

A new gradient-corrected exchange functional

By PETER M. W. GILL

Department of Chemistry, Massey University, Palmerston North, New Zealand

(Received 12 December 1995; accepted 21 February 1996)

A new gradient-corrected exchange functional (G96) is introduced. While similar to Becke's B88 functional, it is much simpler and its potential in finite systems is asymptotically unbounded. The mean absolute deviations of the B88 and G96 exchange energies from the corresponding Hartree-Fock values for the atoms H to Ar are 12.5 and 8.5 mE_h, respectively. In combination with the LYP correlation functional, it yields a density functional (G-LYP) that performs similarly to B-LYP on the standard G2 benchmark and we infer that the usefulness of a functional for molecular calculations does not depend critically on its asymptotic behaviour.

1. Introduction

As an approach to the electronic structure problem, Kohn–Sham density functional theory (DFT) [1–3] combines the virtues of comparative computational inexpense with commendable accuracy for a wide range of physically interesting properties. An intensive research effort has yielded an impressive variety of exchange and correlation functionals [4–19], some of which have shown considerable promise in recent comparisons [20–23] between DFT predictions and reliable experimental data on molecular structure and energetics. Not surprisingly, DFT has been widely embraced by physicists and chemists but fundamental questions about the origin of its success remain unanswered [24] and the trite remark that “DFT gets the right answers for the wrong reasons” is not far from the truth. If we are to improve this unsatisfactory situation, the veil of mystery that envelops modern DFT practice must be pierced and we propose that Occam's Razor [25] may be a potent weapon in this effort.

A major obstacle to progress is the arresting complexity of many of the currently popular density functions. It is entirely reasonable, and it is good science, to ask whether or not such baroque tendencies are necessary in order to obtain good agreement with experiment. In this spirit, we have initiated a minimalist search for simplicity in DFT. Our goal is the construction of extremely simple functionals that perform as well as their more complicated brethren when applied to atomic and molecular problems. For example, in work with Stewart [26], we have recently found that the Lee–Yang–Parr (LYP) [15, 16] correlation functional is only marginally superior to the very much simpler Wigner [5] functional buried within it and we have investigated the Becke–Wigner (B–W) model as an alternative to the more complicated B-LYP procedure.

In this paper, we turn our attention to the exchange energy. We introduce and examine a novel functional that, while comparable to the Becke [13] and Perdew–Wang [18] functionals, enjoys a peerless simplicity of form that may eventually allow it to be used without resort to the grid-based quadrature that bedevils current DFT practice.

We conjecture that it is the simplest possible exchange functional that affords a high-quality theoretical model chemistry.

The original exchange functional of Dirac [4],

$$E_X^{D_{30}} = C_X \int \rho^{4/3}(\mathbf{r}) d\mathbf{r}, \quad (1)$$

is intuitively comprehensible and conceptually attractive. However, although the functional is exact for the homogeneous electron gas, it is insufficiently accurate in molecular systems to yield an entirely satisfactory theoretical model chemistry. Most attempts to generalize and improve upon it introduce a gradient-dependent function $g(x)$ to the integrand, yielding

$$E_X = \int \rho^{4/3}(\mathbf{r}) g(x) d\mathbf{r}, \quad (2)$$

where $\rho(\mathbf{r})$ is a *spindensity* and its dimensionless reduced gradient is given by $x = |\nabla\rho| \rho^{-4/3}$. All of the exchange functionals that we will consider henceforth are of form (2) and, for the sake of brevity, we will therefore often discuss a functional in terms of its $g(x)$.

A number of authors have emphasized the importance of the *potential* that an exchange functional yields when applied in the classically forbidden outer regions of a molecule where the spindensity decays exponentially. Since the density of the hydrogen atom is exponential

$$\rho_H(r) = \pi^{-1} \exp(-2r), \quad (3)$$

and its *exact* exchange potential (which cancels its Coulomb potential) is easily shown to be

$$V_H^{\text{exact}}(r) = \exp(-2r) \left(1 + \frac{1}{r} \right) - \frac{1}{r}, \quad (4)$$

it follows that one can obtain a useful diagnostic gauge of the performance of functional (2) in classically forbidden regions by comparing (4) with the *approximate* exchange potential [27]:

$$V_H^{\text{DFT}}(r) = \frac{2x}{3} \frac{dg}{dx^2} + \left(\frac{2}{r} - \frac{8}{3} \right) \frac{dg}{dx} + \frac{8}{3x} g, \quad (5)$$

(where $x = 2\pi^{1/3} e^{2/3}$) that results when the density is given by (3).

The spin-polarized Dirac functional is a special case of (2) in which $g(x)$ is constant, i.e.

$$g^{D_{30}}(x) = \alpha = -\frac{3}{2} \left(\frac{3}{4\pi} \right)^{1/3}, \quad (6a)$$

$$V_H^{D_{30}}(r) = -\left(\frac{6}{\pi^2} \right)^{1/3} \exp(-2r/3). \quad (6b)$$

In an attempt to correct the tendency of (6a) to underestimate the Hartree-Fock exchange energy by roughly 10% in molecular systems, Slater [8] and others proposed that the constant α be increased by such a factor. This approach leads to the famous X_α theory and was a popular choice for many years despite being necessarily inexact for the homogeneous electron gas.

By examining the slowly-varying infinite electron gas, Sham [7] and Kleinman [10] were able to derive from first principles the second-order gradient-corrected functional

$$g^{S71}(x) = \alpha - \beta x^2, \quad (7a)$$

$$V_H^{S71}(r) = V_H^{D30}(r) - 8\pi^{1/3}\beta \exp(+2r/3) \left(\frac{1}{r} - \frac{1}{3} \right), \quad (7b)$$

where $\beta = 5(36\pi)^{-5/3} = 0.00189$. Moreover, although S71 yields improved energies over D30, Herman *et al.* found [6] that replacing β with the semiempirical value $b = 0.0044$ is even better. However, the Sham–Kleinman–Herman functionals have been criticized for several reasons, the most serious of which is that their potential (7b) is unbounded for large r .

