5.88				
Si	8.15	8.02	8.04				
P	10.49	10.34	10.39				
S	10.36	10.36	10.32				
Cl	12.97	12.94	12.93				
Ar	15.76	15.70	15.73				
CH_4	12.62	12.42	12.45				
NH_3	10.18	10.20	10.06				
OH	13.01	13.12	12.94				
H_2O	12.62	12.62	12.46				
HF	16.04	16.09	15.90				
SiH_4	11.00	10.65	10.78				
PH	10.15	10.06	10.12				
PH_2	9.82	9.76	9.81				
PH_3	9.87	9.80	9.75				
SH	10.37	10.34	10.31				
$SH_2(^2B_1)$	10.47	10.33	10.33				
$SH_2(^2A_1)$	12.78	12.50	12.54				

[a]Expt: from Ref. 1.
[b]Bx88/Bc95: Present work, no exact-exchange mixing.
[c]Equation (14): Present work, with exact-exchange mixing parameter $a_0=0.28$.

continuum of *partially* interacting systems, all with the same density, spans these limits. E_{XC}, through Eq. (12), is related to the *coupling-strength averaged* exchange-correlation hole.

Thus E_{XC} samples h_{XC}^λ, or equivalently the pair density P_2^λ, at *all values* of the coupling-strength parameter λ. This is the price we pay for circumventing explicit computation of the interacting *kinetic* energy! Unfortunately, local density-functional h_{XC}^λ models poorly represent *molecular* holes in the noninteracting $\lambda=0$ limit. This is most easily visualized

by considering the prototypical molecular bond, H_2. Let us recall the arguments in Part III (see also Ref. 18) relating to the nature of correlation in this simplest conceivable bond.

In the noninteracting $\lambda=0$ limit, h_{XC}^λ is the pure exchange hole of the Slater determinant of the Kohn–Sham orbitals. In H_2, it is just the negative of the σ_g orbital density (i.e., a pure one-orbital self-interaction correction). This hole is *delocalized*, extending equally over both centers, and is *reference point independent*. A static, delocalized hole implies total absence of long-range, ''left–right'' correlation in the molecular bond! Density-functional *model* holes, on the

TABLE V. Proton affinities (kcal/mol).

	Expt.[a]	Bx88/Bc95[b]	Eq. (14)[c]
H_2	100.8	99.9	99.7
C_2H_2	152.3	155.3	156.7
NH_3	202.5	201.8	203.8
H_2O	165.1	163.3	165.3
SiH_4	154.0	154.3	153.0
PH_3	187.1	183.1	185.4
H_2S	168.8	168.9	168.6
HCl	133.6	134.7	133.9

[a]Expt: from Ref. 1.
[b]Bx88/Bc95: Present work, no exact-exchange mixing.
[c]Equation (14): Present work, with exact-exchange mixing parameter $a_0=0.28$.

TABLE VI. Deviations from experiment. Average absolute (maximum absolute).

		Bx88/Bc95[a]	Eq. (14)[b]
Atomization energies	(kcal/mol)	8.6(28.6)	2.0(7.5)
Ionization potentials	(eV)	0.15(0.47)	0.12(0.41)
Proton affinities	(kcal/mol)	1.5(4.0)	1.3(4.4)

[a]Bx88/Bc95: Present work, no exact-exchange mixing.
[b]Equation (14): Present work, with exact-exchange mixing parameter $a_0=0.28$.

TABLE VII. Deviations from experiment for Eq. (14). Average absolute (maximum absolute).

		Bx88/Bc95[a]	Bx86/Bc95[b]	PWx86/Bc95[c]
Mixing parameter a_0		0.28	0.28	0.29
Atomization energies	(kcal/mol)	2.0(7.5)	1.8(6.9)	2.0(5.8)
Ionization potentials	(eV)	0.12(0.41)	0.11(0.33)	0.11(0.32)
Proton affinities	(kcal/mol)	1.3(4.4)	1.4(4.0)	1.5(3.2)

[a]Present correlation functional, with exchange functional of Ref. 8.
[b]Present correlation functional, with exchange functional of Ref. 14.
[c]Present correlation functional, with exchange functional of Ref. 28.

other hand, are localized near each reference point, and consequently nonstatic (i.e., "attached" to the reference electron). Thus DFT exchange-correlation models mimic long-range left–right correlation in a trivial, albeit crude, manner. Though desirable in the *interacting* system, this simulation of nondynamical correlation extends, unfortunately, all the way to the $\lambda=0$ limit. The overbinding tendency of local density-functional theories, with or without gradient corrections, is thus explained.

