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Assessment of the Perdew–Burke–Ernzerhof exchange-correlation functional

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In order to discriminate between approximations to the exchange-correlation energy $E_{xc}[\rho_{\uparrow}, \rho_{\downarrow}]$, we employ the criterion of whether the functional is fitted to a certain experimental data set or if it is constructed to satisfy physical constraints. We present extensive test calculations for atoms and molecules, with the nonempirical local spin-density (LSD) and the Perdew–Burke–Ernzerhof (PBE) functional and compare our results with results obtained with more empirical functionals. For the atomization energies of the G2 set, we find that the PBE functional shows systematic errors larger than those of commonly used empirical functionals. The PBE ionization potentials, electron affinities, and bond lengths are of accuracy similar to those obtained from empirical functionals. Furthermore, a recently proposed hybrid scheme using exact exchange together with PBE exchange and correlation is investigated. For all properties studied here, the PBE hybrid gives an accuracy comparable to the frequently used empirical B3LYP hybrid scheme. Physical principles underlying the PBE and PBE hybrid scheme are examined and the range of their validity is discussed. © 1999 American Institute of Physics. [S0021-9606(99)30510-9]

I. INTRODUCTION

In the Kohn–Sham¹ approach the ground-state energy is written as

$$E = T_s + \int d^3r \rho(\mathbf{r}) v(\mathbf{r}) + \frac{1}{2} \int d^3r d^3r' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{xc}[\rho_{\uparrow}, \rho_{\downarrow}]. \quad (1)$$

T_s denotes the kinetic energy of a noninteracting system yielding the exact ground-state density ρ . Numerous approximations to the exchange-correlation energy $E_{xc}[\rho_{\uparrow}, \rho_{\downarrow}]$ as a functional of the spin-densities ρ_{\uparrow} and ρ_{\downarrow} ($\rho = \rho_{\uparrow} + \rho_{\downarrow}$) have been developed and tested. The first of these approximations, the local spin-density approximation (LSD),¹ yields results of good or moderate accuracy for a variety of properties such as lattice constants, bulk moduli, equilibrium geometries, and vibrational frequencies.² Binding energies are usually much better reproduced by LSD than by Hartree–Fock,³ but LSD is not accurate enough for reliable results in thermochemistry. There is no straightforward procedure to improve upon the LSD approximation. Various extensions to the LSD approximation have been proposed, among them those in Refs. 3–13, but there is no unique answer to the question of which one is the best.

One possible criterion for the discussion of approximations to $E_{xc}[\rho_{\uparrow}, \rho_{\downarrow}]$ is whether the functional is fitted to experimental data or if it is constructed to satisfy physical constraints. Most existing functionals combine these two approaches, i.e., while they are subject to physical constraints, parameters are added to better fit the experimental data. In the search for higher accuracy, we have recently observed

the appearance of functionals with an increasing number of fitted parameters.^{11–15} Often physical constraints on the functional are abandoned^{14,15} in favor of higher accuracy on the selected experimental data set. Increasingly, parameters are recommended^{14,15} which are constructed to absorb technical problems in the solution of the Kohn–Sham equations. Basis set deficiencies, for example,¹⁴ are assimilated in the fitted coefficients. These schemes are of great practical value. They show a very high accuracy when applied to systems which are represented by the fitted data set. On the other hand, heavily parametrized functionals cannot be analyzed in terms of physical concepts. Often little is known about empirical functionals applied to systems which are very different from those in the fitted set. However, for widely used fitted functionals a wealth of applications has been reported in the literature, assessing the performance of these functionals.

Functionals which do not rely on empirical adjustments but on universal physical constraints are expected to give more predictable accuracy for all systems at the price of being less accurate for systems similar to or contained in the fitted set of the empirical functionals. An example for an important physical constraint is the normalization condition on the exchange-correlation hole $\rho_{xc}(\mathbf{r}, \mathbf{r}')$, i.e., $\int d^3r' \rho_{xc}(\mathbf{r}, \mathbf{r}') = -1$. The hole is related to E_{xc} by

$$E_{xc} = \frac{1}{2} \int d^3r d^3r' \frac{\rho(\mathbf{r})\rho_{xc}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \quad (2)$$

Other examples of physical constraints are scaling conditions.¹⁶ In the present paper, we focus on the nonempirical Perdew–Burke–Ernzerhof (PBE)³ generalized gradient approximation (GGA) and apply the PBE functional to the G2 data set.^{17–20} We do not expect to improve upon functionals being fitted to this data set. However, we want to determine how far the physical constraints included in the

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PBE functional are sufficient to achieve reliable results for thermochemistry, and we want to identify important features of density functionals for future development of new approximations.