In recent years, the evolution of improved exchange functionals has been partly guided by an impressive piece of literature [28] on the scaling and asymptotic behaviour of the exact functional. This knowledge has been used to infer that $g(x)$ should reduce to $g^{S71}(x)$ as $x \rightarrow 0$ and that the potential (5) should decay as $1/r$ as $x \rightarrow \infty$. We designate these the ‘Sham-quadratic’ and ‘Coulombic’ asymptotic properties, respectively, and note that any functional possessing *both* is likely to be fairly complicated.

The first functional developed with both of these properties in mind

$$g^{B88}(x) = \alpha - \frac{bx^2}{1 + 6bx \sinh^{-1} x} \\ = \alpha - bx^2 + 6b^2x^4 - \dots, \quad (8a)$$

$$V_H^{B88}(r) = V_H^{D30}(r) - r^{-2} - O(r^{-3}), \quad (8b)$$

was published in 1988 by Becke [13]. He chose the parameter $b = 0.0042$ to fit the known Hartree–Fock exchange energies of the noble gas atoms He to Rn and the similarity of this to the Herman value follows from the similarity between the Taylor series in (7a) and (8a). It is sobering to note that, despite being neither Sham-quadratic nor Coulombic, B88 yields very useful theoretical model chemistries [22] when paired with competent functionals.

Following Becke’s work, Perdew and Wang constructed another functional

$$g^{PW91}(x) = \alpha - \frac{bx^2 - (b - \beta)x^2 \exp(-1.6455x^2) - 10^{-6}x^4}{1 + 6bx \sinh^{-1} x - 10^{-6}x^4/\alpha} \\ = \alpha - \beta x^2 - 0.00375x^4 - \dots, \quad (9a)$$

$$V_H^{PW91}(r) = V_H^{D30}(r) - \text{small terms}, \quad (9b)$$

that is also widely used and is frequently referred to as the GGA91 exchange functional [18]. Although based on B88, it has been refined in the small- and large- x limits. In particular, the Gaussian term in the numerator renders it Sham-quadratic while the x^4 terms ensure that (9a) tends to zero in the high-gradient limit. However, although such modifications produce a functional that is theoretically superior, PW91 is not found in practice (as we will see later) to yield systematically better chemical predictions. (The referee of this paper has informed us that the 1986 functional of Perdew [11] is preferable to PW91. Few direct comparisons between P86 and B88 have appeared in the literature but such work would obviously be valuable.)

Recently, Gill and Pople found a functional that yields the exact wavefunction and energy for the hydrogen atom and showed [27] that it is the unique functional of form (2) to do so. Their functional is complicated and is most conveniently written as

$$g^{\text{GP93}}(x) = \frac{x\Gamma(1/3)}{4} \left[U(-2/3, 2, 2r) \int_0^{2r} t(t+2) \exp(-2t) M(-2/3, 2, t) dt \right. \\ \left. + M(-2/3, 2, 2r) \int_{2r}^{\infty} t(t+2) \exp(-2t) U(-2/3, 2, t) dt \right] - \frac{x}{2}, \quad (10a)$$

$$V_{\text{H}}^{\text{GP93}}(r) = V_{\text{H}}^{\text{exact}}(r), \quad (10b)$$

where U and M are confluent hypergeometric functions. It is Coulombic (necessarily) but not Sham-quadratic. Regrettably, it performs extremely poorly for all but the simplest of systems and we will not consider it further here.

What, then, can we conclude from the observed performance of the existing functionals? The question is a confusing one because B88, which is neither Sham-quadratic nor Coulombic, performs at least as well as PW91 (which is Sham-quadratic but otherwise very similar) and very much better than S71 (which is Sham-quadratic) and GP93 (which is Coulombic and, indeed, exact for the hydrogen atom). An objective observer must conclude, on the weight of evidence but contrary to conventional wisdom, that an exchange functional need *not* necessarily possess the Sham-quadratic and Coulombic properties in order to perform well. If this is true, it is frustrating for it tells us only what is *not* important. If we wish to develop an improved functional, it would be much more helpful to know what *is* important. Nonetheless, if nothing else, it should at least make us receptive to slightly unconventional suggestions. One follows.

2. A new exchange functional

The functional that this paper introduces is defined by

$$g^{\text{G96}}(x) = \alpha - bx^{3/2}, \quad (11a)$$

$$V_{\text{H}}^{\text{G96}}(r) = V_{\text{H}}^{\text{D90}}(r) - 3\sqrt{2}\pi^{1/6}b \exp(+r/3) \left(\frac{1}{r} - \frac{5}{18} \right), \quad (11b)$$

and we will refer to it as G96. We choose the value $b = 1/137$ to reproduce the Hartree–Fock exchange energy for the Ar atom using the HF/6-311++G density [29, 30] and SG-1 grid [31]. Before examining the quantitative performance of the G96 functional, we note that it is neither Sham-quadratic nor Coulombic but, for the reasons below, this is unlikely to be important.

