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Investigation of Exchange Energy Density Functional Accuracy for Interacting Molecules

Éamonn D. Murray,* Kyuho Lee, and David C. Langreth

Department of Physics and Astronomy, Rutgers University, 136 Frelinghuysen Road, Piscataway, New Jersey 08854-8019

Abstract: We present a comparison of exchange-only interaction energies obtained using several standard exchange functionals in the generalized gradient approximation to Hartree−Fock results for interacting molecules. We observe that functionals with an enhancement factor using a 2/5 power dependence on the gradient of the density for large density gradients offer consistently better agreement with Hartree−Fock calculations than that of alternative functionals. We revisit the functional offering the closest agreement and recalculate it to include its exact large gradient dependence.

There has recently been a large interest and some progress in the treatment of van der Waals or dispersion interactions within or as an adjunct to density functional theory (DFT) calculations. These include empirical functionals,[1−4] a collection of methods of the DFT-D type,[5−9] a modified atomic potential method,[10−14] the Becke−Johnson method,[15−22] a nonempirical van der Waals density functional (vdW-DF)[23−28] and variants,[29] and a number of others.[30−43] The development and application of such methods are beginning to allow the application of density functional theory to new classes of matter and are of great importance. Some of these methods calculate the exchange energy within Hartree−Fock (HF), while others use some form of generalized gradient approximation (GGA). For the former, as the DFT methods for including dispersion become more efficient, one may look for a GGA method for replacing the less efficient HF part of the calculation. For the latter, one may also wish to find the GGA for exchange which best mimics HF. The evaluation of some of the common GGAs for exchange in comparison with HF is an aim of this work. As pointed out by Lacks and Gordon,[44] the functionals which are most accurate out on the long-range tail of the wave function and so important for van der Waals complexes may be quite different from those which are most successful for isolated molecules or dense condensed matter. A systematic study of the performance of exchange functionals for such systems of interest will be detailed here.

One important issue which is not addressed here is the compatibility of a particular exchange functional and the corresponding approximation for correlation. It is well-known that one of the reasons for the great success of DFT is the cancellation of errors between exchange and correlation. Each can have long-range parts which cancel in their sum, a fact that can be especially important for developing approximations for open shell systems. The sole criterion used in this work is how well each of the tested GGA exchange functionals reproduce the results of HF. The user will have to judge whether that is the correct criterion for the matching correlation approximation to be used.

We begin this paper with a brief description of the issue of spurious exchange binding and how it may be overcome by the generalized gradient approximation (GGA). This is followed by a summary of the exchange functionals we will be using in our calculations. These exchange functionals are: PBE,[45] revPBE,[46] PW86,[47] Becke86b,[48] and Becke88.[49] This is followed by a comparison of the calculated interaction energy as a function of molecular separation for pairs of molecules of various sizes. These calculations are performed using both HF and exchange-only density functional theory. The systems we examine are dimers consisting of pairs of the following atoms: H_2, N_2, CO_2, ammonia, methane, ethene, benzene and pyrazine. We conclude the paper with a re-examination of the PW86 functional, which, as we will show, offers the most consistent agreement with HF interaction energies. This work follows the pioneering work of Lacks and Gordon[44] and the recent work of Kannemann and

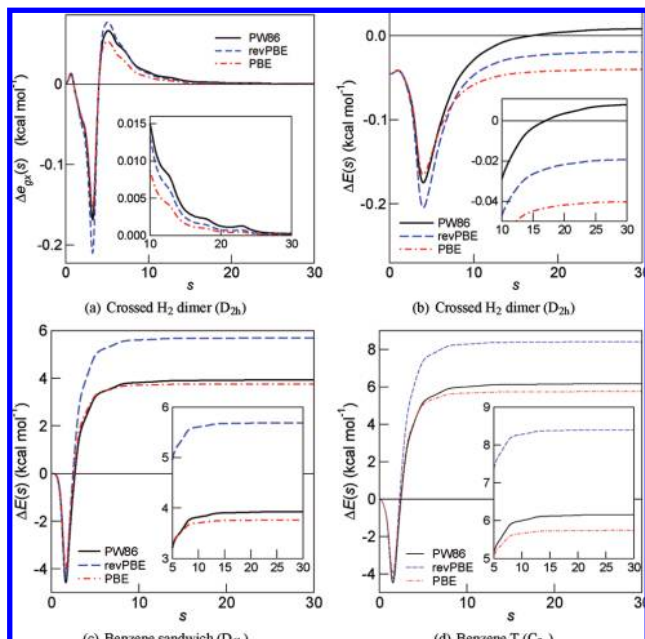* Corresponding author. E-mail: emurray@physics.rutgers.edu.

