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Exchange-Correlation Functional with Broad Accuracy for Metallic and Nonmetallic Compounds, Kinetics, and Noncovalent Interactions

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Abstract. By incorporating kinetic energy density in a balanced way in the exchange and correlational functionals and removing self-correlation effects, we have designed a density functional that is broadly applicable to organometallic, inorganometallic, and nonmetallic bonding, thermochemistry, thermochemical kinetics, and noncovalent interactions as well as satisfying the uniform electron gas limit. The average error is reduced by a factor of 1.3 compared to the best previously available functionals, but even more significantly, we find a functional that has high accuracy for all four categories of interaction.

Although the density functional theory (DFT) of electronic structure was developed 40 years ago, progress was slow until the development of modern functionals in the last 20 years (*1,2*). Now density functional theory is the method of choice for most applications involving metals, catalysis, dynamics, nanotechnology, and large or complex molecules. The key to progress is the design of new functionals incorporating correct mathematical properties and improved physical descriptions of exchange and correlation (*3–16*) and stringently testing them against well validated, diverse, and representative data. Although a few density functionals are determined entirely from first principles, most successful functionals in chemistry have the values of one or more parameters determined by fitting (*4,5,7–9,12–14,17–28*). None of the available functionals, though, is universally accurate. The variables used to construct most functionals are the local spin density ρ_σ, its gradient $\nabla\rho_\sigma$, and two quantities that can be constructed from the Kohn-Sham orbitals: Hartree-Fock (HF) exchange and, most recently, kinetic energy density, represented here by the variable called τ_σ which equals the kinetic energy density for spin σ, where $\sigma = \alpha$ (up) or β (down).

Local spin density approximations lead to significant overbinding of molecules and solids (*1*). Although this is largely corrected by including $\nabla\rho_\sigma$ for metals or including $\nabla\rho_\sigma$ and 20–25% HF exchange for molecules, chemical reaction barrier heights are still systematically underestimated. The results can be improved by using ~40% HF exchange (*22*). However including even much smaller amounts of Hartree-Fock exchange (> 10%) degrades the accuracy of many metal-metal (*29*) and metal-ligand (*30*) bond energies. Thus for systems like metalloenzymes, heterogeneous and homogeneous catalysts involving metals or metal compounds, and nanotechnological devices with metalorganic components, one cannot achieve a uniformly satisfactory description of all bonds in the system. Furthermore, only very recently have functionals been obtained that give satisfactory practical accuracy for weak dispersion-like interactions (*19,27,28*).

Many different aspects of density functionals have been singled out in trying to understand these performance issues. In wave function theory (WFT), both electron exchange and electron correlation require at least two electrons, but most density functionals include artificial and incorrect self-exchange and self-correlation. Since kinetic energy density, in conjunction with $\nabla\rho_\sigma$, can "detect" one-electron regions (*13*), one hopes it can be used to ameliorate these problems. However, so far, kinetic energy density has usually been included separately in either the exchange (*24,26*) or correlation (*9,28*) functional, whereas a more balanced treatment may be required (*15*). This requirement is signaled by the fact that DFT exchange potentials include some effects that appear in WFT as correlation (*14,31*), in particular static correlation (also called near-degeneracy correlation). It is sometimes stated that one could include a larger fraction of self-exchange-free Hartree-Fock exchange if one had a more accurate correlation functionals (*16*), but with an inaccurate correlation functional, one cannot replace local exchange by Hartree-Fock exchange because most correlation functionals are more compatible (due to cancellation of errors) with local exchange calculated from ρ_σ and $\nabla\rho_\sigma$ than with HF exchange (*2,16,31*). In the present work we present a more complete treatment of kinetic energy density in the exchange and correlation functionals.