Hybrid methods which mix exact exchange with density functional approximations to exchange and correlation have become a standard tool in quantum chemistry. Becke^{21–23} noticed that utilizing a portion of the exact exchange energy together with density functional exchange and correlation, significantly improves the accuracy of GGAs. In the present work, we also combine the PBE functional with exact exchange by using a very simple one-parameter formula.^{23–26} The value of the parameter is set based on the assumption that fourth-order perturbation theory is sufficient to obtain accurate atomization energies.²⁴ Our study is the first extensive assessment of this hybrid scheme. During the course of this work, we learned that another study on the accuracy of the PBE and PBE hybrid has been conducted simultaneously by Adamo and Barone.²⁷

A number of studies on the performance of the PBE functional have already been published. Patton, Porezag, and Pederson²⁸ reported calculations of the equilibrium bond lengths, vibrational frequencies, and atomization energies of a number of small molecules, including transition metal compounds. Zhang, Pan, and Yang²⁹ studied rare gas dimers with various functionals and found that the PBE performs the best for these systems. Rare gas dimers have also been investigated by Patton and Pederson³⁰ and rare gas complexes by Wesolowski *et al.*³¹ Weakly bonded polyethylene chains have been studied with different functionals by Montanari, Ballone, and Jones.³² The PBE functional gives a qualitative correct description of the interchain interaction. The LSD, PBE, and BLYP^{33,34} approximations have been applied to properties of simple metals³⁵ where the PBE functional shows the best overall performance. Lee and Martin applied the PBE approximation to atoms, clusters and solids.³⁶ The hydrogen bonds in ice are accurately described by PBE, as has been shown by Hamann.³⁷ This list, although far from being complete, covers a wide range of electronic systems and illustrates the reliability of the PBE.

II. THE PERDEW–BURKE–ERNZERHOF FUNCTIONAL

The success of the LSD approximation has been justified in a number of articles (among them are Refs. 2,38–40) arguing that LSD obeys various physical constraints such as the above mentioned normalization condition on the exchange–correlation hole. Recently, it has been shown³⁹ that the LSD approximation to the on-top ($\mathbf{r}=\mathbf{r}'$) value of the exchange–correlation hole $\rho_{XC}(\mathbf{r},\mathbf{r}')$ is very accurate for all electronic systems and that this together with the normalization condition on the exchange–correlation hole makes the LSD approximation a fairly successful one.³⁹ The PBE functional is constructed in such a way that all the essential conditions for the reliability of the LSD approximation are preserved. Further physical constraints are satisfied using the dependence on the reduced density gradient $s=|\nabla\rho|/(2k_F\rho)$, with $k_F=(3\pi^2\rho)^{1/3}$. The PBE exchange–correlation energy depends on ρ , s , and ζ .

$$E_{XC}^{PBE} = \int d^3r \rho(\mathbf{r}) \epsilon_{XC}^{PBE}(r_s(\mathbf{r}), s(\mathbf{r}), \zeta(\mathbf{r})), \quad (3)$$

where $\zeta=(\rho_{\uparrow}-\rho_{\downarrow})/\rho$ is the spin-polarization and $r_s=(4\pi\rho/3)^{-1/3}$ is the Wigner–Seitz radius. For the interpretation of the numerical results given below, we review some of the important features of the PBE functional. (A detailed discussion of the physical ideas used to construct the PBE and the consequences for practical calculations is given in Refs. 41 and 42). For fixed s and ζ , $|E_{XC}^{PBE}|$ increases with increasing density since the exchange–correlation hole becomes deeper and more localized. Consider for instance the binding energies in the LSD approximation (to which PBE reduces for $s=0$). On average, we obtain an increase in the electron density upon bond formation and a corresponding increase in $|E_{XC}^{LSD}|$. This increase of $|E_{XC}^{LSD}|$ is usually exaggerated. The decrease of ζ upon bond formation reduces $|E_{XC}^{LSD}|$ of the molecule compared to the atoms, but not enough to give good binding energies. Finite s causes an increase in the kinetic energy of the electrons compared to the homogeneous electron gas ($s=0$) and valence and core electrons become more localized. As a consequence, $|E_{XC}^{PBE}|$ increases. Applied to the atomization process this means, the more inhomogeneous system (the separated atoms) with the bigger average s -value will experience a lowering of the exchange–correlation energy relative to the less inhomogeneous system (the molecule), reducing the atomization energy. For typical valence and core densities there is no mechanism in the PBE functional to raise the exchange–correlation energy above that of LSD. In a molecule, the exchange–correlation hole can become arbitrarily extended and thus E_{XC} can go to zero. This behavior cannot be correctly reproduced by any GGA, so that even GGAs tend to overbind.

For valence densities, the ζ -dependence of the PBE exchange–correlation functional changes only little with varying s . This implies that for valence densities the dependence of LSD and PBE on ζ is very similar; $|E_{XC}^{PBE}|$ increases with increasing spin-polarization.