Figure 1. Large s contribution to exchange repulsion of (a–b) crossed H_2 dimer 4 Å apart, (c) parallel benzene molecules 3.75 Å apart, and (d) benzene molecules in the T configuration 5.0 Å apart. (a) The differential exchange energy of crossed H_2 dimer showing the *explicitly* gradient-dependent contribution to the exchange interaction energy from each s value. (b) The interaction energy $\Delta E(s)$ of the crossed H_2 dimer as a function of s, showing the convergence of the exchange energy as a function of s. Results obtained from PW86, revPBE, and PBE are compared. Note that, of these, only PW86 gives correct repulsive interaction (positive ΔE). (c–d) The interaction energy $\Delta E(s)$ of parallel benzene molecules and benzene molecules in the T configuration as a function of s, respectively.
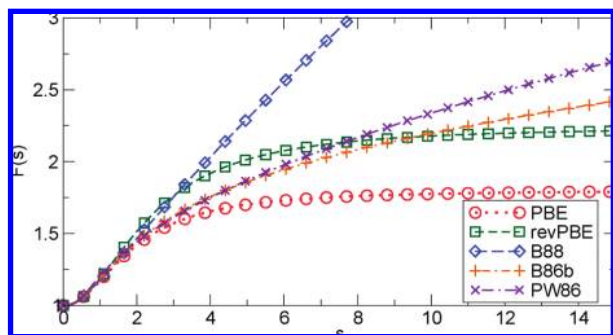

Figure 2. Enhancement factors $F(s)$ plotted for the exchange functionals discussed in this paper.

Becke,[50] who have come to a similar conclusion for the case of interacting rare gas atoms.

All of the exchange functionals discussed in this paper use the generalized gradient approximation (GGA) to exchange, so can be written in terms of an enhancement factor $F(s)$, where the exchange energy of a system with density $n(\mathbf{r})$ is given by

$$E_x^{GGA}[n(\mathbf{r}), \nabla n(\mathbf{r})] = A_x \int d^3r\, n^{4/3} F_x^{GGA}(s) \tag{1}$$

with $s = (\nabla n)/(2k_F n)$, where $k_F \equiv (3\pi^2 n)^{1/3}$ is the local Fermi wavevector, and $A_x = -(3/4)(3/\pi)^{1/3}$.

The issue of this spurious exchange binding has been studied previously by Harris[51] in the case of two interacting He atoms. In examining the system in terms of the first-order change in the potential due to the overlap in the densities:

$$M = \int d^3r\, \psi_{He}(\mathbf{r} - \mathbf{R}_1)\psi_{He}(\mathbf{r} - \mathbf{R}_2) \tag{2}$$

where $\mathbf{R}_1$ and $\mathbf{R}_2$ are the nuclear locations and

$$\psi_{He}(\mathbf{r}) = \frac{1}{\sqrt{2}} n^{1/2}(\mathbf{r}) \tag{3}$$

He noted that the leading contribution to the change in the energy comes from competition between the kinetic and the exchange–correlation terms. In HF, both the kinetic term, which is repulsive, and the exchange term, which is attractive, are proportional to M^2. This yields an interaction energy which is monotonic in $|\mathbf{R}_1 - \mathbf{R}_2|$ and always repulsive, and which may be written schematically as

$$\delta E \simeq (C_T^{HF} - C_x^{HF})M^2 \tag{4}$$

However, in the case of LDA, the exchange term is proportional to $M^{4/3}$, leading to a situation where LDA can yield an attractive interaction for small overlaps (small values of M), so that eq 4 is replaced by

$$\delta E \simeq C_T M^2 - C_x M^{4/3} \tag{5}$$

The second term of eq 5 dominates at large separations and gives spurious binding from exchange alone. This shortcoming of the LDA is generally counteracted to an extent by GGAs due to the enhancement factor, increasing the exchange contribution in regions of small density overlap. This is because an increasing density overlap decreases the value of s in the overlap region, thus reducing the enhancement of a negative contribution to the energy and thereby giving repulsion, which can compensate for the LDA's spurious attraction. However in a highly inhomogeneous region, a GGA functional whose enhancement factor becomes flat for large s will give an exchange energy with the same dependence on the overlap as in LDA, so that the LDA's spurious exchange binding will be exacerbated instead of ameliorated in regions of inhomogeneous low density.