$g^{\text{G96}}(x)$ is not analytic at $x = 0$ and its second and higher derivatives there are infinite. Becke contends [13] that this deficiency may be significant but we do not agree. Indeed, there is evidence that non-analyticity of $g(x)$ at the origin may in fact be *necessary* for high accuracy. Not long ago, we showed [27] that there exists a unique functional of the form (2) that yields the correct Kohn–Sham energy ($-1/2$ hartree) and density ($\pi^{-1} \exp(-2r)$) for a hydrogen atom. We were able to construct and plot the corresponding $g(x)$ and show that it is singular at the origin. This surprising result is, however, not particularly profound. It simply reflects the fact that the form (2),

while very attractive from a computational and conceptual viewpoint, is not infinitely flexible and it shows clearly that, if one wishes to adopt the constraints inherent in (2), one can not rule out the possibility that the optimal $g(x)$ may behave quite strangely.

The fact that the potential (11*b*) of G96, like that of S71, is asymptotically unbounded in the classically forbidden region of a molecule is actually of little practical significance for it can be seen that, where the potential grows as $\exp(+r/3)$, the corresponding spindensity decays as $\exp(-2r)$ and annihilates any spurious effects that might otherwise have arisen.

3. Results and discussion

All of the calculations described below were performed using the Q-Chem program [32].

Table 1 contains the proper UHF/6-311++G exchange energies [24, 29, 30] for the atoms H to Ar, and the signed differences between these and the improper values afforded by the Dirac, Sham, Perdew, Becke and G96 functionals when applied non-self-consistently to the UHF/6-311++G densities and integrated using the SG-1 grid [31].

It has been known for many years that the Dirac functional systematically underestimates UHF exchange energies and the data in table 1 show this error decreasing from 14% for H to 8% for Ar. This functional constitutes the exchange component of the widely used local spin density approximation (LSDA).

The inclusion of a gradient correction for the inhomogeneity of the electron density has a marked and beneficial effect. Although the straightforward Sham functional yields exchange energies that are still too small, the errors are now only 2–3%. Given the popularity that the LSDA has enjoyed, it is surprising that the Sham functional has received such scant attention. This may reflect more on early density-functional programs than on the functional itself!

The Becke functional is semiempirical in that the value of its b parameter was chosen to fit, in a least-squares sense, the exchange energies of the six noble gas atoms from He to Rn. The return for this single degree of ‘*ab initio* empiricism’, however, is that it is 1–2 orders of magnitude more accurate than the Sham functional for predicting atomic exchange energies. Its mean absolute deviation (MAD) from the UHF value is just $12.5\text{ m}E_{\text{h}}$.

The Perdew–Wang functional is a little more complicated than Becke’s but the results in table 1 show that it is also somewhat less accurate: for the 18 atoms tested, its mean absolute deviation from the UHF values is $24\text{ m}E_{\text{h}}$. This is very interesting. PW91 was carefully constructed to mimic B88 for intermediate x values but to correct it elsewhere. It raises the intriguing possibility that, in order to perform well for finite systems, it may be unimportant, or even undesirable, for an exchange functional to be Sham-quadratic.

The G96 functional contains a semiempirical parameter chosen to fit the exchange energy of the Ar atom. The mean absolute deviation of G96 exchange energies from the UHF values is small, only $8.5\text{ m}E_{\text{h}}$. That such agreement can be achieved is itself significant, especially given the functional’s simplicity, non-analyticity and unbounded potential.

The deviations of the Becke, Perdew and G96 functionals are plotted in figure 1. The most interesting feature of this figure is the striking similarity between the three graphs and, in particular, the ‘neon dip’ that they all display. The obvious parallels

Table 1. Atomic exchange energies (millihartrees) using various functionals.^a

Atom	$E_X(\text{UHF})^b$	$\Delta(\text{D30})^c$	$\Delta(\text{S71})^d$	$\Delta(\text{B88})^e$	$\Delta(\text{PW91})^f$	$\Delta(\text{G96})^g$
H	−312.32	44.43	7.01	+2.74	+5.58	+1.28
He	−1024.81	141.55	18.71	+0.26	+8.81	−3.15
Li	−1781.03	243.23	46.56	+6.01	+18.06	+2.59
Be	−2666.17	354.30	86.02	+9.04	+21.67	+9.02
B	−3759.01	469.17	120.04	+6.71	+21.82	+7.72
C	−5066.06	585.65	159.09	+5.95	+23.24	+6.67
N	−6603.54	705.25	203.84	+9.95	+29.32	+8.43
O	−8203.17	828.59	240.70	−8.70	+12.06	−9.09
F	−10028.34	950.01	282.42	−23.47	−1.60	−25.04
Ne	−12098.93	1073.14	329.95	−31.13	−8.06	−36.63
Na	−14017.57	1233.20	408.94	−10.99	+12.33	−17.38
Mg	−15991.69	1382.59	484.66	−5.82	+15.00	−9.65
Al	−18079.79	1537.02	549.52	+1.38	+23.97	−5.42
Si	−20293.16	1691.61	616.05	+9.20	+33.42	−1.55
P	−22641.01	1848.91	685.11	+19.94	+45.49	+4.36
S	−25019.77	2005.71	750.24	+20.71	+47.83	+0.78
Cl	−27528.64	2160.70	816.57	+22.33	+50.51	−2.92
Ar	−30183.28	2321.83	891.42	+31.35	+61.26	−0.67
MAD ^h	—	1087.6	372.0	12.5	24.4	8.5

^a All energies obtained using the UHF/6-311++G density.
^b UHF/6-311++G exchange energy.
^c Difference between $E_X(\text{UHF})$ and energy from equation (6*a*) (Dirac).
^d Difference between $E_X(\text{UHF})$ and energy from equation (7*a*) (Sham).
^e Difference between $E_X(\text{UHF})$ and energy from equation (8*a*) (Becke).
^f Difference between $E_X(\text{UHF})$ and energy from equation (9*a*) (Perdew–Wang).
^g Difference between $E_X(\text{UHF})$ and energy from equation (11*a*) (present).
^h Mean absolute deviation from $E_X(\text{UHF})$.