Note that the PBE exchange–correlation functional is a continuous extrapolation of the exchange–correlation energy of the homogeneous electron gas. As such, the PBE (and other GGAs) cannot be self-exchange free,^{43,44} i.e., for a one-electron system the PBE exchange energy does not properly cancel the self-interaction term $\frac{1}{2}\int d^3r d^3r' [\rho(\mathbf{r})\rho(\mathbf{r}')/|\mathbf{r}-\mathbf{r}'|]$. Furthermore, the PBE correlation energy does not vanish for a one-electron density. The elimination of the self interaction requires a completely nonlocal functional, which goes beyond the simple ansatz of Eq. (3) and employs for instance the kinetic energy density.^{11,23}

III. APPLICATION TO THE EXTENDED G2 SET

A. Atomization energies

The extended G2 set^{17–20} represents an extensive collection of thermochemical data which meets the requirement that the experimental results are reliable within relatively small error bars. Unfortunately, a variety of electronic systems such as transition metal compounds, weakly bonded

systems, and extended systems are not represented in this data set. It is, however, very convenient to have this compilation of accurate experimental data available. Since in PBE no parameters are optimized to reproduce experimental results, we do not need to worry about the diversity of the G2 data set.

In the present work, we use the second-order Møller–Plesset (MP2) geometries of Refs. 17–20 and perform self-consistent calculations with the 6311+G(3df,2p) basis set. According to our experience the 6311+G(3df,2p) basis set is large enough to give dissociation energies per (single or multiple) bond within ~ 2 kcal/mol of the basis set limit. The PBE functional has been implemented in the development version of the GAUSSIAN suite of programs⁴⁵ and all the standard features for geometry optimization and property calculations (including frequencies) are available for this functional. The present choice of geometries and basis sets allows a direct comparison of our results with previously published data obtained with other functionals.^{11,19} In particular, we compare the PBE to SVWN [LSD exchange + correlation energy density of the homogeneous electron gas in the random phase approximation (RPA)⁴⁶], BLYP (Becke88 exchange³³+Lee–Yang–Parr correlation³⁴), LSD (local spin-density approximation¹ with the parametrization of the exact correlation energy density of the homogeneous electron gas by Vosko, Wilk, and Nusair;⁴⁶ this functional is SVWN5 in GAUSSIAN), and the recently developed VSXC functional.¹¹ The latter functional does not only depend on the density and its gradient but also on the kinetic energy density. With the exception of SVWN and LSD the above functionals are constructed semiempirically or empirically. The results for the hybrid scheme B3LYP²² are also quoted and compared to the one-parameter PBE hybrid. (The keyword for the PBE hybrid in the GAUSSIAN program is PBE1PBE.) To the best of our knowledge, the LSD approximation has not yet been applied to this data set. In view of the fact that PBE is a refinement of the LSD approximation (to which it reduces in the zero gradient limit) it will be helpful for this and other systematic assessments of functionals to have these results available. Note that the SVWN results reported in Refs. 19 and 20 do not correspond to the usual LSD definition. This is because the SVWN option in GAUSSIAN employs the parametrization⁴⁶ of the correlation energy density of the homogeneous electron gas in the random phase approximation. The keyword in GAUSSIAN for the correct LSD approximation (with the parametrization⁴⁶ of an almost exact⁴⁷ correlation energy density of the homogeneous electron gas) is SVWN5. Spin unrestricted calculations have been performed to obtain the LSD, PBE, and PBE hybrid results, and nonspherical densities and Kohn–Sham potentials have been used for the open-shell atoms. The original G2 set^{17,18} consisting of 55 molecules is denoted by G2-1 and the extended G2 set^{17–19} containing 148 molecules is denoted by G2.

In Table I we compare “experimental” electronic atomization energies (D_e) with LSD, PBE, and PBE hybrid results. These experimental atomization energies with the zero point energy subtracted were taken from Ref. 19. In light of the discussion given above, it is not surprising that

LSD overbinds all systems but Li_2 . The more bonds are broken, the bigger this systematic overbinding becomes. Thus, the LSD approximation performs particularly poorly for the larger molecules. However, the total atomization energy of a large molecule might not play an important role in practical applications. Any method with a statistical rather than a systematic error is likely to better reproduce the atomization energy of a large molecule due to error cancellation. A method with a systematic error might, however, be more predictable for relevant properties.

Overall, the PBE functional significantly reduces, but does not eliminate the overbinding tendency of the LSD approximation. For small molecules with many hydrogen atoms (e.g., CH_4 and SiH_4) the PBE tends to give accurate or too small atomization energies. This finding is easily rationalized by noting that the hydrogen atoms have self-correlation energy in the PBE approximation (3.6 kcal/mol for H), which leads to a spurious lowering of the energy of H. This effect compensates or overcompensates the overbinding tendency of the PBE. For small multiply-bonded systems we observe a strong overbinding tendency because of the orbital nodality problem.^{26,48} This problem appears when spatially overlapping orbitals are created upon molecule formation. There are a few larger systems in Table I where new phenomena appear which are not present in small molecules. For example, the aromatic systems show unexpectedly large overbinding in the PBE approximation. The exchange hole in these systems is very delocalized and extends over the whole ring system. As described above, the PBE functional has an exchange hole which cannot become arbitrarily delocalized for finite densities;^{40,49} $|E_X^{\text{PBE}}|$ is therefore, too large, explaining the significant overbinding for these systems. In Table II, we compare the mean absolute error (mae) of the LSD and PBE functional to the mae of the functionals tested in Refs. 11 and 19. We find that the empirical functionals perform significantly better on this specific data set. Note that due to the systematic errors in the LSD and PBE functional the mae increases drastically if we go from the original G2-1 data set, containing only small molecules, to the current G2 set. The best performance is obtained with the VSXC scheme.¹¹ Note that LSD (SVWN5) performs better than SVWN.

