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Becke–Wigner: A Simple but Powerful Density Functional

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The construction of the Becke–Wigner (B–W) density functional for electronic structure calculations, a simplification of the B–LYP (Lee–Yang–Parr) functional, is examined. The performance of B–W is investigated with both small and large basis sets on a wide range of molecules and produces results similar in accuracy to B–LYP. However, the simplicity of B–W means that it is both more conceptually pleasing and more amenable to interpretation than B–LYP.

Density functional theory (DFT) has in recent years attracted the attention of quantum chemists, offering the promise of accurate exchange and correlation energies at a reasonable cost.[1–6] However, the putative 'exact' exchange-correlation functional[7] has not yet been discovered, and current DFT must content itself with imperfect approximations to its elusive ideal.

One of the more widely used of these lesser theories is the B–LYP model,[8] comprising the Becke exchange functional[9] and the correlation functional due to Lee *et al.*[10] In many cases, the B–LYP model gives results in remarkably good agreement with experiment.[1–6] However, B–LYP, and indeed DFT in general, can fail dramatically in the prediction of certain chemical data.[5,11,12]

The factors underlying the successes and failures of DFT must be determined in order to define (and hopefully extend) the realm of applicability of DFTs in general. Unfortunately, these determinations are obscured by the complicated form of the functionals. In the quest for accuracy, density functionals such as LYP have become intricate and unwieldy constructions. Simplicity of form has been lost, and their analysis and physical interpretation have become difficult or impossible. There is clearly a need for alternative functionals which, while offering comparable performance, are simpler in form and thereby more physically comprehensible. It is not unreasonable to expect that, as in other spheres, Occam's Razor will yield new insights into DFT. In this paper we discuss a simple but effective density functional denoted B–W. We examine the construction of this functional and investigate its performance relative to B–LYP.

Method

Since the B–LYP theoretical model chemistry often affords useful molecular energies when used with a fairly large basis set, we take it as the starting point for our simplified density functional. The Becke exchange functional is relatively simple as it stands and we choose not to modify it. In contrast, the LYP functional contains numerous terms and we decided to discard all but the first of them. Using ρ_α and ρ_β to represent spin densities, we will refer to the resulting exchange-correlation functional,

$$E_{\mathrm{XC}} = -\frac{3}{2}\left(\frac{3}{4\pi}\right)^{1/3} \sum_{\sigma=\alpha,\beta} \int \rho_\sigma^{4/3}\,\mathrm{d}\mathbf{r} - b \times \sum_{\sigma=\alpha,\beta} \int \rho_\sigma^{4/3} \frac{x_\sigma^2}{1+6bx_\sigma \sinh^{-1} x_\sigma}\,\mathrm{d}\mathbf{r} - 4a \int \frac{1}{1+d\rho^{-1/3}} \frac{\rho_\alpha \rho_\beta}{\rho}\,\mathrm{d}\mathbf{r} \qquad (1)$$

$$x_\sigma = \frac{|\nabla \rho_\sigma|}{\rho_\sigma^{4/3}} \qquad (2)$$

comprising the Becke 88 exchange functional[9] and the spin-polarised Wigner[13] correlation functional as B–W. While the B–LYP functional contains five parameters, B–W has only three; *b*, *a* and *d*.

Having thus chosen the form of our simplified functional, we have investigated a number of schemes for modifying the values of *b*, *a* and *d* in order to obtain a functional that predicts chemical behaviour accurately.

We initially determined the parameter values by minimising a quantity representing the error in the B–W functional. Specifically, we sought to minimise

$$Z = \sum_{i=1}^{10} (E_i^{\mathrm{exact}} - E_i^{\mathrm{B-W}})^2 \qquad (3)$$

where E_i^{exact} denotes the total energy[14] of the atom with atomic number *i* and $E_i^{\mathrm{B-W}}$ is the corresponding B–W/6-311++G energy obtained by the self-consistent Kohn–Sham procedure.[15] This basis set is of quadruple split-valence quality for each of the atoms H to Ne. Because the solution of the Kohn–Sham equations is iterative, the minimisation of *Z* cannot easily be achieved analytically and numerical techniques were employed.

Optimisation of the B–W parameters may be achieved by several methods. Perhaps the most intuitively appealing of these is to optimise all three parameters together, a process we call full optimisation. That is, one searches for the minimum point of the $Z = Z(b, a, d)$ hypersurface. Any multidimensional minimisation technique, such as the method of steepest descent, may be employed for this purpose.