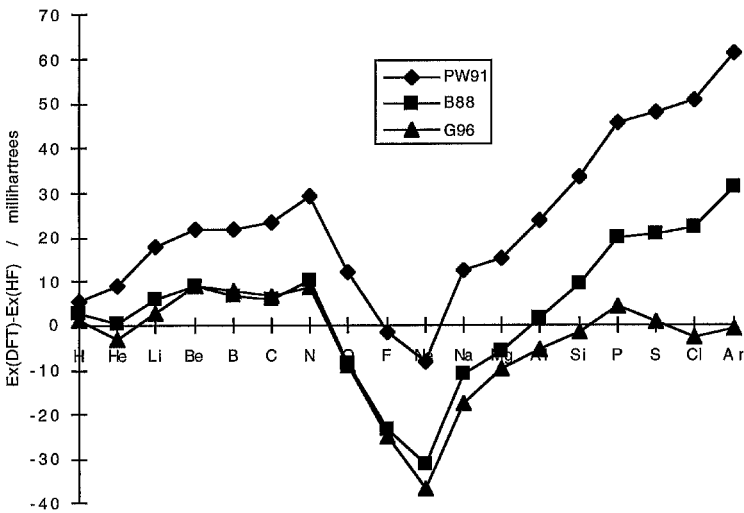


Figure 1. Differences between Hartree–Fock atomic exchange energies and those afforded by the PW91, B88 and G96 exchange functionals.

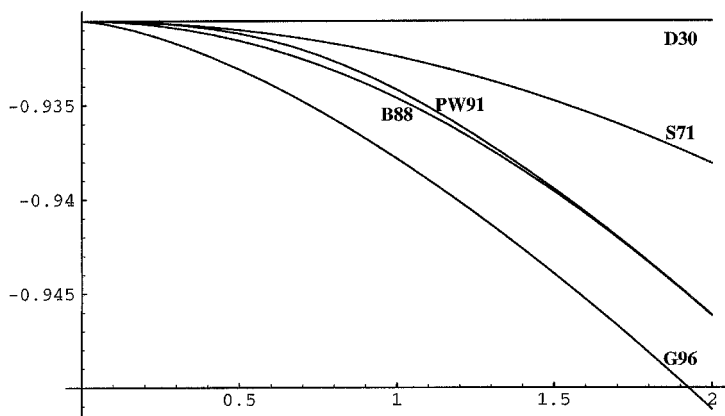


Figure 2. The $g^{D30}(x)$, $g^{S71}(x)$, $g^{B88}(x)$, $g^{PW91}(x)$ and $g^{G96}(x)$ functions ($0 < x < 2$).

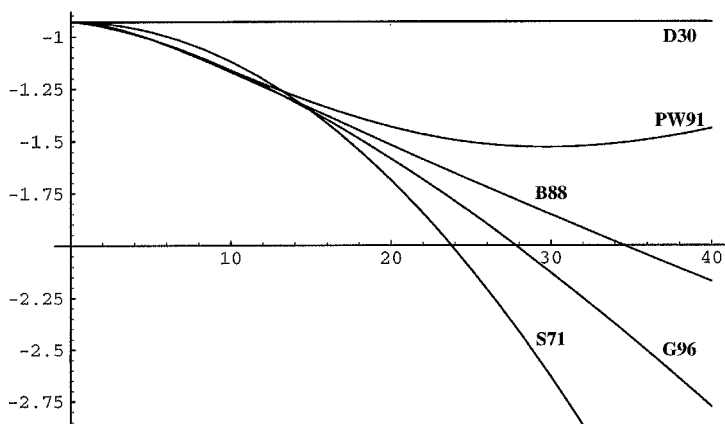


Figure 3. The $g^{D30}(x)$, $g^{S71}(x)$, $g^{B88}(x)$, $g^{PW91}(x)$ and $g^{G96}(x)$ functions ($0 < x < 40$).

between the energies that they yield suggest that the underlying functionals may be more closely related than a cursory inspection of (8), (9) and (11) would suggest. Fortunately, since all three are of the form (3), it is easy to compare them by comparing their respective $g(x)$ functions as in figures 2 and 3.

Because it is Sham-quadratic, PW91 decreases more slowly than B88 for $0 < x < 2$ but then becomes almost identical to it until $x \approx 10$ after which it reaches a minimum and then increases. Because of its infinite curvature at the origin, G96 decreases more rapidly initially than B88, but they subsequently intersect twice (at $x \approx 5.1$ and $x \approx 13.2$) before the $x^{-3/2}$ of G96 eventually prevails over the $x/\ln x$ of B88. Although the behaviours of the functionals in the small- and large- x regions have been studied in detail by asymptotic analysis, the differences between them turn out to be relatively unimportant. Of much greater significance practically is the striking similarity between all three functionals in the intermediate- x region, for it is there that their performances in most chemical applications are determined.

Having identified B88, PW91 and G96 as the most accurate of the functionals examined, we were interested to compare their strengths and weaknesses when applied to the prediction of accurately known chemical reaction energetics. In order to do this, we had to pair each of the exchange functionals with a correlation functional and we

Table 2. Atomization energies (kcal mol⁻¹) from experiment, G-LYP, B-LYP and GGA91.