In order to estimate the error introduced by employing the MP2 geometries of Ref. 19 instead of the self-consistent PBE geometries, geometry optimizations for the G2-1 set have been carried out. The resulting mean absolute error is 8.8 kcal/mol compared to 8.6 kcal/mol for the MP2 geometries. We conclude that the inconsistency introduced by employing MP2 geometries is insignificant.

It has been argued^{21–23} that density functional theory (DFT) exchange energies in molecules such as H_2 are too negative compared to the separated atoms, since the approximate exchange hole is too localized in the molecule. This is often used to explain the need for adding a certain fraction of exact exchange to the density functional exchange correlation energy. However, since the GGA binding energy of the H_2 molecule is already too small and since the exchange contribution to the binding energy is correctly reproduced^{26,50} by GGAs, the exact exchange mixing is nec-

TABLE I. Electronic atomization energies for the molecules in the extended G2 set (Ref. 19). Energies are given in kcal/mol. For the various methods we list the deviations from experiment (theory-exp.). The empty line in the table marks the end of the G2-1 set.

Molecule	Exp.	LSD (SVWN5)	PBE	PBE1PBE
LiH	58	2	-5	-6
BeH	48	12	7	8
CH	84	8	0	-1
CH ₂ (³ B ₁)	189	24	5	5
CH ₂ (¹ A ₁)	182	21	4	2
CH ₃	306	33	4	2
CH ₄	420	43	0	-2
NH	82	13	6	3
NH ₂	182	26	7	2
NH ₃	297	40	5	-2
OH	107	17	3	-1
H ₂ O	233	34	2	-6
HF	142	21	0	-5
SiH ₂ (¹ A ₁)	154	12	-6	-7
SiH ₂ (³ B ₁)	131	16	1	1
SiH ₃	226	21	-3	-3
SiH ₄	324	24	-9	-8
PH ₂	153	21	2	0
PH ₃	241	29	-2	-3
SH ₂	182	25	0	-2
HCl	107	13	1	-2
Li ₂	26	-2	-6	-7
LiF	139	18	0	-7
C ₂ H ₂	404	57	11	0
C ₂ H ₄	562	71	9	2
C ₂ H ₆	711	84	6	1
CN	179	40	17	0
HCN	313	48	13	-2
CO	261	39	9	-6
HCO	279	55	17	2
H ₂ CO	376	59	11	-3
H ₃ COH	513	74	7	-3
N ₂	227	38	15	-4
N ₂ H ₄	437	79	16	1
NO	153	46	19	1
O ₂	118	55	25	4
H ₂ O ₂	268	66	14	-6
F ₂	38	39	14	-5
CO ₂	392	83	26	1
Na ₂	19	1	-1	-3
Si ₂	74	19	8	-3
P ₂	116	28	6	-5
S ₂	98	39	16	8
Cl ₂	57	24	10	2
NaCl	99	5	-3	-5
SiO	191	33	6	-9
SC	172	32	7	-4
SO	122	45	18	3
ClO	62	40	19	4
FCI	62	32	11	-2
Si ₂ H ₆	533	48	-11	-10
CH ₃ Cl	395	53	6	1
CH ₃ SH	473	65	5	0
HOCl	165	45	11	-2
SO ₂	253	81	26	-4
BF ₃	470	75	12	-3
BCl ₃	325	58	16	7
AlF ₃	425	56	0	-14
AlCl ₃	309	35	2	-2
CF ₄	482	122	25	0
CCl ₄	316	86	23	6
COS	336	76	25	3

TABLE I. (Continued.)