Alternatively, the optimisation may be achieved by holding one or more of the parameters constant and minimising *Z* with respect to the remaining variable parameters. For example, holding *b* constant, we can minimise

$$Y = \sum_{i=1}^{10} (E_{c_i}^{\mathrm{exact}} - E_{c_i}^{\mathrm{B-W}})^2 \qquad (4)$$

where the E_{c_i} are atomic correlation energies and the B–W energies are calculated using the 6-311++G basis set. The exact correlation energy is defined to be the difference between the Hartree–Fock energy and the exact energy (see Table 1). Because of the low dimensionality of the B–W functional, curve-fitting schemes lend themselves to this constrained optimisation approach.

Finally, one may investigate the behaviour of the unadulterated B–W functional, *i.e.* the functional defined with the values of the corresponding constants in the B–LYP functional: $b = 0.0042$, $a = 0.04918$ and $d = 0.349$.

We examine the exchange-correlation functionals resulting from each of these approaches by applying them to the G2 set of atoms, ions and molecules,[8] using the SG-1 grid[16] to

Table 1 Energies (in E_h) of first-row atoms

atom	exact[a]	UHF[b]	correlation	B-W/6-311++G[c]
H	−0.500000	−0.4998	−0.0002	−0.4977
He	−2.903724	−2.8599	−0.0438	−2.9194
Li	−7.47806	−7.4320	−0.0461	−7.4963
Be	−14.66736	−14.5719	−0.0955	−14.6744
B	−24.65393	−24.5311	−0.1228	−24.6590
C	−37.8450	−37.6903	−0.1547	−37.8434
N	−54.5893	−54.3989	−0.1904	−54.5734
O	−75.067	−74.8093	−0.258	−75.0639
F	−99.734	−99.4018	−0.332	−99.7333
Ne	−128.939	−128.527	−0.412	−128.9276

[a] Ref. 14. [b] Ref. 18. [c] Present work, see eqn. (1).

integrate the exchange-correlation functionals.† After correction for zero-point vibrational effects,[8] 56 atomisation energies, 39 ionisation potentials, 25 electron affinities and 8 proton affinities may be computed. The discrepancies between the predicted B–W energies and accurate experimental data can then be used as a measure of the usefulness of the B–W functional.

Results and Discussion

We attempted a multidimensional minimisation of Z with respect to all three of the B–W parameters, using the Q-CHEM program[17] and a method of steepest descent, but it proved impossible to determine a unique minimum in this way. Noting that the d parameter changed very little during the steepest descent procedure, we constructed a two-dimensional (2D) slice of the 3D hypersurface (by holding d constant at the B-LYP value of 0.349). A contour plot of the resulting surface is shown in Fig. 1. A relatively flat 'channel' runs through the Z-surface, sloping gently downwards in the direction of decreasing a and increasing b. The value of Z may be decreased by following the channel's slight downhill gradient. While this leads to a better fit of first-row atomic B–W energies to known exact energies, it gives a progressively worsening predicted chemistry. For example, proceeding until Z has been halved yields a functional whose errors in molecular atomisation energies are of the order of 100 kJ mol^{-1}. It appears that the first-row atoms sacrifice 'correlation', for 'exchange' energy in order to fit the exact total energies better. While this trade-off goes unnoticed in the computation of total atomic energies, it produces gross inaccuracies in the molecular chemistry of the functional. The curious relationship between the DFT 'exchange' and 'correlation' energies implied by the near-linear dependence of b on a has been reported by previous researchers.[18] It appears that exchange-correlation functionals of this type cannot be usefully calibrated by a full optimisation of all parameters.