We begin with the PBE (*11*) exchange functional, $F_{X\sigma}^{\mathrm{PBE}}$. This is a theoretically sound starting point because it satisfies the correct uniform electron gas (UEG) limit and also has a reasonable form at large values of the reduced density x_σ (which equals $\left.|\nabla\rho_\sigma|\right/\rho_\sigma^{4/3}$), which is important for treating noncovalent interactions (*19,27,28*). The exchange energy is then approximated as

$$E_x^{(0)} = \sum_\sigma \int d\mathbf{r} \; F_{X\sigma}^{\mathrm{PBE}}\left(\rho_\sigma,\nabla\rho_\sigma\right)\left(\sum_{i=0}^{m} a_i w_\sigma^i\right) \tag{1}$$

where w_σ is the function of τ_σ suggested by Becke (*14*) because it reduces to 0 for a uniform electron gas, but becomes negative in regions of delocalized one-electron exchange holes. The static correlation contribution to the exchange functional must be

different in such negative-w_σ regions, typically associated with fractionally occupied single orbitals, then in more typical regions where $w_\sigma \approx 1$. Since we do not know the dependence on w_σ *a priori*, we take the coefficients a_i as fitting parameters. We require $a_i = 1$ to constrain the exchange functional to have the correct UEG limit. The power series in eq. (1) is similar to that employed by Becke (*13*) in earlier work with older expressions for $F_{X\sigma}$ and w_σ, but we changed the form and use more terms in the series. The motivation here is that combining a very flexible representation of inhomogeneity with a well validated function of ρ_σ and $\nabla\rho_\sigma$ can lead to a more accurate exchange functional that corrects the treatment of delocalization, thereby requiring less cancellation of errors by the correlation functional. However, as first pointed by Becke (7), the density-based exchange is still not correct for weak electron-electron coupling, and this can be corrected (*2,7,9,14,17*) by mixing in a small percentage X of HF exchange:

$$E_X = \left(1 - \frac{X}{100}\right) E_X^{(0)} + \frac{X}{100} E_X^{HF} \tag{2}$$

The correlation energy is a sum of opposite-spin and same-spin components (*9,12,21,24–28*):

$$E_C = E_C^{opp}\left(\rho_\sigma, \nabla\rho_\sigma\right) + \sum_{\sigma=\alpha,\beta} E_C^{\sigma\sigma}\left(\rho, \nabla\rho_\sigma, \tau_\sigma\right)$$

The form of the opposite-spin functional is the same as used in the τHCTH (*24*) and BMK (*26*) functionals, and it contains five parameters $\gamma_{C\alpha\beta}$ and $c_{C\alpha\beta,i}$ with $i = 0,1,2,3,4$. The parallel-spin term is based on the work of Becke (*9, 12*), who introduced a parameter (*9*)

$$D_\sigma = 2\left(\tau_\sigma - \frac{|\nabla\rho_\sigma|^2}{8\rho_\sigma}\right)$$

and used $D_\sigma / D_\sigma^{UEG}$ to remove self-correlation error. In the present work we replace $D_\sigma / D_\sigma^{UEG}$ by the variable $D_\sigma / 2\tau_\sigma$ (also suggested by Becke (*13*) who relabels $2\tau_\sigma$ as τ_σ) because it eliminates the integration grid instabilities noted by Johnson *et al*. (*32*). The form of the $\nabla\rho$ dependence of $E_C^{\sigma\sigma}$ is the same as in the τHCTH and BMK

functionals and involves five parameters $\gamma_{C\sigma\sigma}$ and $c_{C\sigma\sigma, i}$, with $i = 0,1,2,3,4$. For both E_C^{opp} and $E_C^{\sigma\sigma}$, the $\nabla\rho$ dependence differs from the original formulation of Becke (12) by increasing the number of terms in a power series from three to four and in that we require $c_{C\alpha\beta, 0} = c_{C\sigma\sigma, 0} = 1$. In agreement with the philosophy of the B95 functional (9), this forces the correlation functionals to have the correct UEG limit, which is not enforced in a considerable body of work (12,21,23,24,26) using similar correlation functionals. (The new correlation functional also differs from the τHCTH and BMK functionals by including the $D_\sigma/2\tau_\sigma$ factor for the parallel-spin case.) In addition to giving the correct UEG limit, our correlation functionals has two other theoretically important features: a rational polynomial in $\nabla\rho$ that accounts for the leading inhomogeneity correction to the correlation energy and a τ-dependent factor that eliminates self-correlation energy.