Molecule	Exp.	LSD (SVWN5)	PBE	PBE1PBE
CS ₂	280	68	22	5
CF ₂ O	423	105	28	2
SiF ₄	566	88	3	-15
SiCl ₄	387	56	4	-3
N ₂ O	270	90	40	3
CINO	192	73	34	0
NF ₃	209	106	38	2
PF ₃	359	84	16	-5
O ₃	148	92	36	-7
F ₂ O	94	77	29	-4
ClF ₃	126	103	40	3
C ₂ F ₄	592	159	42	8
C ₂ Cl ₄	471	120	36	12
CF ₃ CN	645	150	40	2
CH ₃ CCH (propyne)	703	101	19	5
CH ₂ CCH ₂ (allene)	702	106	23	8
C ₃ H ₄ (cyclopropene)	679	108	23	10
CH ₃ CHCH ₂ (propylene)	859	114	15	5
C ₃ H ₆ (cyclopropane)	851	120	18	9
C ₃ H ₈ (propane)	1005	125	10	3
CH ₂ CHCHCH ₂ (butadiene)	1009	144	26	9
C ₄ H ₆ (2-butyne)	1001	144	25	9
C ₄ H ₆ (methylene cyclopropane)	990	151	29	14
C ₄ H ₆ (bicyclobutane)	983	155	30	16
C ₄ H ₆ (cyclobutene)	998	150	27	12
C ₄ H ₈ (cyclobutane)	1147	160	21	10
C ₄ H ₈ (isobutene)	1156	156	20	7
C ₄ H ₁₀ (trans butane)	1299	165	14	5
C ₄ H ₁₀ (isobutane)	1301	165	13	4
C ₅ H ₈ (spiropentane)	1281	197	36	19
C ₆ H ₆ (benzene)	1362	216	48	24
CH ₂ F ₂	439	80	13	-1
CHF ₃	462	101	19	-1
CH ₂ Cl ₂	370	64	13	4
CHCl ₃	344	75	19	6
CH ₃ NH ₂ (methylamine)	581	81	10	0
CH ₃ CN (methyl cyanide)	615	92	21	2
CH ₃ NO ₂ (nitromethane)	603	142	40	2
CH ₃ ONO (methyl nitrite)	601	137	37	0
CH ₃ SiH ₃ (methyl silane)	627	65	-4	-6
CHOOH (formic acid)	503	97	21	-1
HCOOCH ₃ (methyl formate)	788	137	26	0
CH ₃ CONH ₂ (acetamide)	867	146	30	6
C ₂ H ₄ NH (aziridine)	719	115	22	8
NCCN (cyanogen)	501	100	38	3
(CH ₃) ₂ NH (dimethylamine)	869	122	15	2
CH ₃ CH ₂ NH ₂ (trans ethylamine)	877	122	15	3
CH ₂ CO (ketene)	533	97	27	6
C ₂ H ₄ O (oxirane)	651	108	20	4
CH ₃ CHO (acetaldehyde)	677	103	18	1
HCOCOH (glyoxal)	636	119	29	0
CH ₃ CH ₂ OH (ethanol)	810	116	12	0
CH ₃ OCH ₃ (dimethylether)	799	115	12	-1
C ₂ H ₄ S (thiooxirane)	624	99	17	7
(CH ₃) ₂ SO (dimethyl sulfoxide)	853	142	21	2
CH ₃ CH ₂ SH (ethanethiol)	767	106	10	2
(CH ₃) ₂ SO (dimethyl sulphide)	766	106	11	2
CH ₂ CHF	573	93	18	3
CH ₃ CH ₂ Cl (ethyl chloride)	691	94	11	3
CH ₂ CHCl (vinyl chloride)	542	84	17	5
CH ₂ CHCN (acrylonitrile)	761	121	31	6
CH ₃ COCH ₃ (acetone)	978	145	23	4
CH ₃ COOH (acetic acid)	804	139	26	2
CH ₃ COF (acetyl fluoride)	707	125	26	3
CH ₃ COCl ₃ (acetyl chloride)	669	117	26	5
CH ₃ CH ₂ CH ₂ Cl (propyl chloride)	985	134	15	5

TABLE I. (Continued.)

Molecule	Exp.	LSD		
		(SVWN5)	PBE	PBE1PBE
(CH ₃) ₂ CHOH (isopropanol)	1108	157	16	1
CH ₃ CH ₂ OCH ₃ (methyl ethyl ether)	1096	156	17	1
(CH ₃) ₃ N (trimethylamine)	1160	163	18	3
C ₄ H ₄ O (furan)	992	177	41	15
C ₄ H ₄ S (thiophene)	960	166	37	17
C ₄ H ₅ N (pyrrole)	1068	185	44	19
C ₅ H ₅ N (pyridine)	1234	211	52	22
H ₂	110	3	-6	-6
HS	87	13	1	0
CCH	262	48	14	4
C ₂ H ₃ (² A')	443	66	15	7
CH ₃ CO (² A')	581	98	24	6
H ₂ COH (² A)	409	70	13	3
CH ₃ O (² A')	400	65	13	3
CH ₃ CH ₂ O (² A'')	696	106	18	5
CH ₃ S (² A')	381	56	9	3
C ₂ H ₅ (² A')	601	77	11	6
(CH ₃) ₂ CH (² A')	898	120	17	9
(CH ₃) ₃ C (t-butyl radical)	1195	162	22	12
NO ₂	228	95	43	5
mae	...	83.7	17.1	4.8

essary only in cases^{26,49} where we encounter orbital nodality problems.⁴⁸ Examples for such systems are the multiply-bonded molecules. For these systems, mixing of exact exchange ensures that the long-range component of the exchange hole is accounted for and we obtain significant improvements for the atomization energies. In a paper by Perdew, Ernzerhof, and Burke²⁴ it has been argued that a mixing coefficient $a = \frac{1}{4}$ used in the hybrid formula^{23,25}

$$E_{XC}^{hyb} = a(E_X - E_X^{DFT}) + E_{XC}^{DFT}, \quad (4)$$

should give improved results for atomization energies of systems for which fourth-order perturbation theory is adequate. Following this suggestion, we have examined the performance of the PBE functional if used in the simple hybrid scheme [Eq. (4)] (PBE1PBE). As can be seen from Table I, the results of these self-consistent calculation show a significant improvement for the congested systems, such as F₂ or N₂, with many overlapping orbitals whose overlap disappears upon atomization. The largest errors within the PBE

TABLE II. Mean absolute errors (mae) for atomization energies in kcal/mol, obtained from various DFT schemes. G2 denotes the extended G2 set (148 molecules) (Ref. 19) and G2-1 the original G2 set (55 molecules) (Refs. 17 and 18). The maximum absolute errors (max ae) are also listed.