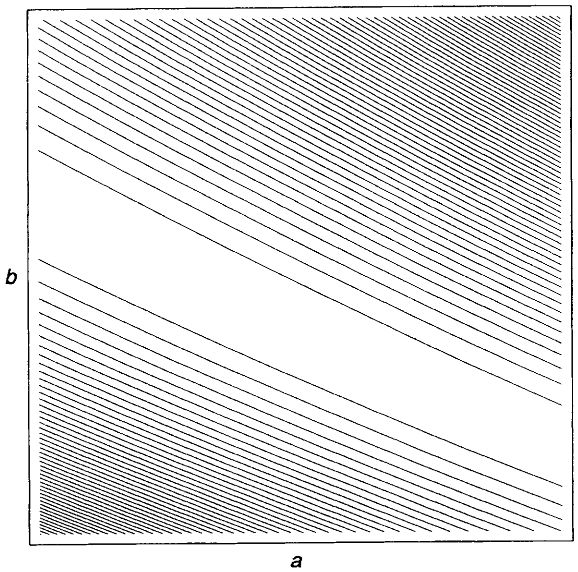

Fig. 1 Portion of the $Z = Z(b, a, 0.349)$ surface showing the flat channel. The parameter a runs from 0.030 to 0.069 units, b from 0.00300 to 0.00612 units. Contour lines are marked at 0.01 unit intervals.

To investigate a possible constrained approach to optimisation, we examined the behaviour of the B–W functional when the b and d parameters are held constant at their B-LYP values, and only the parameter a is allowed to vary. We evaluated Y at 50 points where a takes values from 0.028 to 0.077. A quadratic polynomial was fitted to the resulting data points (Fig. 2) and yields the optimal value $a = 0.0526$. We will call the functional with this value of a B–O(W) to indicate that only the Wigner correlation functional has been optimised. Calculations were performed on the G2 set using B–O(W) and both the 6-31+G(d) and 6-311+G(3df,2p) basis sets. A summary of the performance of B-LYP and B–O(W) is given in Table 2. The table shows the mean absolute deviation from experiment of the atomisation energy (E_{at}), the ionisation potential (E_i), the electron affinity (E_{ea}) and the proton affinity (E_{pa}). It can be seen that B–O(W) affords better overall proton affinities than B-LYP, but fares worse in the prediction of the other data. The overall mean absolute deviation for B–O(W) is within 6 kJ mol^{-1} of B-LYP, a remarkably close result considering the severely abbreviated form of the B–W functional.

We present a detailed examination of the unadulterated

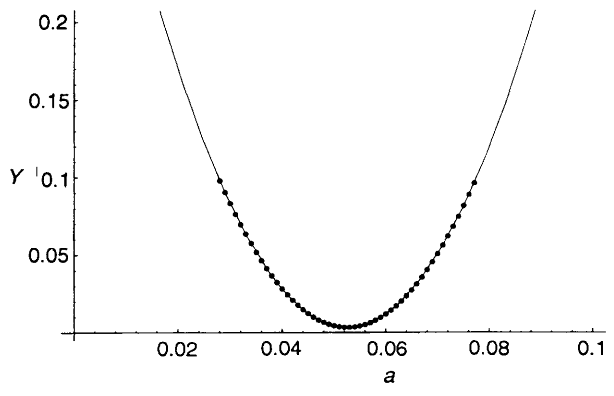

Fig. 2 Parabola obtained by evaluating Y as a function of a with minimum at $a = 0.00526$

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† For technical reasons, we have excluded the N_2^+ ($^2\Pi_u$) and SH_2^+ ($^1A_1$) ions from the G2 set.

Table 2 Mean absolute deviations of B–LYP and B–O(W) results from experiment

	E_{at}/kJ mol^{-1}	E_i/kJ mol^{-1}	E_{ea}/kJ mol^{-1}	E_{pa}/kJ mol^{-1}	$E_o{}^a$/kJ mol^{-1}
6-31 + G(d):					
B–O(W)	23.39	22.15	15.30	10.08	20.60
B–LYP	18.80	17.92	12.55	18.09	17.27
6-311 + G(3df,2p):					
B–O(W)	28.40	22.42	13.29	7.86	22.34
B–LYP	19.51	18.69	10.15	8.17	16.72

[a] Overall energy.

B–W density functional. No optimisation was attempted in this study. The parameters $b = 0.0042$, $a = 0.04918$ and $d = 0.349$ were retained from the more elaborate B–LYP functional. We give results for both the 6-31 + G(d) and 6-311 + G(3df,2p) basis sets in Tables 3–7. The deviation from experiment is defined as $\Delta E^{\text{theory}} - \Delta E^{\text{expt}}$ (*i.e.* the result predicted by the DFT minus the experimentally determined result) and is a measure of the predictive power of the functional.