Molecule	Expt.	6-311 + G(2df,p)			6-31G(d)		
		G-LYP	B-LYP	GGA91	G-LYP	B-LYP	GGA91
H	103.3	103.6	103.2	99.1	103.6	103.4	99.5
LiH	56.0	54.6	56.0	52.6	53.3	55.0	51.6
BeH	46.9	54.3	54.2	53.2	54.0	54.1	53.5
CH	79.9	80.2	81.3	81.5	78.3	79.6	80.1
CH ₂ (³ B ₁)	179.6	178.4	179.0	184.3	176.8	177.8	183.8
CH ₂ (¹ A ₁)	170.6	167.4	169.1	170.1	163.6	165.7	167.3
CH ₃	289.2	287.2	288.9	293.7	285.7	288.1	293.8
CH ₃	392.5	387.1	389.2	395.0	387.4	390.5	397.5
NH	79.0	82.8	84.4	84.7	79.8	81.5	82.1
NH ₂	170.0	174.1	176.6	178.3	167.7	170.4	172.6
NH ₃	276.7	276.6	279.4	283.1	267.0	270.1	274.6
OH	101.3	102.9	103.8	105.3	97.5	98.4	100.1
OH	219.3	217.1	218.1	222.0	206.0	207.1	211.4
FH	135.2	134.4	134.4	136.6	124.3	124.2	126.8
SiH ₂ (¹ A ₁)	144.4	143.2	144.1	142.3	141.2	142.3	141.4
SiH ₂ (³ B ₁)	123.4	122.6	122.6	125.0	121.1	121.4	124.5
SiH ₃	214.0	209.9	210.7	211.2	207.9	209.2	210.7
SiH ₃	302.8	296.6	298.0	297.1	294.4	296.4	297.1
PH	144.7	147.4	148.5	148.1	143.6	145.0	145.0
PH ₂	227.4	225.3	226.6	227.0	220.7	222.6	223.6
SH	173.2	169.4	169.9	173.3	164.5	165.5	169.0
ClH	102.2	99.6	99.5	102.3	95.3	95.6	98.2
Li	24.0	16.0	20.4	21.2	16.0	19.8	20.4
LiF	137.6	135.9	138.6	139.8	132.0	135.6	136.4
HCCCH	388.9	384.0	387.6	400.4	378.3	382.8	396.8
H ₂ CCH ₂	531.9	524.8	528.9	543.7	522.8	528.4	544.5
H ₂ CCH ₃	666.3	653.6	658.3	675.4	655.0	661.8	680.4
CN	176.6	182.6	186.3	195.4	178.7	182.9	192.3
HCN	301.8	305.0	309.2	319.0	301.2	306.0	316.5
CO	256.2	256.1	258.3	268.0	254.7	257.3	267.2
HCO	270.3	276.1	278.6	289.4	274.6	278.0	288.9
H ₂ CO	357.2	358.0	360.9	372.6	357.4	361.4	373.5
H ₂ COH	480.8	474.8	478.4	492.2	470.2	475.3	489.7
N ₂	225.1	230.1	235.1	242.5	225.5	230.9	238.7
H ₂ NNH ₂	405.4	406.7	412.8	424.9	394.9	401.7	414.7
NO	150.1	159.7	162.9	171.9	157.5	161.3	170.2
O	118.0	131.2	132.8	142.0	134.0	136.4	145.2
HOOH	252.3	255.3	258.1	268.3	248.2	251.7	262.0
F	36.9	45.4	46.8	52.3	51.7	54.2	59.0
CO	381.9	389.6	392.7	413.2	388.2	392.6	413.0
Na ₂	16.6	12.9	17.8	18.8	12.3	17.3	18.5
Si ₂	74.0	71.3	75.2	79.1	71.4	72.5	78.7
P ₂	116.1	118.3	120.2	124.3	112.1	114.1	118.2
S ₂	100.7	104.6	105.4	114.8	99.0	100.2	108.7
Cl ₂	57.2	56.1	56.5	65.2	49.7	50.8	58.2
NaCl	97.5	90.4	91.5	96.0	87.3	88.8	93.4
SiO	190.5	190.4	192.2	196.6	185.6	187.8	192.5
SC	169.5	168.1	169.9	179.5	164.7	166.8	176.5
SO	123.5	130.4	131.7	139.8	123.8	125.6	133.4
ClO	63.3	71.1	72.5	80.5	65.7	67.7	75.3
ClF	60.3	63.8	64.7	71.3	61.2	63.0	69.2
SiH ₆	500.1	485.6	488.7	494.6	482.3	486.4	494.7
CH ₃ Cl	371.0	363.7	366.1	379.3	363.2	366.9	380.6
CH ₃ SH	445.1	435.2	438.2	452.8	432.5	436.9	452.1
HOCl	156.3	157.4	159.0	168.3	150.5	152.8	161.8
SO ₂	254.0	253.8	256.4	274.4	237.9	241.6	259.4

Table 3. Ionization potentials (eV) from experiment, G-LYP, B-LYP and GGA91.