In order to illustrate the importance of the asymptotic behavior of the enhancement factor $F_x(s)$ for large s, we analyze the gradient exchange energy contribution from each s for the case of the crossed H_2 dimer with the PBE, revPBE, and PW86 exchange functionals. In Figure 1(a), we show the *explicitly* gradient-dependent component of the differential exchange interaction energy:

$$\Delta e_{gx}(s) = e_{gx}^{2H_2}(s) - 2e_{gx}^{H_2}(s) \tag{6}$$

where the gradient component of the differential exchange energy $e_{gx}(s)$ is defined by

$$e_{gx}(s) = A_x \int d^3r\, n^{4/3}[F_x(s(\mathbf{r})) - 1]\delta(s - s(\mathbf{r})) \tag{7}$$
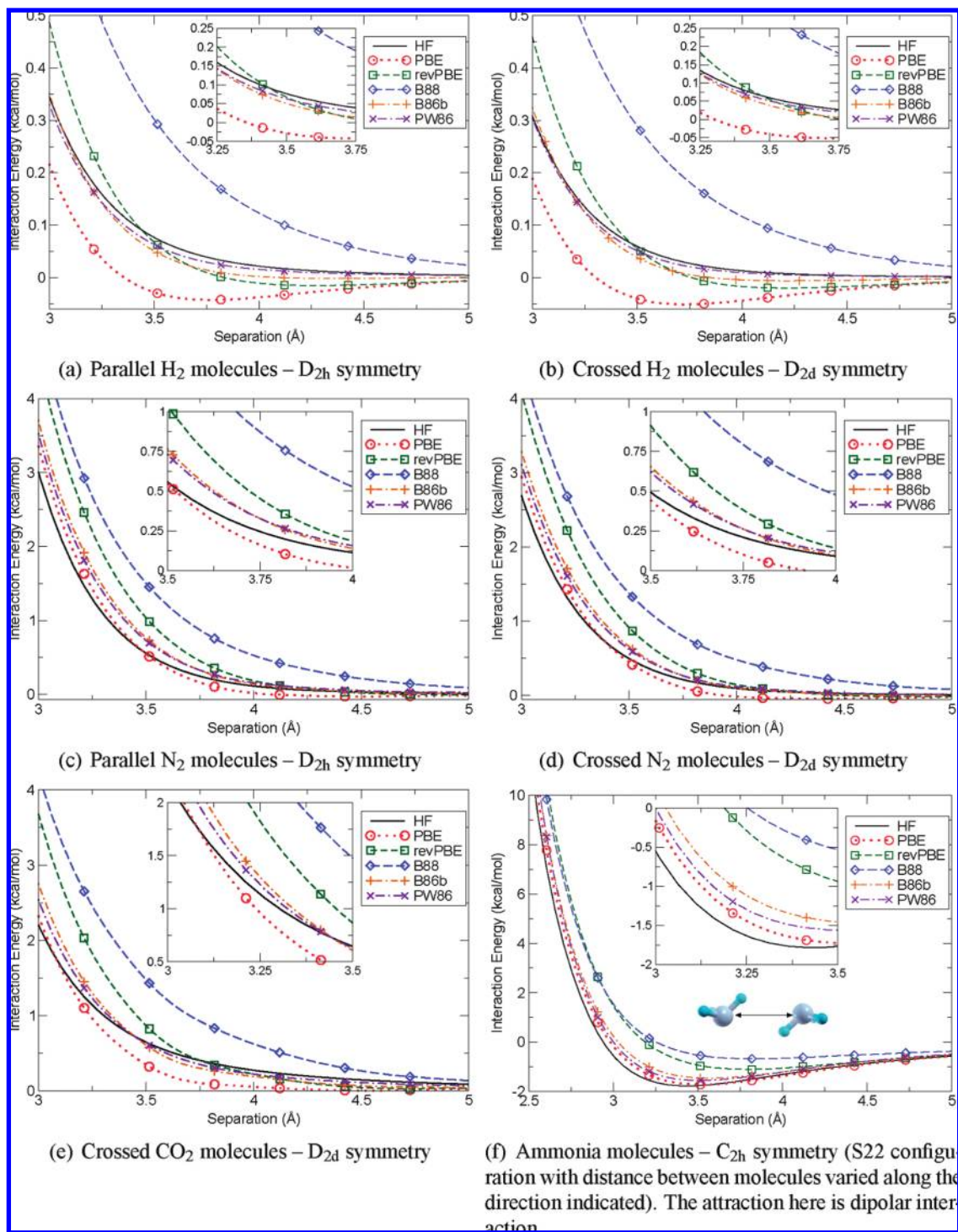
Figure 3. DFT exchange-only interaction energies calculated using several different exchange functionals compared to HF results for pairs of interacting molecules. Those structures marked as S22 use geometries taken from ref 58. The separations refer to the distance between the centers of mass of the molecules.