Table 3 shows the deviations from experiment of the 56 atomisation energies studied. We affirm the findings of other researchers:[4] an increase in the size of the basis set used does not always lead to a more accurate predicted chemistry. In approximately half of the cases studied, for both the B–W and the B–LYP functionals, use of the larger basis set leads to greater errors in predicted atomisation energies, implying that in these cases errors introduced by a limited basis set are cancelled by errors in the density functionals themselves. We find significant differences between B–W and B–LYP in the prediction of specific atomisation energies. Each of these differences must be directly attributable to the inclusion of the non-Wigner terms of the LYP functional. The B–LYP functional is known to perform relatively poorly for systems with multiple bonds.[8] We see that both functionals produce large errors (greater than 25 kJ mol^{-1}) for most molecules containing nitrogen, although B–LYP is usually nearer the mark than B–W for such compounds. However, B–W outperforms B–LYP in the prediction of atomisation energies of carbonyl-like molecules: formaldehyde, CO, CO_2 and HCO, as well as most of the sulfur and silicon-based compounds. Interestingly, for both functionals, there is difference of *ca.* 42 kJ mol^{-1} between the deviations in diatomic halogens Cl_2 and F_2. For B–W this energy difference manifests as a 22 kJ under-binding of Cl_2 and an over-binding of F_2 by a similar amount, while B–LYP achieves a near perfect description of chlorine dissociation, but overbinds fluorine by more than 40 kJ mol^{-1}. The largest atomisation energy error for B–W with the large basis set is 64 kJ mol^{-1} (N_2) and that for B–LYP is also 64 kJ mol^{-1} (O_2).

Deviations of ionisation potentials are given in Table 4. As with atomisation energies, errors in the functionals can be seen to compensate for basis set incompleteness. An examination of the figures for the 6-311 + G(3df,2p) basis set shows that in the majority of cases ionisation potentials are underestimated by both functionals. B–W predicts a lower ionisation potential than B–LYP in all but a handful of cases (He and O are two notable exceptions). Both B–W and B–LYP produce their largest errors for atomic oxygen: 62 and 54 kJ mol^{-1}, respectively.

Table 5 shows electron affinity data. B–W tends to predict lower affinities than B–LYP. Although this feature is sometimes desirable (B–LYP overestimates electron affinities in approximately half of the molecules studied), it is disastrous when B–LYP predicts a sub-experimental result. Neither functional is able to predict the electron affinity of the Cl_2 molecule adequately, large basis set notwithstanding.

Table 3 Deviations from experimental atomisation energies (in kJ mol^{-1})

	6-31 + G(d)		6-311 + G(3df,2p)	
molecule	B–W	B–LYP	B–W	B–LYP
BeH	32.59	29.18	33.85	31.10
CH	16.09	1.16	21.92	7.56
$CH_2(^1A_1)$	5.88	−16.76	18.69	−2.66
$CH_2(^3B_1)$	−6.85	−7.77	0.30	0.04
CH_3	0.53	−6.49	8.29	1.89
CH_3Cl	−45.36	−29.87	−31.46	−15.43
CH_3SH	−53.27	−46.30	−29.64	−21.24
CH_4	−5.65	−16.18	0.02	−9.97
Cl_2	−51.95	−32.10	−21.57	−1.25
ClF	−18.95	3.56	1.03	23.57
ClH	−24.90	−27.04	−4.62	−6.30
ClO	−4.01	14.62	25.42	44.45
CN	12.03	15.49	38.26	43.21
CO	−19.91	−10.28	3.13	13.43
CO_2	−28.01	11.72	12.81	52.91
F_2	17.65	37.99	20.84	40.72
FH	−25.11	−22.13	−1.18	1.89
H_2	29.27	0.57	28.89	0.96
H_2CCH_2	−41.19	−29.13	−20.91	−7.27
H_2OO	−7.07	4.10	9.35	20.89
H_2NNH_2	12.76	0.55	50.12	40.31
H_3CCH_3	−49.88	−39.74	−39.22	−27.99
H_3COH	−42.25	−28.84	−16.20	−1.91
HCCH	−49.19	−35.16	−16.84	−1.01
HCN	12.14	8.71	37.15	35.09
HCO	0.78	18.63	21.40	40.01
HOCl	−33.27	−16.98	1.61	18.67
HOOH	−13.81	−2.13	19.00	31.33
Li_2	−19.87	−17.62	−17.46	−15.22
LiF	−27.02	−9.59	−11.91	6.43
LiH	10.26	−4.19	14.53	0.22
N_2	39.89	18.72	64.04	44.12
Na_2	−3.47	2.83	−1.27	5.10
NaCl	−39.64	−30.92	−32.03	−23.78
NH	28.47	14.84	38.54	25.23
NH_2	31.38	10.74	53.23	33.66
NH_3	9.63	−10.77	37.25	18.19
NO	34.26	35.56	55.62	57.57
O_2	32.13	54.75	41.48	63.94
OH	3.11	−3.03	20.08	14.25
OH_2	−27.23	−31.77	6.67	2.75
P_2	2.21	−10.47	31.27	20.48
PH_2	25.20	2.76	41.22	20.13
PH_3	10.68	−18.26	30.32	2.94
S_2	−26.13	−7.76	3.94	23.30
SC	−21.61	−15.25	−2.11	5.05
SH_2	−19.41	−31.63	4.09	−7.10
Si_2	−13.95	−8.09	−0.60	−5.96
Si_2H_6	−24.27	−55.41	−13.20	−42.77
$SiH_2(^1A_1)$	18.01	−6.19	24.03	0.87
$SiH_2(^3B_1)$	3.83	−7.29	8.81	−1.64
SiH_3	3.05	−18.55	9.60	−11.23
SiH_4	6.66	−24.96	13.59	−17.19
SiO	−24.73	−14.91	−0.28	10.63
SO	−17.41	4.55	17.55	40.36
SO_2	−106.54	−68.24	−10.08	29.59