Following Becke (13), we pre-optimized the γ parameters to the correlation energies of He and Ne in a preliminary fit. All other parameters were optimized with a genetic algorithm to minimize the training function

$$F = \text{RMSEPB(AE6)} + \text{RMSE(IPEA8)}$$
$$+ \text{RMSE(K9)} + 10\text{RMSE(NB4)}$$
$$+ 0.2\,\text{RMSE(AAE5)} + \text{RMSE(MBE3)}$$

The first term is the root-mean-square error (RMSE) per bond in the atomization energies of propyne (C_3H_4), cyclobutane (C_4H_8), glyoxal ($C_2H_2O_2$), silane (SiH_4), silicon dioxide (SiO_2), and disulfur (S_2). The second term is the RMSE for the ionization potentials of C, Cr, Cu, O, and OH and the electron affinities of C, O, and OH. The third term is the RMSE for the forward and reverse barrier heights and energies of reaction of $H + OH \rightarrow O + H_2$, $OH + CH_4 \rightarrow H_2O + CH_3$, and $H + H_2S \rightarrow H_2 + HS$. The fourth term is ten times the RMSE for four noncovalent complexation energies: $(H_2O)_2$, $(CH_4)_2$, $(C_2H_4)_2$, and $(C_2H_4)(F_2)$. The fifth terms is 0.2 times the RMSE in the absolute energies of H, C, O, S, and Si. The sixth term is the RMSE of the bond energies of Cr_2 and V_2 and the Cr–

C bond of $CrCH_3^+$. Thus the training set consists of 35 data. References for training set data are in supporting information.

Geometries and the treatment of spin-orbit terms are explained in previous papers (*28–30*). During parametrization, we used the DZQ basis set (*29*) for the calculations involving transition metals and the MG3S basis set (*33*) for other calculations. We used $m = 11$. The optimized parameters are in Table 1.

To assess the accuracy of the resulting density functional, we tested the results against a much larger set of 231 data. To gauge the performance for main group thermochemistry we use the mean unsigned error (MUE) on 135 data consisting of the MGAE109/04 database of 109 main-group atomization energy, the IP13/3 database of 13 main-group ionization potentials, and the AE13/3 database of 13 main-group electron affinities; this is called TMUE. For kinetics we use the average MUE of 38 chemical barrier heights and 19 energies of reaction of 19 hydrogen atom transfer reactions in the HTBH38/04 database; this is called AMUE. For noncovalent interactions, the question of whether to include counterpoise (CP) corrections for basis set superposition error is controversial. Because it is important to obtain accurate results both in cases where it is used to improve performance and in cases (e.g., condensed phases) where it is impractical and because CP corrections often overestimate the correction, we measure performance on noncovalent interactions by

$$\text{MMMUE} \equiv [\text{MMUE(no-CP)} + \text{MMUE(CP)}]/2$$

where each MMUE is averaged over individual MUEs for five kinds of noncovalent interaction represented by the HB6/04, CT7/04, DI6/04, WI7/05, and PPS5/05 databases of noncovalent complexation energies for, respectively, 6 hydrogen bonding dimers, 7 charge transfer complexes, 6 dipole interaction energies, 7 weakly bound dimers governed by dispersion-like interactions, and 5 $\pi-\pi$ stacking complexes. Performance for metals is the average of the mean unsigned errors for the TMAE9/05 database of 9 transition metal dimer atomization energies and the MLBE22/05 database of 22 metal-

ligand bond energies. This was further averaged over the DZQ and TZQ (*29*) bases sets; this average is called MMUE. References for databases, counterpoise corrections, and software are in supporting information (*34*).

Results. Table 2 shows the results for the four error quantities and compares them to 16 of the most popular and best performing density functionals in the literature. For this purpose the results are divided into groups depending on the variables included in the functional. For each of the four categories of interaction we have put the results for the four best performing functionals in bold. The new functional, denoted M05 (for Minnesota 2005), is in the top four in all four categories, and it is the only functional to appear in the top 4 in more than two categories. The simultaneous good performance for kinetics (barriers) and metallic binding is especially encouraging; no previous functional with Hartree-Fock exchange has ever performed well for metals, and no functional without Hartree-Fock exchange has ever performed well for hydrogen transfer barrier heights. The second last column of Table 2 is an average of the four mean unsigned errors. The M05 functional has an average error 1.3 times smaller than the second best performing method (B97-2). Because the errors for metal binding are much larger than the others, we also computed a weighted average where each error is divided by the average error of all 17 functionals for that quantity; this is shown in the last column. With this fitness function, the M05 functional performs 1.4 times better than the second best performing functional (which is now PW6B95).