The term $\delta(s - s(\mathbf{r}))$ has been employed previously in ref 52. Note that in eq 7 the larger LDA component of the differential exchange energy:

$$e_{LDAx}(s) = A_x \int d^3r n^{4/3} \delta(s - s(\mathbf{r})) \qquad (8)$$

has been explicitly subtracted out, so that the difference between each GGA flavor is more visible. Figure 1(a) shows the contribution of gradient exchange energy $\Delta e_{gx}(s)$ to the interaction energy from each value of s.

By integrating $\Delta e_{gx}(s)$ over s and adding all the remaining energy terms ΔE_R, the interaction energy ΔE as a function of s is obtained, i.e.,

$$\Delta E(s) = \int_0^s ds' \Delta e_{gx}(s') + \Delta E_R \qquad (9)$$

Note that ΔE_R also contains the LDA exchange energy contribution arising from $\int_0^\infty ds e_{LDAx}(s)$. The convergence of interaction energy ΔE as a function of s is shown in
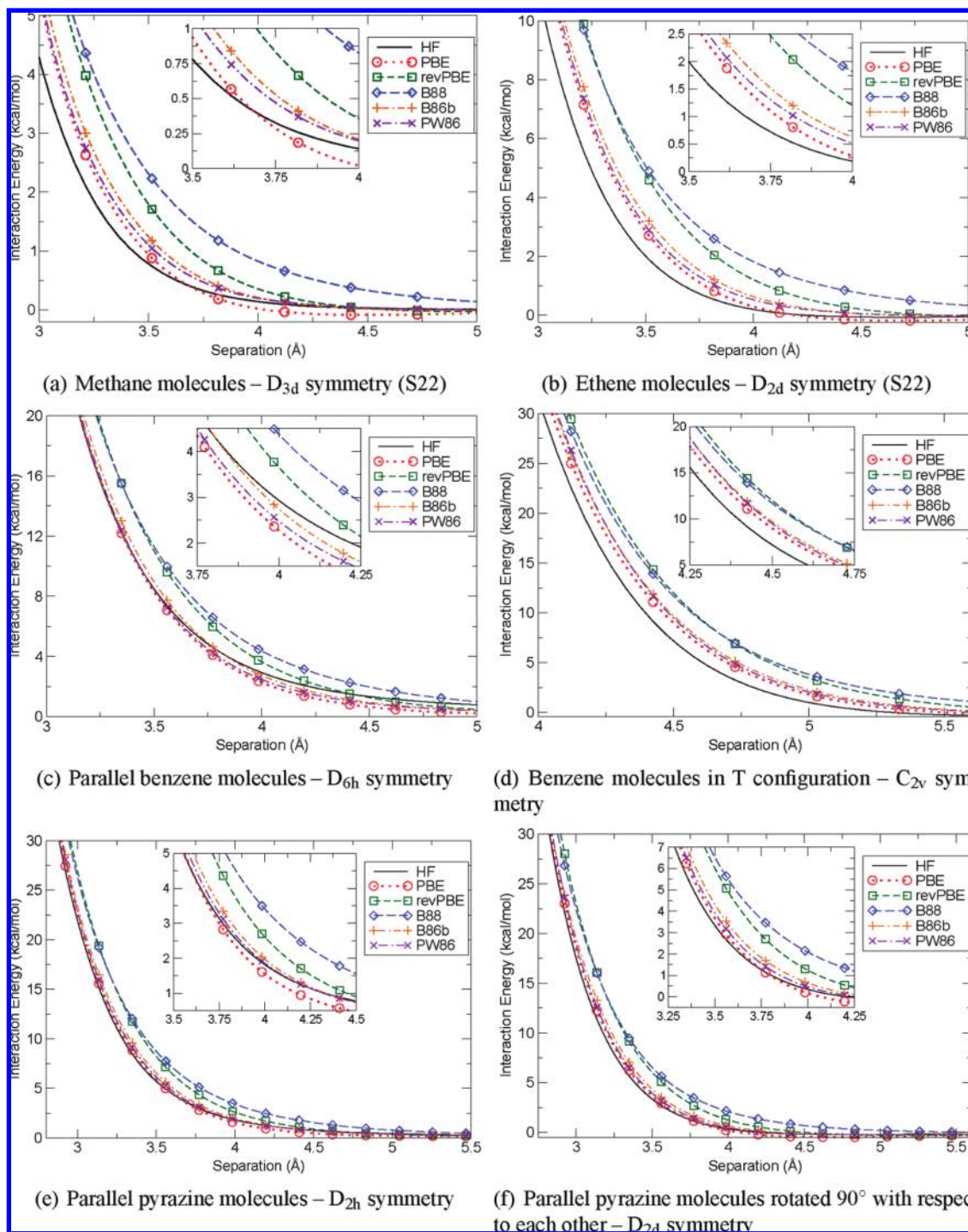
Figure 4. DFT exchange-only interaction energies calculated using several different exchange functionals compared to HF results for pairs of interacting molecules. Those structures marked as S22 use geometries taken from ref 58. The separations refer to the distance between the centers of mass of the molecules.