Given any local exchange-correlation DFT, here is a simple correction for the $\lambda=0$ problem:

$$E_{XC} = E_{XC}^{DFT} + a_0 (E_X^{Exact} - E_X^{DFT}). \tag{14}$$

In other words, replace the qualitatively incorrect DFT behavior near $\lambda=0$ (namely, the DFT pure exchange part) with *exact* $\lambda=0$ behavior (namely, the exact exchange energy of the Kohn–Sham Slater determinant) to properly represent the $\lambda=0$ region of Eq. (12). Parameter a_0, reflecting a system's "Hartree–Fock character," controls the amount of this replacement. Assuming, as a first approximation, that a_0 is a universal constant, we determine its value by fitting to the G2 thermochemical data.

First, consider the functional Bx88/PWc91. A least-squares fit to the G2 atomization energies, ionization potentials, and proton affinites yields a rather small exact-exchange mixing parameter of $a_0=0.16$. The resulting

TABLE VIII. Total atomic energies (hartrees).

	Exact[a]	Bx88/Bc95[b]	Eq. (14)[c]
H	−0.500	−0.497	−0.498
He	−2.904	−2.904	−2.903
Li	−7.478	−7.481	−7.482
Be	−14.667	−14.657	−14.658
B	−24.654	−24.645	−24.645
C	−37.845	−37.840	−37.839
N	−54.589	−54.588	−54.587
O	−75.067	−75.081	−75.074
F	−99.734	−99.761	−99.748
Ne	−128.938	−128.975	−128.959

[a]Exact: from Ref. 22.
[b]Bx88/Bc95: Present work, no exact-exchange mixing.
[c]Equation (14): Present work, with exact-exchange mixing parameter $a_0=0.28$.

average absolute deviations from experiment are 3.1 kcal/mol, 0.14 eV, and 1.5 kcal/mol, respectively. These errors are only slightly smaller than for the functional itself (i.e., 5.7 kcal/mol, 0.15 eV, and 1.5 kcal/mol without exact-exchange mixing[3]). For the sake of brevity and clarity, the results of this unimpressive fit are not tabulated here.

In Part III, we reported a notably better fit involving two additional parameters: one adjusting the magnitude of the gradient correction for exchange, and the other the gradient correction for correlation. The *three* parameter G2 fit of Part III achieved average absolute errors of 2.4 kcal/mol, 0.14 eV, and 1.2 kcal/mol (atomization energies, ionization potentials, and proton affinites, respectively).

The functional Bx88/Bc95 performs considerably better in conjunction with Eq. (14) than does Bx88/PWc91. With a best-fit value of $a_0=0.28$, and no further alterations whatsoever, we obtain the G2 data in the final columns of Tables III, IV, and V. The average absolute error in the atomization energies is reduced dramatically to 2.0 kcal/mol, from 8.6 in Sec. IV. The ionization potential and proton affinity errors are 0.12 eV and 1.3 kcal/mol, also improved. The present one-parameter fit is of higher quality than our previous three-parameter fit of Part III. Average and maximum absolute errors are collected in Table VI. Note, also, that the proportion of exact exchange in the present work (28%) is greater than in Part III (20%). Baker and co-workers[5] have speculated that this is the desired direction for improvement of DFT reaction barrier heights.

How sensitive are these tests to the choice of *exchange* functional? Despite the fact that exchange dominates correlation in E_{XC}, the results are essentially unchanged when our older 1986 exchange functional (Bx86)[14] or the 1986 exchange GGA of Perdew and Wang (PWx86)[28] replace Bx88. All three of these functionals exactly contain the uniform electron gas limit, as is necessary if this requirement is placed on correlation. The effects of these substitutions are summarized in Table VII.

Finally, total energies of the atoms H through Ne are presented in Table VIII. These should not be taken too seriously given the post-LSDA nature of the calculations. Nevertheless, our atomic total energies are seen to be quite reasonable, with a maximum error of order 20 mH for Bx88/Bc95 with exact-exchange mixing.

VI. CONCLUSIONS

We have constructed a new dynamical correlation functional (Bc95) rectifying certain major deficiencies in previous popular functionals. Bc95 exactly contains the uniform electron gas limit, distinctly treats opposite and parallel spins, and is perfectly self-interaction free. With two fitted parameters, one for opposite and one for parallel spins, correlation energies of atoms are similar to those of previous functionals.[23]

In the one-parameter exact-exchange mixing formula, Eq. (14), the exchange-correlation combination Bx88/Bc95 performs significantly better in the G2 thermochemical tests than Bx88/PWc91. This ranking is opposite to that of Sec.

IV, where the functionals were tested by themselves. If exact-exchange mixing is justified (and we strongly believe that it is) then future assessments of exchange-correlation functionals must incorporate Eq. (14). This, unfortunately, complicates matters somewhat, but the higher thermochemical precision thus made possible is worth the effort.

The ultimate outcome of this work is a much more satisfying exact-exchange mixing theory, Eq. (14), than that of Part III. The three parameters in Part III are reduced to one, the exact-exchange mixing fraction a_0 itself. Though the present functional contains explicit kinetic-energy dependence, through Eq. (4), self-consistent computations of this kind are already possible.[29] In future work, system or (even more likely) position dependence of the exact-exchange mixing parameter will be explored.

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