Molecule	Expt.	6-311 + G(2df,p)			6-31G(d)		
		G-LYP	B-LYP	GGA91	G-LYP	B-LYP	GGA91
H	13.60	13.57	13.54	13.64	13.53	13.48	13.58
He	24.59	24.80	24.79	24.55	24.74	24.71	24.47
Li	5.39	5.44	5.52	5.60	5.44	5.52	5.61
Be	9.32	8.84	8.98	9.07	8.81	8.92	9.01
B	8.30	8.58	8.62	8.70	8.40	8.41	8.51
C	11.26	11.39	11.41	11.57	11.25	11.23	11.41
N	14.54	14.52	14.51	14.76	14.50	14.46	14.71
O	13.61	14.05	14.17	14.20	13.86	13.93	13.98
F	17.42	17.67	17.74	17.81	17.26	17.25	17.38
Ne	21.56	21.69	21.71	21.81	21.17	21.10	21.28
Na	5.14	5.22	5.35	5.37	5.20	5.33	5.36
Mg	7.65	7.45	7.63	7.67	7.45	7.63	7.67
Al	5.98	5.66	5.87	6.10	5.86	5.86	6.10
Si	8.15	7.94	7.94	8.22	7.94	7.93	8.21
P	10.49	10.19	10.18	10.50	10.18	10.17	10.50
S	10.36	10.37	10.41	10.54	10.31	10.32	10.45
Cl	12.97	12.88	12.91	13.07	12.84	12.84	13.03
Ar	15.76	15.60	15.61	15.81	15.58	15.56	15.78
CH ₄	12.62	12.33	12.38	12.47	12.40	12.41	12.56
NH ₃	10.18	10.04	10.09	10.22	9.69	9.71	9.87
OH	13.01	13.10	13.18	13.26	12.76	12.78	12.91
OH ₂	12.62	12.49	12.53	12.66	12.03	12.02	12.20
FH	16.04	16.01	16.03	16.16	15.31	15.26	15.46
SiH ₄	11.00	10.63	10.67	10.79	10.74	10.75	10.92
PH	10.15	9.98	9.98	10.27	9.97	9.96	10.26
PH ₂	9.82	9.74	9.75	10.01	9.72	9.72	9.99
PH ₃	9.87	9.66	9.71	9.85	9.61	9.63	9.79
SH	10.37	10.27	10.31	10.47	10.21	10.23	10.39
SH ₂	10.47	10.22	10.25	10.44	10.17	10.18	10.37
ClH	12.75	12.55	12.57	12.75	12.50	12.49	12.70
HCCH	11.40	11.08	11.12	11.30	10.79	10.79	11.03
H ₂ CCH ₂	10.51	10.23	10.28	10.48	9.97	9.98	10.22
CO	14.01	13.86	13.92	13.97	13.77	13.78	13.86
N ₂	15.58	15.34	15.37	15.48	15.22	15.19	15.34
O ₂	12.07	12.47	12.48	12.52	12.38	12.33	12.41
P ₂	10.53	10.12	10.13	10.40	10.17	10.16	10.46
S ₂	9.36	9.26	9.28	9.50	9.36	9.34	9.56
Cl ₂	11.50	11.05	11.08	11.24	11.15	11.14	11.34
ClF	12.66	12.32	12.36	12.48	12.13	12.12	12.28
SC	11.33	11.23	11.28	11.39	11.21	11.22	11.36

chose to use LYP with B88 and G96 (giving B-LYP and G-LYP) and the PW91 correlation functional with PW91 (giving GGA91). All calculations were performed self-consistently [33] and used the SG-1 grid [31].

In tables 2–5, we compare the predictions of G-LYP, B-LYP and GGA91 with accurate experimental data for the G2 set of molecules [34]. We present results obtained with both the large 6-311 + G(2df,p) basis set and the smaller 6-31G(d) set. We expect the former to be close to the basis set limit while the latter are indicative of the quality that could be anticipated if one wished to apply the functionals to large systems where a modest basis set would be mandated. MP2/6-31G(d) geometries were

Table 4. Electron affinities (eV) from experiment, G-LYP, B-LYP and GGA91.

Molecule	Expt.	6-311 +G(2df,p)			6-31G(d)		
		G-LYP	B-LYP	GGA91	G-LYP	B-LYP	GGA91
C	1.26	1.29	1.32	1.57	- 0.21	- 0.28	0.07
CH	1.24	1.27	1.31	1.54	- 0.05	- 0.11	0.21
CH ₂	0.65	0.68	0.79	0.82	- 0.64	- 0.63	- 0.52
CH ₃	0.08	- 0.06	0.02	0.12	- 1.41	- 1.43	- 1.25
CN	3.82	3.75	3.82	3.91	2.82	2.78	2.95
NH	0.38	0.40	0.50	0.56	- 1.28	- 1.29	- 1.13
NH ₂	0.74	0.65	0.73	0.83	- 0.95	- 0.97	- 0.78
NO	0.02	0.20	0.26	0.31	- 0.75	- 0.81	- 0.69
O	1.46	1.61	1.70	1.77	- 0.34	- 0.37	- 0.19
OH	1.83	1.77	1.83	1.93	- 0.17	- 0.21	- 0.01
O ₂	0.44	0.42	0.52	0.53	- 0.74	- 0.77	- 0.66
F	3.40	3.50	3.56	3.65	0.93	0.85	1.07
Si	1.385	1.17	1.19	1.47	0.78	0.74	1.11
SiH	1.277	1.10	1.12	1.39	0.74	0.71	1.04
SiH ₂	1.124	1.00	1.05	1.29	0.67	0.66	0.96
SiH ₃	1.44	1.25	1.33	1.45	0.97	0.98	1.16
P	0.746	0.81	0.87	0.93	0.14	0.13	0.28
PH	1.00	0.95	1.01	1.11	0.32	0.31	0.50
PH ₂	1.26	1.09	1.15	1.29	0.52	0.50	0.73
PO	1.09	1.05	1.10	1.28	0.33	0.31	0.55
S	2.077	2.05	2.10	2.22	1.49	1.47	1.68
SH	2.314	2.17	2.22	2.37	1.64	1.61	1.85
S ₂	1.663	1.46	1.51	1.64	1.21	1.20	1.40
Cl	3.615	3.54	3.57	3.72	2.97	2.94	3.18
Cl ₂	2.39	2.70	2.78	2.70	2.61	2.62	2.65

used for all calculations. We note that a major investigation of the B-LYP procedure has previously been published by Johnson *et al.* [22]. These authors, however, confined their attention to the 6-31G(d) basis set and did not present comparisons of B-LYP with the GGA91 (or G-LYP) procedure. Our results are summarized in table 6.