	Mae (G2)	Mae (G2-1)	Max ae (G2)	Max ae (G2-1)
SVWN ^a	121.2	39.6	229	94
LSD(SVWN5)	83.7	36.4	216	84
PBE	17.1	8.6	52	26
BLYP ^a	7.1	4.7	28	15
VSXC ^b	2.7	2.5	12	8
B3LYP ^a	3.1	2.4	20	10
PBE1PBE	4.8	3.5	24	10

^aReference 19.

^bReference 11.

hybrid scheme are again observed for the aromatic systems. For these systems the exact exchange hole is probably very delocalized over the ring system and a fixed mixing coefficient of $\frac{1}{4}$ is too small. There is no universal mixing coefficient^{26,51,52} applicable to all systems and methods with mixing coefficients adjustable to the problem at hand have been proposed.^{24,26,51-53} These schemes are based on density functional perturbation theory.⁵⁴ Adjustable mixing coefficients are meaningful only if the hybrid scheme is applied to a particular energy difference (e.g., an atomization energy) rather than to the total energy of the individual constituents. This, however, makes it difficult to perform self-consistent calculations. In Ref. 52 it has also been shown that nonempirical hybrid schemes employing a system- and property-dependent mixing coefficient can often be approximated to a good accuracy by Eq. (4), and the limitations of this approximation have been discussed in detail.

A comparison of the mean absolute errors (mae) obtained with the present hybrid scheme and B3LYP investigated in Ref. 19 is shown in Table II. In particular, we obtain a drastic improvement with PBE1PBE compared to PBE. The largest absolute deviation obtained with the PBE1PBE is only slightly largest than the biggest absolute deviation observed for the B3LYP scheme which has eight empirical parameters.

Inspection of the results in Ref. 19 reveals that the BLYP functional often underbinds, particularly in big molecules. This is a somewhat surprising result and it is clear that hybrid schemes employing the BLYP functional worsen the results further. The good performance of the B3LYP functional is due to the fact that in its implementation in the GAUSSIAN program this hybrid scheme employs the SVWN formula⁵⁵ for the local correlation energy density instead of the local part of LYP.³⁴

B. Ionization potentials

Ionization potentials in the LSD approximation turn out to be difficult to improve upon. Whereas gradient approximations drastically reduce the LSD error for atomization energies, comparable small improvement are obtained for ionization energies. In Table III we compare the experimental and our theoretical results for the ionization potentials in the G2-1 set.^{17,18,20} Electronic ionization potentials are listed, i.e., the zero point energy corrections of Refs. 17 and 18 have been subtracted from the experimental results. We see that the PBE approximation gives an overall improvement for the ionization energies compared to LSD. In LSD, the ionization energies are usually overestimated since the LSD approximation overbinds. The ion is often more inhomogeneous compared to the neutral system and consequently the overbinding is reduced in the PBE approximation. Note that PBE underestimates the ionization potential of Be. This is due to the strong correlation in the neutral system coming from the near degeneracy of the *s* and *p* orbitals.⁵⁶

Some cases of underbinding of an electron in the PBE approximation can again be explained with the self-correlation error made by the PBE. The cation of SiH₄, for example, has a single unpaired electron and the PBE assigns too much exchange-correlation energy to this electron. The

TABLE III. Experimental and calculated electronic ionization potentials for the G2-1 data set (Refs. 17,18, and 20) in eV. For the various methods we list the deviations from experiment (theory-exp.).

