Validation and assessment of an accurate approach to the correlation problem in density functional theory: The Kriger–Chen–Iafrate–Savin model

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In the present paper, we validate and assess a correlation functional based on the so-called meta generalized gradient approximation, whose form and parameters are entirely derived only from first-principles criteria. In particular, we have carried out a detailed comparison with the most common, parametrized correlation functionals. Next, we propose a new model in which the correlation functional proposed by Kriger, Chen, Iafrate, and Savin is integrated in a hybrid Hartree–Fock/density functional theory scheme. In such approach only one, or two in the G2-optimized version, parameters are adjusted on experimental data, all the others being derived from purely theoretical considerations. The results obtained for a set of molecular properties, including H-bonded complexes, proton transfer model, S_N2 reaction and magnetic properties, are satisfactory and comparable, if not better, with those delivered by the most common functionals including heavy parametrization. The way in which the whole functional is derived and the few empirical parameters used make the new exchange–correlation functional widely applicable. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1521432]

I. INTRODUCTION

Density functional theory (DFT), combining good performances and low computational costs, is nowadays one of the most powerful and reliable tools of quantum chemistry for the computation of the electronic structure of atoms, molecules or solids.[1] In the application of this theory within the Kohn–Sham formalism, the total electronic energy can be expressed as a functional of the electron density, the only contribution that needs to be approximated being the exchange–correlation term.[2] Finding improved approximations to this contribution is therefore of vital importance in chemical applications to obtain accurate molecular properties.[3,4]

A large number of approximations have been developed, ranging from the simple local density approximation (LDA) involving only the electron density ρ to the generalized gradient approximations (GGAs) where the gradient of the density $\nabla\rho$ has been introduced to model the inhomogeneous character of molecular and real chemical systems. More recently, a new generation of functionals, called meta-GGAs and including the Laplacian of the density ($\nabla^2\rho$) and/or the kinetic energy density (τ), have attracted increasing attention.

Introducing more semilocal or nonlocal information compared to previous approximations, these meta-GGA functionals are very promising.[5]

Two extreme strategies can be defined in designing new approximations. The first approach consists in proposing an empirical formula containing some parameters fitted on experimental data, with the related danger of obtaining functionals adapted only to the applications for which they have been developed. The second way is represented by designing a mathematical form which satisfies some (eventually the largest possible number of) rigorous theoretical conditions of the exact exchange–correlation functional. This approach does not assure the "chemical" applicability of the developed functional. Of course the two philosophies are compatible and can be mixed.[6,7]

In practice, any functional is arbitrarily separated into an exchange and a correlation contributions, the approximated forms for each of them being often developed in an independent way. A relatively large number of approximations have been proposed for the exchange term representing the major part of the combined contribution to the total electronic energy (see, for instance, Refs. 8–12). In contrast, relatively few forms have been proposed for correlation functionals, perhaps due to the greater difficulty to represent this contribution. Here we recall some of the most common correlation forms, like those developed by Perdew and co-workers (like the P86, PW91 or PBE),[13–15] which are based on a GGA

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philosophy, while, only more recently, meta-GGA correlations appeared.[16–19]

Aside from these expressions, all rooted on the free-electron gas, several functionals based on the Colle–Salvetti approach[20] have been proposed, where the inhomogeneity of the systems is introduced via the second-order reduced density matrix.[21–23] The most known derivation has been developed by Lee, Yang, and Parr and it is one of the most common and successful correlation functionals (usually referred to as LYP).[21]

In this context, Krieger, Chen, Iafrate, and Savin have recently proposed a new meta-GGA approach (hereafter referred to as KCIS), based on the idea of a uniform electron gas with a gap in the excitation spectrum.[24,25] The KCIS functional is, in our opinion, particularly appealing since it is built only from physical considerations, it preserves many of the know properties of the exact correlation energy and it has no empirical parameters. Despite its promising features, the KCIS functional has never been tested beyond atomic or small molecular systems.[26]

The aim of this paper is, therefore, to explore the limits of the applicability of such a functional to chemical systems and to compare the KCIS performances with those provided by the most common correlation functionals. To this end, several exchange functionals have been chosen as counter part either in pure DFT approaches or in a hybrid HF/DFT schemes.[27] As in our previous works,[7,10] we have tested the exchange–correlation functionals obtained in these ways by computing properties concerning a number of chemical systems or processes involving both covalent and weak interactions.