Table 4 Deviations from experimental ionisation potentials (in kJ mol^{-1})

	6-31 + G(d)		6-311 + G(3df,2p)	
molecule	B–W	B–LYP	B–W	B–LYP
Al	−20.84	−10.15	−21.61	−10.66
Ar	−20.85	−11.22	−23.90	−14.44
B	8.93	26.01	13.27	31.32
Be	−31.76	−32.26	−32.11	−32.62
C	−10.25	12.46	−8.72	14.23
CH_4	−16.82	−12.75	−27.61	−24.10
Cl	−8.90	−6.31	−8.74	−5.97
Cl_2	−36.79	−28.67	−50.31	−42.29
ClF	−25.31	−18.13	−38.71	−32.00
ClH	−27.38	−19.22	−25.98	−17.71
CO	−2.37	−1.22	−10.62	−9.46
F	29.42	31.57	28.16	30.54
FH	−17.66	−7.26	−10.08	0.17
H_2CCH_2	−51.51	−34.04	−40.15	−22.17
HCCH	−53.51	−38.41	−42.32	−26.70
He	49.26	11.53	56.52	19.37
Li	0.94	12.88	0.10	12.14
Mg	−10.66	−1.70	−10.68	−1.71
N	−23.99	1.25	−27.72	−2.58
$N_2(^2\Sigma_g)$	−33.29	−23.45	−31.49	−21.27
Na	1.07	18.13	3.03	20.49
Ne	8.32	21.00	2.19	14.53
NH_3	−24.66	−17.87	−13.20	−5.87
O	60.87	52.49	62.05	54.09
O_2	18.99	45.72	11.33	38.38
OH	10.16	10.55	16.59	17.47
OH_2	−25.42	−16.57	−15.63	−6.59
P	−45.19	−27.95	−46.87	−30.02
P_2	−43.88	−31.08	−50.65	−37.80
PH	−33.74	−14.16	−35.38	−16.33
PH_2	−24.83	−4.84	−26.04	−5.90
PH_3	−22.92	−17.74	−20.59	−14.68
S	5.60	0.83	8.80	4.71
S_2	−16.57	2.02	−26.89	−8.07
SC	5.91	5.68	−5.34	−5.98
SH	−10.00	−8.96	−6.73	−4.80
$SH_2(^2B_1)$	−29.66	−23.00	−26.63	−19.48
Si	−33.83	−19.17	−34.54	−20.02
SiH_4	−26.15	−20.52	−37.46	−32.33

Table 5 Deviations from experimental electron affinities (in kJ mol^{-1})