Figure 1(b). Note that $\Delta E(\infty)$ is equal to the total interaction energy.

From this it is clear that there is still a significant contribution for s as large as 25 in the H_2 dimer cases and 15 in the benzene cases. We also note that, as will be shown in our later calculations, the most consistent agreement with HF results is obtained from functionals with an enhancement factor proportional to $s^{2/5}$ at large s. Becke88, which is almost linear in s for large s, yields overly repulsive interaction energies in all cases. PBE and revPBE, which are constructed

to tend to a constant as s is increased yield spurious attractions in several cases.

The PBE and revPBE functionals use a form originally proposed by Becke[53] but with different parameters. The corresponding enhancement factor can be written as

$$F_x(s) = 1 + \frac{\mu s^2}{1 + \mu s^2/\kappa} \tag{10}$$

where both PBE and revPBE set $\mu = 0.2195$ to recover the expected low s limit. In PBE, κ is fixed to be 0.804 so the

local Lieb−Oxford bound is satisfied. This guarantees that the global Lieb−Oxford bound[54] will be satisfied for any possible density, even if the functional is not valid at that density. On the other hand, the other functionals discussed here may exceed the global bound for densities for which they are invalid. In the revPBE functional, this constraint is relaxed, and $\kappa = 1.245$ is obtained by fitting to atomic total energies. The PW86 enhancement factor is given by

$$F_x(s) = (1 + 15as^2 + bs^4 + cs^6)^{1/15} \quad (11)$$

with $a = 0.0864$, $b = 14$, and $c = 0.2$. The value of a was fixed to recover the then expected low-s dependence while b and c are obtained from a fit to the numerical solution of an integral derived from the gradient expansion of the exchange hole with real space cutoffs. The full derivation is discussed in more detail toward the end of this paper. The Becke86b functional was derived by considering highly inhomogeneous systems where it was shown that the large-s dependence of the enhancement factor should be $s^{2/5}$. Its final form was chosen so as to smoothly interpolate between this large s form and the expected small s form. It can be cast into a PBE-like enhancement factor as

$$F_x(s) = 1 + \frac{\mu s^2}{(1 + \mu s^2/\kappa)^{4/5}} \quad (12)$$

where $\mu = 0.2449$ and $\kappa = 0.5757$ are obtained by fitting to noble gas exchange energies. Finally, the Becke88 functional is constructed so as to reproduce the exact asymptotic behavior of a finite many electron system: $\lim_{r \to \infty} U_x^\sigma = -1/r$ with U_x^σ the Coulomb potential of exchange charge density $\rho_x^\sigma(r,r')$. One can also write this in a PBE-like form as

$$F_x(s) = 1 + \frac{\mu s^2}{1 + \frac{9}{4\pi}\mu s \sinh^{-1}(\lambda s)} \quad (13)$$

where $\lambda = 2(6\pi^2)^{1/3}$, and $\mu = 0.2743$ is found by fitting to noble gas exchange energies. $F(s)$ for each of these functionals is plotted in Figure 2.