We found that we could obtain very similar results (average error increases to only 2.53 kcal/mol and the scaled average to 0.44) by employing the same procedure with $m = 10$, $X = 30$, and the PBE exchange functional replaced by the mPW (*19*) one, which is based on the earlier B88 (*5*) and PW91 (*10*) functionals. Thus the treatment of kinetic energy density and optimization of the correlation functional for complementarity to a given exchange functional are the key ingredients in the new functional, not the precise choice of $F_{X\sigma}$.

We checked that we obtain relatively good results for dipole moments as well as dipole-bound complexes (*34*).

We conclude that the new treatments of the exchange and correlation functionals are well balanced in a way that allows accurate Hartree-Fock exchange to be included even for systems with large static correlation. For broad accuracy across the four properties tested (nonmetallic and metallic thermochemistry of molecules, chemical reaction barriers, and noncovalent interaction energies) the new density functional outperforms all previously available density functionals by a significant margin.

1. W. Kohn, A. D. Becke, and R. G. Parr, *J. Phys. Chem.* **100**, 12974 (1996).

2. J. Perdew, in *Density Functional Theory*, edited by P. Geerlings, F. DeProft, and W. Langenaeker (VUB Press, Brussels, 1999), pp. 87–109.

3. J. P. Perdew, *Phys. Rev. B* **33**, 8822 (1986).

4. A. D. Becke, *Phys. Rev. A* **38**, 3098 (1988).

5. C. Lee, W. Yang, and R. G. Parr, *Phys. Rev. B* **37**, 785 (1988).

6. J. P. Perdew and Y. Wang, *Phys. Rev. B* **45**, 13244 (1992).

7. A. D. Becke, *J. Chem. Phys.* **98**, 1372 (1993).

8. P. W. M. Gill, *Mol. Phys.* **89**, 433 (1996).

9. A. D. Becke, *J. Chem. Phys.* **104**, 1040 (1996).

10. J. P. Perdew, K. Burke, and Y. Wang, *Phys. Rev. B* **54**, 16533 (1996).

11. J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996), **78**, 1396(E) (1997).

12. A. D. Becke, *J. Chem. Phys.* **107**, 8554 (1997).

13. A. D. Becke, *J. Chem. Phys.* **109**, 2092 (1998).

14. A. D. Becke, *J. Chem. Phys.* **112**, 4020 (2000).

15. J. Tao, J. P. Perdew, V. N. Staroverov, and G. E. Scuseria, *Phys. Rev. Lett.* **91**, 146401 (2003).

16. A. D. Becke, *J. Chem. Phys.* **122**, 64101 (2005).

17. A. D. Becke, *J. Chem. Phys.* **98**, 5648 (1993).

18. P. J. Stephens, F. J. Devlin, C. F. Chabalowski, and M. J. Frisch, *J. Phys. Chem.* **98**, 11623 (1994).

19. C. Adamo and V. Barone, *J. Chem. Phys.* **108**, 664 (1998).

20. H. L. Schmider and A. D. Becke, *J. Chem. Phys.* **108**, 9624 (1998).

21. F. A. Hamprecht, A. J. Cohen, D. J. Tozer, and N. C. Handy, *J. Chem. Phys.* **109**, 6264 (1998).

22. B. J. Lynch, P. L. Fast, M. Harris, and D. G. Truhlar, *J. Phys. Chem. A* **104**, 4811 (2000).

23. P. J. Wilson, T. J. Bradley, and D. J. Tozer, *J. Chem. Phys*. **115**, 9233 (2001).

24. A. D. Boese and N. C. Handy, *J. Chem. Phys*. **116**, 9559 (2002).

25. V. N. Staroverov, G. E. Scuseria, J. Tao, and J. P. Perdew, *J. Chem. Phys*. **119**, 12129 (2003).

26. A. D. Boese and J. M. L. Martin, *J. Chem. Phys*. **121**, 3405 (2004).