Table 2 lists experimental and theoretical atomization energies for 55 small molecules. In general, the theoretical values follow the pattern $G-LYP < B-LYP \ll GGA91$ and the tendency of GGA91 to overbind is particularly significant for unsaturated systems. The fact that G-LYP atomization energies are usually smaller than those of B-LYP is an asset in the infinite-basis limit (where B-LYP tends to overbind slightly) but a liability in 6-31G(d) calculations (where errors due to the functional and basis set largely cancel and B-LYP's mean error is small). For large-basis calculations, G-LYP is slightly better than B-LYP overall and both are much more accurate than GGA91. For small-basis calculations, B-LYP is better than G-LYP overall and both are more accurate than GGA91.

Table 3 lists experimental and theoretical ionization potentials for 40 atoms and molecules. In general, the theoretical values follow the pattern $G-LYP \approx B-LYP < GGA91$. However, unlike atomization energies, molecular ionization energies are almost invariably underestimated by B-LYP. Consequently, G-LYP is slightly worse overall than B-LYP for calculations with the large basis set and slightly better with the small basis set. Both, however, are much less accurate than GGA91.

Table 5. Proton affinities (kcal mol⁻¹) from experiment, G-LYP, B-LYP and GGA91.

Molecule	Expt.	6-311 + G(2df,p)			6-31G(d)		
		G-LYP	B-LYP	GGA91	G-LYP	B-LYP	GGA91
H ₂	100.8	98.8	97.3	99.2	91.1	90.1	91.4
HCCH	152.3	154.5	152.9	154.6	157.3	156.9	157.2
NH ₃	202.5	202.3	200.4	201.7	208.7	207.7	208.3
H ₂ O	165.1	163.3	161.5	162.9	169.2	168.2	168.7
SiH ₄	154.0	155.1	154.0	152.9	151.4	150.8	148.9
PH ₃	187.1	185.7	184.2	183.4	185.4	184.4	183.7
H ₂ S	168.8	168.6	167.1	167.2	167.5	166.7	166.5
HCl	133.6	133.5	132.1	133.0	130.2	129.6	129.6

Table 6. Mean absolute deviations (kcal mol⁻¹) of functionals from experiment.

	6-311 + G(2df,p)			6-31G(d)		
	G-LYP	B-LYP	GGA91	G-LYP	B-LYP	GGA91
Atomization Energies	4.21	4.39	8.97	6.10	5.04	7.77
Ionization Potentials	4.76	4.40	3.62	5.86	5.97	3.93
Electron Affinities	2.50	2.47	3.45	23.58	24.16	19.43
Proton Affinities	1.13	1.98	1.75	4.25	4.44	4.80
Overall	3.86	3.87	5.80	5.87 ^a	5.35 ^a	6.06 ^a

^a Without inclusion of electron affinity data.

Table 4 lists experimental and theoretical electron affinities for 25 atoms and molecules. It is well known that most anions cannot be adequately described without diffuse functions and, as a result, the 6-31G(d) electron affinities are generally much too low. With the large basis set, the theoretical values invariably follow the pattern G-LYP < B-LYP < GGA91 but the B-LYP values are sometimes above, and sometimes below, experiment. As a result, we find overall that G-LYP and B-LYP are similar and both are much more accurate than GGA91.

Table 5 lists experimental and theoretical proton affinities for eight small molecules. All three functionals perform notably well here. Presumably, this is because, unlike atomization, ionization and electron addition, protonation is an isogyric process. The G-LYP affinities are generally slightly larger than those of B-LYP and GGA91 and this is usually an improvement. Overall, G-LYP is superior to both B-LYP and GGA91, especially with the large basis set.

In an attempt to draw the threads of this paper together, we have constructed a summary of the properties and performance of the six exchange functionals that we have considered and present it in table 7. Careful inspection of this leads to the conclusion that correct behaviour of $g(x)$ in the $x \rightarrow 0$ and $x \rightarrow \infty$ limits is neither necessary nor sufficient to determine whether a functional may be useful in the prediction of chemical energetics. Of much greater significance is the behaviour in the intermediate range, say, $2 < x < 10$. This is a salutary lesson to any who seek to devise accurate exchange functionals in the future.

Table 7. Summary of various exchange functionals.

	D30 ^a	S71 ^b	B88 ^c	PW91 ^d	GP93 ^e	G96 ^f
Sham-quadratic? ^g	×	✓	×	✓	×	×
Intermediate? ^h	×	×	✓	✓	×	✓
Coulombic? ⁱ	×	×	×	×	✓	×
Simple? ^j	✓	✓	×	×	×	✓
Accurate? ^k	×	×	✓	✓	×	✓

^a Dirac functional, equation (6*a*).^b Sham functional, equation (7*a*).^c Becke functional, equation (8*a*).^d Perdew–Wang functional, equation (9*a*).^e Gill–Pople functional, equation (10*a*).^f Present functional, equation (11*a*).^g Correct in low-gradient limit.^h Accurate for moderate gradients.ⁱ Correct in high-gradient limit.^j Corresponding $g(x)$ is of polynomial form.^k Performs well on the G2 dataset when combined with a competent correlation functional.

4. Conclusions

We have introduced and studied the simple G96 exchange functional given by

$$E_X^{\text{G96}} = \int \rho^{4/3} \left(\alpha - \frac{|\nabla \rho|^{3/2}}{137 \rho^2} \right) d\mathbf{r}. \quad (12)$$

A new density-functional procedure, G-LYP, obtained by combining G96 with the LYP correlation functional, has been applied to the G2 molecular dataset and compared with the established B-LYP and GGA91 procedures. Atomization energies from G-LYP are generally slightly lower than those from B-LYP and, as a result, G-LYP is less prone to the overbinding tendency that characterizes B-LYP. Ionization potentials from G-LYP are generally lower, and less accurate, than those of B-LYP. Electron affinities from the two functionals are comparable but the proton affinities afforded by G-LYP with a large basis set are significantly closer to the experimental values than those predicted by B-LYP.