Using each of these functionals, we calculate the exchange-only interaction as a function of separation for pairs of molecules. These calculations are performed using abinit,[55] a plane wave density functional theory code, and a 25 Ha

Figure 5. The exchange-only interaction energy for parallel N$_2$ molecules calculated using both the original and the refit PW86 functionals along with the HF results.

plane wave energy cutoff with the molecules placed in a 30 × 30 × 30 Bohr box (this is increased to 30 × 30 × 40 Bohr for the benzene and pyrazine systems). The corresponding HF calculations are performed using gamess.[56,57] In all of these calculations, the basis set superposition error is counterpoise corrected. All the systems are calculated using the aug-cc-pVTZ basis set with the exception of the benzene and the pyrazine systems, where the aug-cc-pVDZ basis is used. Testing indicates the error in the HF interaction due to use of the smaller basis set is ≲ 1% (see Supporting Information). In each case, we calculate the self-consistent interaction energy for the respective GGA functional and for HF. Because of the importance of the cancellation between kinetic and exchange energies discussed above and hence, preserving it in our comparisons, we believe this procedure is more relevant than a comparison of either exchange energies alone or post process calculations.

The results of these calculations are plotted in Figures 3 and 4. It is clear from the figures that both PW86 and Becke86b offer, for the most part, better agreement with HF than the other functionals, with PW86 performing slightly better. Both of these functionals are proportional to $s^{2/5}$ for large s, with $F_x^{PW86}(s) \sim 0.898s^{2/5}$ and $F_x^{B86b}(s) \sim 0.485s^{2/5}$. A similar conclusion has been reached in previous studies of rare gas diatomics by Lacks and Gordon[44] and more recently by Kannemann and Becke.[50] Here, we find that, while PW86 and Becke86b are consistently the best for systems dominated by large s, we found several cases where PBE was marginally better in the binding region. The error in the interaction energy ($Ex_{GGA} - E_{HF}$) for PBE, revPBE, PW86, and B86b compared to the accurate CCSD(T) calculations of the full binding energy at both the optimal separation and larger separations is shown in Table 1 for several systems. This gives a good indication of the effect on the binding energy of changing the GGA used in the calculation. It is also important to note that, as can be seen in the table, the PW86 functional is the only one of those tested that did not yield spurious exchange binding in any of the systems examined.

Of primary importance is the question of the true large s dependence of the integrals solved to obtain the PW86 functional. These are obtained from the expression for the gradient expansion of the exchange hole density:

$$n_x^{GEA}(\mathbf{r}, \mathbf{r} + \mathbf{R}) = -\frac{1}{2}n(\mathbf{r})y(\mathbf{r}, \mathbf{R}) \quad (14)$$

where

$$y = J + 4L\hat{\mathbf{R}} \cdot \mathbf{s}/3 - 16M(\hat{\mathbf{R}} \cdot \mathbf{s})^2/27 - 16Ns^2/3 \quad (15)$$

with

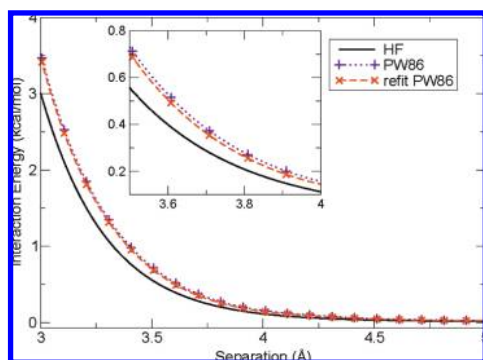$$J = 72[4 + z^2 - (4 - z^2)\cos z - 4z \sin z]z^6 \quad (16)$$