System	Exp.	LSD(SVWN5)	PBE	PBE1PBE
Li	5.39	0.07	0.18	0.17
Be	9.32	-0.30	-0.32	-0.34
B	8.30	0.33	0.37	0.34
C	11.26	0.43	0.28	0.26
N	14.54	0.48	0.20	0.17
O	13.61	0.33	0.46	0.25
F	17.42	0.57	0.26	0.06
Na	5.14	0.23	0.21	0.14
Mg	7.65	0.08	-0.03	-0.11
Al	5.98	0.03	0.07	0.11
Si	8.15	0.08	0.08	0.07
P	10.49	0.12	0.00	0.04
S	10.36	0.13	-0.03	0.04
Cl	12.97	0.19	0.02	-0.01
CH ₄	12.81	-0.11	-0.24	-0.22
NH ₃	10.23	0.28	0.03	-0.15
OH	13.05	0.35	0.16	-0.01
H ₂ O	12.69	0.34	-0.03	-0.17
HF	16.11	0.49	0.03	-0.14
SiH ₄	11.08	-0.13	-0.30	-0.20
PH	10.14	0.19	0.11	0.14
PH ₂	9.81	0.19	0.17	0.19
PH ₃	9.87	0.11	-0.09	-0.14
SH	10.37	0.14	0.01	-0.01
H ₂ S(² B ₁ cation)	10.48	0.14	-0.10	-0.12
H ₂ S(² A ₁ cation)	12.81	-0.18
ClH	12.76	0.25	-0.06	-0.07
C ₂ H ₂	11.43	0.20	-0.16	-0.25
C ₂ H ₄	10.55	0.29	-0.10	-0.23
CO	14.01	0.05	-0.14	-0.08
N ₂ (² Σ cation)	15.59	0.07	-0.20	0.18
N ₂ (² Π cation)	16.74	-0.16
O ₂	12.04	0.54	0.38	0.69
P ₂	10.54	0.10	-0.16	-0.18
S ₂	9.35	0.11	0.13	0.29
Cl ₂	11.49	-0.17	-0.34	-0.15
ClF	12.66	-0.09	-0.27	-0.15
CS	11.34	0.11	-0.03	-0.03
mae	...	0.22	0.16	0.16

large errors obtained for the O₂ molecule have also been observed by other authors using different functionals.¹⁵

The rationalization for the success of the hybrid approach in improving atomization energies is in general not applicable to ionization processes. Consequently, we do not obtain an improvement over PBE by utilizing exact exchange.

In Table IV, we compare our results to previously published²⁰ assessments of other functionals. Surprisingly, the nonempirical schemes PBE and PBE1PBE outperform the empirical schemes except VSXC.

C. Electron affinities and proton affinities

It is well known that pure DFT schemes such as LSD and PBE often do not bind an extra electron.^{44,57,58} This is largely due to the missing derivative discontinuity^{57,58} in the density functionals. The derivative discontinuity ensures that the energy minimizes at integer particle numbers. Let us con-

TABLE IV. Mean absolute errors (mae) for the ionization potentials (in eV) in the G2-1 set Refs. (17,18 and 20) (the 38 atoms and molecules of Table III). Max ae denotes the maximum absolute error. In some cases self-consistent solutions could not be obtained (see Table III).

	Mae (G2-1)	Max ae(G2-1)
SVWN	0.69	1.2
LSD(SVWN5)	0.22	0.6
PBE	0.16	0.5
BLYP ^a	0.20	0.6
VSXC ^b	0.13	0.4
B3LYP ^a	0.17	0.8
PBE1PBE	0.16	0.7

^aReference 20.

^bTaken from Ref. 11. The test set used in this reference deviates slightly from the G2-1 set of ionization potentials.

sider for instance the NaCl molecule. At a large separation between Na and Cl, we find integer particle numbers at the atoms. However, LSD predicts fractional particle numbers at the fragments.⁵⁷

Nevertheless, it is possible to obtain an estimate for the electron affinity by using an artificial stabilization of the anion. In our case this artificial stabilization is simply provided by the finite basis set with functions localized at the molecule. We note, however, that in the majority of the cases listed in Table V (again the zero point energies have been subtracted from the experimental results and electronic electron affinities are compared) the highest occupied orbital has a positive orbital energy, clearly indicating that we are deal-

TABLE V. Electron affinities for the G2-1 data set (Refs. 17,18, and 20) in eV. Deviations from experiment are listed for the various approximations (theory-exp.).

System	Exp.	LSD (SVWN5)	PBE	PBE1PBE
C	1.26	0.55	0.29	0.14
O	1.46	0.55	0.20	-0.14
F	3.40	0.65	0.14	-0.22
Si	1.39	0.20	0.07	0.05
P	0.75	0.22	0.06	0.01
S	2.08	0.30	0.10	-0.03
Cl	3.62	0.44	0.09	-0.04
CH	1.21	0.49	0.28	0.14
CH ₂	0.58	0.32	0.11	-0.10
CH ₃	0.05	0.29	0.00	-0.22
NH	0.36	0.33	0.10	-0.18
NH ₂	0.73	0.37	0.00	-0.26
OH	1.81	0.48	0.04	-0.28
SiH	1.27	0.20	0.11	0.08
SiH ₂	1.09	0.21	0.15	0.14
SiH ₃	1.36	0.20	-0.01	-0.10
PH	1.02	0.24	0.02	-0.07
PH ₂	1.25	0.23	-0.03	-0.11
HS	2.35	0.29	-0.04	-0.13
O ₂	0.41	0.05	-0.04	-0.16
NO	-0.01	0.28	0.22	0.14
CN	3.88	0.15	-0.04	0.01
PO	1.08	0.21	0.19	0.22
S ₂	1.65	-0.02	-0.12	-0.08
Cl ₂	2.37	0.12	0.23	0.20
mae	...	0.30	0.11	0.13

TABLE VI. Mean absolute errors (mae) for electron affinities in eV. G2-1 is the original G2 set (25 systems) (Refs. 17,18, and 20). Max ae denotes the maximum absolute error.