27. Y. Zhao and D. G. Truhlar, *J. Phys. Chem. A* **108**, 6908 (2004).

28. Y. Zhao and D. G. Truhlar, *J. Phys. Chem. A* **109**, 5656 (2005).

29. N. E. Schultz, Y. Zhao, and D. G. Truhlar, *J. Phys. Chem. A* **109**, 4388 (2005).

30. N. E. Schultz, Y. Zhao, and D. G. Truhlar, *J. Phys. Chem. A*, in press (2005).

31. T. A. Ziegler, *Chem. Rev*. **91**, 651 (1991).

32. E. R. Johnson, R. A. Wolkow, and G. A. DiLabio, *Chem. Phys. Lett*. **394**, 334 (2004).

33. B. J. Lynch, Y. Zhao, and D. G. Truhlar, *J. Phys. Chem. A* **107**, 1384 (2003).

34. See EPAPS Document No._____ for references for databases, counterpoise corrections, and software, for dipole moment results, for extra details on the errors in noncovalent interactions, and for ethylene dimer potential. This document can be reached through a direct link in the online article's HTML reference section or via the EPAPS homepage (http://www.aip.org/pubservs/epaps.html).

Table 1. Optimized parameters (unitless).

a_i	1.0, 0.08151, −0.43956, −3.22422, 2.01819, 8.79431, −0.00295, 9.82029, −4.82351, −48.17574, 3.64802, 34.02248
$\gamma_{C\alpha\beta}$	0.0031
$c_{C\alpha\beta,i}$	1.0, 3.78569, −14.15261, −7.46589, 17.94491
$\gamma_{C\sigma\sigma}$	0.06
$c_{C\sigma\sigma,i}$	1.0, 3.77344, −26.04463, 30.69913, −9.22695
X	28

Table 2. Mean unsigned errors in kcal/mol.[a]

Method	Ref.	Thermochemistry TMUE	Kinetics AMUE	Nonbonded interactions MMMUE	Metal binding MMUE	Straight average[b]	Weighted average[c]
ρ_σ, $\nabla\rho_\sigma$, τ_σ in E and C, HF in E							
M05	present	**0.99**	**1.39**	**0.52**	**6.53**	**2.36**	**0.43**
TPSSh	25	1.37	4.31	1.05	9.45	4.05	0.83
ρ_σ, $\nabla\rho_\sigma$, τ_σ in C, HF in E							
PW6B95	28	**0.81**	1.99	**0.62**	13.87	4.32	**0.61**
B1B95	9	**0.96**	**1.79**	1.25	14.78	4.69	0.76
PWB6K	28	1.72	**1.42**	**0.38**	23.77[d]	6.82	0.81
ρ_σ, $\nabla\rho_\sigma$, τ_σ in E, HF in E							
BMK	26	**0.94**	**1.08**	1.10	27.27[d]	7.60	0.92
ρ_σ, $\nabla\rho_\sigma$, HF in E							
B97-2	23	1.02	2.16	1.23	7.55	**2.99**	**0.65**
B97-1	21	1.07	2.94	**0.71**	10.50	3.81	**0.66**
mPW1PW91	19	1.32	2.34	0.95	16.62	5.31	0.81
B3LYP	5,17,18	1.41	3.09	1.13	12.56	4.55	0.83
ρ_σ, $\nabla\rho_\sigma$, τ_σ in E and C							
TPSS	15	1.36	5.12	1.22	**7.41**	**3.78**	0.87
ρ_σ, $\nabla\rho_\sigma$, τ_σ in C							
BB95	9	2.40	4.89	1.67	11.58	5.14	1.14

$\rho_\sigma, \nabla\rho_\sigma$							
BLYP	4,5	1.93	4.90	1.63	**6.55**	**3.75**	0.99
mPWPW91	19	2.24	5.20	1.30	8.57	4.33	1.01
PBE	11	3.01	6.01	1.14	9.53	4.92	1.13
G96LYP	5,8	2.31	4.22	2.75	**6.44**	3.93	1.21
ρ_σ							
SPWL	6	14.70	12.05	2.18	26.87	13.95	3.33
average		2.33	3.82	1.23	12.93	5.08	1.00

[a] The four best entries in each column are in bold.

[b] (TMUE+AMUE+MMMUE+MMUE)/4

[c] ((TMUE/2.33)+(AMUE/3.82)+(MMMUE/1.23)+(MMUE/12.93))/4

[d] For PWB6K and BMK, this value was approximated as the average of the MUEs for TMAE4/05 and MLBE4/05 with the DZQ basis. For the other 15 cases, the MMUE for this smaller test set (29,30) and smaller basis (8 data, 8 calcuations) agrees with that for the larger test set (31 data, 62 calculations) with an average absolute deviation of only 8.9%.