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$$L = 9(2 - 2\cos z - z\sin z)/z^3 \quad (17)$$

$$M = 9(-z\cos z + \sin z)/(16z) \quad (18)$$

$$N = 3[8 - (8 - 4z^2)\cos z - (8z - z^3)\sin z]/(16z^4) \quad (19)$$

and $z = 2k_F R$. In ref 47, it was observed that while n_x^{GEA} violates the following two conditions for exchange hole:

$$n_x(\mathbf{r}, \mathbf{r} + \mathbf{R}) \leq 0 \quad (20)$$

and

$$\int d^3 R n_x(\mathbf{r}, \mathbf{r} + \mathbf{R}) = -1 \quad (21)$$

these could be satisfied by applying cutoffs so that:

$$n_x^{GGA}(\mathbf{r}, \mathbf{r} + \mathbf{R}) = -\frac{1}{2}n(\mathbf{r})y\Theta(y)\Theta(R_c(\mathbf{r}) - R) \quad (22)$$

This yields

$$F_x^{GGA}(s) = \frac{1}{9}\int_0^{z_c} dz z y_{sa}(s, z) \quad (23)$$

where $z_c = 2k_f R_c$ and the spherical average (sa) of the positive part of y is

$$y_{sa}(s, z) = \frac{1}{4\pi}\int d\hat{\mathbf{R}} y\Theta(y) \quad (24)$$

It is possible to obtain an analytic expression for y_{sa}, which is given explicitly in ref 64. However, the value of $z_c(s)$ and the final value of $F_x(s)$ must be found numerically.

To obtain the exact large s behavior, it can be shown that as s becomes large, the value of $z_c(s)$ becomes small, allowing the expression for $y_{sa}(s,z)$ to be replaced by a power series expansion. Retaining the dominant term we obtain $y_{sa} = (s^2 z^2)/(27\sqrt{2})$. With this we can obtain the following analytic expressions for $z_c(s)$ and $F_x(s)$:

Table 1. Error in the Calculated Exchange-Only Interaction Energy ($Ex_{GGA} - E_{HF}$) at Several Separations Alongside the Full CCSD(T) Binding Energy[a]

separation (Å)	binding energy	HF	$Ex_{GGA} - E_{HF}$			
			PBE	revPBE	PW86	B86b
		H₂ Parallel (ref 59)				
3.55	0.04	0.067	-0.100^b	-0.014	-0.013	-0.026
4.05		0.020	-0.056^b	-0.032^b	-0.006	-0.019
4.55		0.008	-0.026^b	-0.021^b	-0.002	-0.010^b
		N₂ Crossed (ref 60)				
3.87	0.28	0.139	-0.078	0.274	0.086	0.100
4.37		0.028	-0.102^b	-0.026	0.014	-0.002
4.87		0.008	-0.057^b	-0.026^b	0.006	-0.011^b
		CO₂ Crossed (ref 61)				
3.25	0.62	1.13	-0.17	0.70	0.10	0.17
3.75		0.40	-0.29	0.01	-0.05	-0.10
4.25		0.20	-0.18	-0.09	-0.04	-0.08
		Ammonia (ref 58)				
3.16	3.17	-1.41	0.25	1.57	0.40	0.60
3.66		-1.66	-0.01	0.60	0.16	0.23
4.16		-1.15	-0.06	0.18	0.09	0.09
		Methane (ref 58)				
3.72	0.53	0.36	-0.12	0.46	0.07	0.13
4.22		0.07	-0.12^b	0.11	0.04	0.03
4.72		0.01	-0.09^b	-0.02^b	0.006	-0.02^b
		Ethene (ref 58)				
3.72	1.51	0.82	0.43	1.86	0.63	0.85
4.22		0.003	-0.02	0.62	0.22	0.27
4.72		-0.08	-0.12	0.12	0.08	0.05
		Benzene Parallel (ref 62)				
3.89	1.74	3.62	-0.63	0.98	-0.44	-0.04
4.39		1.56	-0.71	0.04	-0.48	-0.36
4.89		0.88	-0.60	-0.30	-0.41	-0.39
		Benzene T (ref 58)				
4.91	2.74	1.55	0.96	2.80	1.22	1.46
5.26		0.10	0.46	1.60	0.70	0.84
5.61		-0.30	0.17	0.84	0.41	0.46
		Pyrazine Parallel (ref 63)				
3.6	2.5	4.50	0.01	2.02	0.29	0.61
4.1		1.49	-0.35	-0.86	0.11	-1.37
4.6		0.67	-0.30	0.05	-0.04	-0.06

[a] Except in the CO₂ case where the result quoted is from MP2 calculations and the N₂ case where an experimental result is given. Energies are given in kcal/mol. [b] Values are cases of spurious exchange binding. Several dimers have attractive electrostatic interactions which dominate at large distances.