Although the exchange potential of G96 is unbounded in an exponential density and its $g(x)$ is not analytic at $x = 0$, the results presented here suggest that these deficiencies may be of little significance for chemical purposes. Indeed, one of the most important conclusions of the present work is that surprisingly accurate agreement with experiment can be achieved using an extremely simple exchange functional. In devising a simple functional with the same predictive power as a more complex one, we feel (with William of Occam) that progress has been made.

We thank Dr Benny Johnson of Q-Chem Inc. for help in the preparation of this paper and Dr Terry Adams for his enthusiastic encouragement of this work. This research was funded in part by New Zealand Lottery Science Grant No. 45088.

References

- [1] HOHENBERG, P., and KOHN, W., 1964, *Phys. Rev. B*, **136**, 864.
- [2] KOHN, W., and SHAM, L. J., 1965, *Phys. Rev. A*, **140**, 1133.
- [3] PARR, R. G., and YANG, W., 1989, *Density-Functional Theory of Atoms and Molecules* (Oxford: Clarendon).
- [4] DIRAC, P. A. M., 1930, *Proc. Camb. Phil. Soc.*, **26**, 376.
- [5] WIGNER, E., 1938, *Trans. Faraday Soc.*, **34**, 678.
- [6] HERMAN, F., VAN DYKE, J. P., and ORTENBURGER, I. B., 1969, *Phys. Rev. Lett.*, **22**, 807.
- [7] SHAM, L. J., 1971, *Computational Methods in Band Theory*, edited by P. M. Marcus, J. F. Janak and A. R. Williams (New York: Plenum).
- [8] SLATER, J. C., 1974, *Quantum Theory of Molecules and Solids*, Vol. 4: *The Self-Consistent Field for Molecules and Solids* (New York: McGraw-Hill).
- [9] VOSKO, S. J., WILK, L., and NUSAIR, M., 1980, *Can. J. Phys.*, **58**, 1200.
- [10] ANTONIEWICZ, R., and KLEINMAN, L., 1985, *Phys. Rev. B*, **31**, 6779.
- [11] PERDEW, J. P., 1986, *Phys. Rev. B*, **33**, 8822.
- [12] GHOSH, S. K., and PARR, R. G., 1986, *Phys. Rev. A*, **34**, 785.
- [13] BECKE, A. D., 1988, *Phys. Rev. A*, **38**, 3098.
- [14] BECKE, A. D., 1988, *J. chem. Phys.*, **88**, 1053.
- [15] LEE, C., YANG, W., and PARR, R. G., 1988, *Phys. Rev. B*, **37**, 785.
- [16] MIEHLICH, B., SAVIN, A., STOLL, H., and PREUSS, H., 1989, *Chem. Phys. Lett.*, **157**, 200.
- [17] WILSON, L. C., and LEVY, M., 1990, *Phys. Rev. B*, **41**, 12930.
- [18] PERDEW, J. P., 1991, *Electronic Structure of Solids '91*, edited by P. Ziesche and H. Eschrig (Berlin: Akademie Verlag).
- [19] LAMING, G. J., TERMATH, V., and HANDY, N. C., 1993, *J. chem. Phys.*, **99**, 8765.
- [20] ANDZELM, J., and WIMMER, E., 1992, *J. chem. Phys.*, **96**, 1280.
- [21] BECKE, A. D., 1992, *J. chem. Phys.*, **96**, 2155.
- [22] JOHNSON, B. G., GILL, P. M. W., and POPL, J. A., 1993, *J. chem. Phys.*, **98**, 5612.
- [23] MURRAY, C. W., HANDY, N. C., and AMOS, R. D., 1993, *J. chem. Phys.*, **98**, 7145.
- [24] POPL, J. A., ADAMSON, R. D., and GILL, P. M. W., 1996, *J. Phys. Chem.*, **100**, 6348, for a description of the distinction between 'proper' and 'improper' exchange energies.
- [25] WILLIAM OF OCCAM; "For the purposes of explanation, things not known to exist should not, unless it is absolutely necessary, be postulated as existing."
- [26] STEWART, P. A., and GILL, P. M. W., 1995, *Faraday Trans. Chem. Soc.*, **91**, 4337.
- [27] GILL, P. M. W., and POPL, J. A., 1993, *Phys. Rev. A*, **47**, 2383.
- [28] LEVY, M., 1987, *Single-Particle Density in Physics and Chemistry*, edited by N. H. March and B. M. Deb (London: Academic).
- [29] KRISHNAN, R., BINKLEY, J. S., SEEGER, R., and POPL, J. A., 1980, *J. chem. Phys.*, **72**, 650.
- [30] MCLEAN, A. D., and CHANDLER, G. S., 1980, *J. chem. Phys.*, **72**, 5639.
- [31] GILL, P. M. W., JOHNSON, B. G., and POPL, J. A., 1993, *Chem. Phys. Lett.*, **209**, 506.
- [32] JOHNSON, B. G., GILL, P. M. W., HEAD-GORDON, M., WHITE, C. A., MAURICE, D. R., ADAMSON, R. D., ADAMS, T. R., and OUMI, M., 1995, *Q-Chem* (Pittsburgh, PA: Q-Chem Inc.).
- [33] POPL, J. A., GILL, P. M. W., and JOHNSON, B. G., 1992, *Chem. Phys. Lett.*, **199**, 557.
- [34] CURTISS, L. A., RAGHAVACHARI, K., TRUCKS, G. W., and POPL, J. A., 1991, *J. chem. Phys.*, **94**, 7221.