	Mae (G2-1)	Max ae(G2-1)
SVWN ^a	0.74	1.2
LSD (SVWN5)	0.30	0.7
PBE	0.11	0.3
BLYP ^a	0.11	0.4
B3LYP ^a	0.11	0.5
PBE1PBE	0.13	0.3

^aReference 20.

ing with unstable systems. (This conclusion is in disagreement with Ref. 59 and supported by Ref. 60.) As expected, the LSD approximation overbinds (relative to the neutral system) the extra electron and the gradient correction removes most of this error. Again, we note that the justification for exact exchange mixing is not applicable to the electron capturing and consequently, the hybrid approach leaves the electron affinities essentially unaffected. Table VI shows that the PBE and PBE hybrid are of accuracy similar to the empirical functionals.

Now we discuss the proton affinities (Table VII). Protonization makes the molecules more inhomogeneous and the LSD approximation misses the corresponding increase in $|E_{XC}|$ so that the LSD results are systematically too small. Again, the PBE and the PBE hybrid scheme remove most of this error.

D. Bond lengths in diatomic molecules

LSD is known to give accurate bond lengths and this is supported by Table VIII. The alkaline dimers show the biggest errors. Since the inclusion of gradient corrections usually favors the more inhomogeneous system we observe an overall lengthening of the bonds with PBE compared to LSD. The mean absolute error is essentially the same for LSD and PBE. Inclusion of exact exchange tends to shorten the bonds again and reduces the overall error. The mean absolute errors for the bond lengths of the molecules in Table VIII obtained with other popular functionals are given in Table IX. The PBE and PBE1PBE compare very favorably with the more empirical approximations.

TABLE VII. Electronic proton affinities for the G2 data set (Refs. 17 and 18) in kcal/mol. For the different methods we list the deviations from experiment (theory-exp.).

System	Exp.	LSD (SVWN5)	PBE	PBE1PBE
NH ₃	211	-5	-1	2
H ₂ O	174	-6	-3	-1
C ₂ H ₂	156	-2	3	5
SiH ₄	159	-10	-2	-2
PH ₃	196	-12	-5	-3
H ₂ S	177	-9	-3	-2
HCl	140	-6	-1	-1
mae	...	7.1	2.7	2.4

TABLE VIII. Calculated and experimental bond lengths for diatomics in Å. For the different methods we list the deviations from experiment (theory-exp.).

System	Exp.	LSD (SVWN5)	PBE	PBE1PBE
BeH	1.343	0.019	0.014	0.007
CH	1.120	0.020	0.017	0.004
Cl ₂	1.988	-0.008	0.018	-0.008
CIF	1.628	0.026	0.026	-0.006
CIO	1.570	0.014	0.010	-0.012
CN	1.172	-0.006	0.002	-0.012
CO	1.128	-0.001	0.008	-0.005
F ₂	1.412	-0.029	0.000	-0.038
FH	0.917	0.015	0.013	0.001
HCl	1.275	0.015	0.012	0.002
Li ₂	2.673	0.034	0.054	0.055
LiF	1.564	-0.004	0.019	0.006
LiH	1.595	0.016	0.010	0.000
N ₂	1.098	-0.003	0.005	-0.008
Na ₂	3.079	-0.095	-0.001	0.008
NaCl	2.361	-0.026	0.014	0.003
NH	1.036	0.018	0.014	0.002
NO	1.151	-0.005	0.006	-0.012
O ₂	1.208	-0.005	0.009	-0.016
OH	0.971	0.014	0.011	-0.001
P ₂	1.893	-0.003	0.011	-0.013
S ₂	1.889	0.006	0.022	-0.004
CS	1.535	-0.002	0.011	-0.006
SiO	1.510	0.005	0.019	-0.003
SO	1.481	0.008	0.023	-0.002
mae	...	0.016	0.014	0.009

IV. CONCLUSIONS

We have applied the physical principles underlying the PBE functional and the PBE hybrid to interpret the results obtained for the extended G2 data set. We find that the physical ideas used to construct the PBE hybrid scheme are sufficient to achieve an accuracy comparable to that of the B3LYP functional which is biased towards the G2 set. The PBE density functional and hybrid scheme seem to be a good compromise for those who want to obtain fair accuracy for systems ranging from molecules to solids, and at the same time have a direct connection to physical principles.

Limitations of the PBE functional and PBE hybrid have been identified. Further improvement in accuracy requires the elimination of the self interaction and the development of self-consistent hybrid schemes which account for varying nonlocality of the exchange energy.

TABLE IX. Mean absolute error (mae) in Å for the bond lengths of the diatomics in Table VIII. Max ae denotes the maximum absolute error.

	Mae	Max ae
LSD (SVWN5)	0.016	0.095
PBE	0.014	0.054
BLYP ^a	0.019	0.045
VSXC ^a	0.013	0.075
B3LYP ^a	0.009	0.039
PBE1PBE	0.009	0.055

^aReference 11.

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