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$$z_c(s) = \frac{3^{4/5}\sqrt{2}(5\pi)^{1/5}}{s^{2/5}} \simeq \frac{5.908}{s^{2/5}} \qquad (25)$$

and

$$F_x(s) = \frac{(5\pi/3)^{4/5}s^{2/5}}{3\sqrt{2}} \simeq 0.8863s^{2/5} \qquad (26)$$

Thus, we have shown that the exact large s dependence of the enhancement factor obtained from the PW86 integrals is $s^{2/5}$. The coefficient of 0.8863, obtained by exact evaluation the PW86 analytic expressions, is within 2% of the value implied by PW86's fitted parametrization (eq 11). Still, it is undoubtedly desirable to use rigorously correct results, wherever possible, and to that end, we use this result to refit the numerical results of the integration. We also correct the small s behavior which was originally constrained to recover $1 + (7/81)s^2$ (ref 65) but was later shown to correctly be $1 + (10/81)s^2$ (see, for example, refs 66 and 67). We keep the original form of the functional as given in eq 11, where a is set by the small s limit to be $10/81(= 0.1234)$, c is set by the large s behavior derived above to be 0.163 $(= 0.8863)$,[15] and the remaining parameter $b = 17.33$ is used to smoothly interpolate between the two limits and is obtained by fitting to the numerical solution for $F_x(s)$ for $0 \le s \le 10$. This constitutes a minor modification to the original PW86 form and does not have a substantial impact on the already good agreement PW86 exchange energies yielded with HF in the systems we have looked at. This can be seen in Figure 5 where the interaction energy of parallel N_2 molecules is shown for both the refit and the original PW86 functionals along with the HF results. The functional parameters are compared in Table 2. The large s asymptote derived here is probably the most robust feature of the analytic form for PW86, as it depends on the sum rule for the exchange hole but not on any of the other cutoffs that were necessarily imposed for evaluations for smaller reduced gradient. The situation may be different for some other functionals.[68] As s increases, it passes a threshold value above which the cutoff that enforces the negativity of the exchange hole is inoperative. We have calculated this threshold value numerically to be $s = 0.874$. The value of z_c, which enforces the second cutoff in eq 22, reduces with increasing s. At this threshold s value, z_c becomes low enough so that the function y_{sa}, described in eq 24, is restricted to a region where it is always positive, guaranteeing a negative exchange hole without any additional cutoffs.

Our analysis of the exchange-only interaction energy for a series of interacting molecules has shown that exchange functionals, which behave as $s^{2/5}$ at large s, offer a consistent improvement over other commonly used exchange functionals, with the PW86 functional being marginally better than Becke86b in the systems we have examined. The underlying origin of this $s^{2/5}$ dependence remains to be explained, although an enhancement factor that increases with s is necessary to mitigate the spurious LDA-like behavior identified by Harris (see discussion

Table 2. Parameters for the Original and Refit PW86 Functional As Described by Equation 11

	original PW86	refit PW86
a	0.0864	0.1234
b	14	17.33
c	0.2	0.163

following eq 5). We also note that, aside from B88, which is overly repulsive in these systems, the PW86 functional was the only functional tested that never yielded spurious exchange binding in the systems and the separations we examined. While B86b has a similar form to PW86, this indicates that the lower rate at which it increases with s, as can be seen in Figure 2, is not sufficiently large to rule out this type of spurious binding. Our analysis of the s-dependence of the exchange energies shows significant contributions are coming from highly inhomogeneous regions where s is $\gtrsim 10$, showing that the large s behavior is particularly important. We have derived the exact large s behavior of the integrals solved to obtain the PW86 functional and used this along with corrected small s behavior to refit the functional to the numerical results used to derive it. This is not a substantial change to the functional but allows it to more accurately reproduce the features of importance in the types of systems of interest.

Supporting Information Available: We have tabulated the errors incurred in the HF interaction energy by basis sets of increasing size relative to the CBS result for benzene in the T configuration and pyrazine in the parallel configuration. Full author list for reference 26. This material is available free of charge via the Internet at http://pubs.acs.org.

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