	6-31 + G(d)		6-311 + G(3df, 2p)	
molecule	B–W	B–LYP	B–W	B–LYP
C	−6.98	7.01	−8.70	5.36
CH	−11.85	6.61	−11.23	7.29
CH_2	8.09	7.04	15.51	15.19
CH_3	−18.40	−13.74	−9.95	−4.37
Cl	−9.41	−1.18	−12.16	−4.31
Cl_2	63.08	66.15	33.97	36.38
CN	2.49	5.54	−3.38	−0.47
F	9.86	21.03	4.68	15.30
NH	6.43	6.28	11.79	12.30
NH_2	−15.19	−8.04	−7.39	0.20
NO	18.08	35.78	4.12	21.80
O	23.92	25.40	22.12	23.54
O_2	13.33	13.43	5.72	5.84
OH	−10.98	−2.19	−7.65	1.16
P	13.67	9.43	15.77	12.08
PH	−1.86	−1.38	0.22	1.44
PH_2	−16.90	−11.64	−15.17	−9.43
PO	−10.57	4.69	−15.54	−0.22
S	1.79	3.48	0.79	2.58
S_2	−8.19	−6.30	−17.51	−15.69
SH	−13.84	−7.09	−14.56	−7.90
Si	−27.05	−18.08	−27.72	−18.98
SiH	−25.91	−13.95	−26.21	−14.60
SiH_2	−21.63	−7.67	−21.23	−7.30
SiH_3	−15.14	−10.72	−14.82	−9.90

Table 6 Deviations from experimental proton affinities (in kJ mol^{-1})

	6-31 + G(d)		6-311 + G(3df, 2p)	
molecule	B–W	B–LYP	B–W	B–LYP
ClH	−12.85	−23.52	7.21	−3.36
H_2	−36.58	−44.67	−5.75	−12.93
HCCH	7.87	−2.16	13.79	3.62
NH_3	3.70	−4.64	−1.15	−10.03
OH_2	−15.16	−22.24	−9.21	−16.22
PH_3	−3.33	−16.47	1.86	−12.28
SH_2	−2.54	−14.09	5.73	−6.18
SiH_4	−0.86	−16.92	16.44	0.74

The set of proton affinities (Table 6) is too small for any general trends to be apparent. However, we may observe that for the HCCH, SiH_4 and SH_2 molecules, moving to a larger basis set improves the estimate of B–LYP but impairs the performance of B–W. Conversely, in the case of the ammonia molecule, B–W benefits and B–LYP is hindered by extension of the basis set. This suggests that the B–W and B–LYP functionals suffer from different deficiencies.

A summary of mean absolute deviations from experiment is given in Table 7. It is apparent that, within a large basis set, B–W affords comparable (within 3 kJ mol^{-1}) overall accuracy to B–LYP. It is interesting to compare the results of Tables 2 and 7. The deviations of Table 2 were achieved by optimising the performance of the B–W functional for first-row atomic energies, yet the unoptimised functional (Table 7) gives closer agreement to experimental results. It appears that fitting density functional parameters to atomic data is an imperfect method of optimisation.

Conclusion

The B–W functional, constructed by removing from B–LYP all but the first term of the LYP correlation functional, yields an overall performance comparable to, but without the complexity of, B–LYP. The B–W functional is the simplest high-quality density functional hitherto discovered and, as such, may constitute a useful starting point for the development of still better ones.

Table 7 Mean absolute deviations of B–LYP and B–W results from experiment

	E_{at}/kJ mol^{-1}	E_i/kJ mol^{-1}	E_{ea}/kJ mol^{-1}	E_{pa}/kJ mol^{-1}	$E_o{}^a$/kJ mol^{-1}
6-31 + G(d):					
B–W	23.04	23.80	14.98	10.36	20.91
B–LYP	18.80	17.92	12.55	18.09	17.27
6-311 + G(3df, 2p):					
B–W	20.33	24.58	13.12	7.64	19.42
B–LYP	19.51	18.69	10.15	8.17	16.72

[a] Overall energy.

While similar in overall agreement, the B–W and B–LYP functionals behave very differently in the prediction of individual molecular data. This suggests that, although the non-Wigner terms of the LYP correlation functional provide significant contributions to the predicted energy barriers of unimolecular chemistry, they have little overall value as their contributions are as often detrimental as advantageous.

Density functionals whose parameters are chosen to perform well for atoms may be less successful in predicting the chemistry of molecules. While it is true that the Becke *b* is determined from the noble gases helium to radon, and the Wigner *a* and *d* parameters are from helium, there is a limit to the extent that molecular functionals can be derived entirely from atomic data.

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