II. EXCHANGE AND CORRELATION FUNCTIONALS USED

The KCIS correlation functional has the following expression:[5]

$$E_c[\rho_\alpha, \rho_\beta] = \int F(\rho_\alpha, \rho_\beta, \nabla\rho_\alpha, \nabla\rho_\beta, \tau_\alpha, \tau_\beta) d\mathbf{r}, \quad (1)$$

where

$$F = \rho \varepsilon_c^{\text{GGAGAP}}(\rho_\alpha, \rho_\beta, \nabla\rho)$$
$$- \sum_{\sigma=\alpha,\beta} \frac{\tau_\sigma^W}{\tau_\sigma} \rho_\sigma \varepsilon_c^{\text{GGAGAP}}(\rho_\sigma, 0, \nabla\rho_\sigma). \quad (2)$$

In Eq. (2), $\varepsilon_c^{\text{GGAGAP}}$ is the correlation energy per particle of a uniform electron gas with a gap in the excitation spectrum and including gradient corrections, and τ_σ^W is the Weizsäcker kinetic energy density

$$\tau_\sigma^W(\mathbf{r}) = \frac{1}{8} \frac{|\nabla\rho_\sigma(\mathbf{r})|^2}{\rho_\sigma(\mathbf{r})}. \quad (3)$$

Correlation functionals usually transfer the correlation energy from a uniform electron gas to the real system, eventually adding some gradient corrections. However, these two systems are very different: the spectrum of the uniform electron gas is a continuum of states which are occupied up to the Fermi level and unoccupied above. On the contrary, the molecular or atomic spectrum is made of discrete states which are occupied up to the HOMO orbital and unoccupied up to the ionization threshold, followed by a continuum of unoccupied states. It is therefore more judicious to model the correlation energy by starting from a uniform electron gas with a gap in the excitation spectrum roughly corresponding to the difference between the HOMO energy and the ionization threshold of the real system. It has been chosen to express this gap as the simplest semilocal functional positive everywhere and reducing to the ionization potential in the large r limit:

$$G[\rho] = \frac{1}{8} \frac{|\nabla\rho|^2}{\rho^2}. \quad (4)$$

Furthermore, $\varepsilon_c^{\text{GGAGAP}}$ has been built so as to the three PBE theoretical conditions are fulfilled by the KCIS functional. Besides, the second term in expression (2) ensures the self-interaction correction (SIC) of the functional which enables the correlation energy to vanish in the case of one-electron systems.[28] The details concerning the form of the KCIS functional are reported in the appendix.

Since, no specific form for exchange functional have been proposed to be used in conjunction with the KCIS correlation, we have tested in this work several combinations using already existing exchange functionals. It is worth to notice that these tests are essential because the arbitrary association between an exchange and a correlation functional, developed separately, can in principle lead to any kind of numerical results. In fact, the quality of exchange–correlation functionals is almost always due to quite unpredictable compensations of errors of each contribution. Among the most common GGA approaches, we have chosen the Perdew–Wang 91 (PW91) functional,[29] the Perdew–Burke–Ernzerhof (PBE) form[15] and the widely-used Becke 88 (B) exchange.[9] Concerning the meta-GGA approach, only the exchange part of the Perdew–Kurth–Zupan–Blaha (PKZB) model was tested.[18]

Furthermore in this paper, the KCIS correlation functional has been also cast in a hybrid model of the general formula:[30]

$$E_{xc}^{\text{hyb}} = a(E_x^{\text{exact}} - E_x^B) + E_{xc}^{\text{BKCIS}}. \quad (5)$$

The constant a can be fixed *a priori* to 1/4 by using nonempirical considerations, or fitted to experimental data.[30–32] When using the Becke 88 exchange,[9] the former approach willbe named B0KCIS, whereas, when using a fitted value for a, will be referred as B1KCIS (see below).

III. COMPUTATIONAL DETAILS

All the DFT computations have been carried out within the unrestricted Kohn–Sham formalism as implemented in our development version of the GAUSSIAN 99 package.[33] We have added the KCIS correlation functional, as well as its first and second derivatives with respect to all the required variables so that all the available exchange functionals as well as all the standard features of the package (as geometry optimization, computation of excitation energies, magnetic properties) can be used in conjunction with KCIS.

TABLE I. Exact correlation energies of atoms belonging to the first two rows of the periodic table and differential energies (hartree) computed with the $6\text{-}311+G(3df,3pd)$ basis set and HF densities.

Atoms	Exact[a]	PBE	PW91	LYP	PKZB	KCIS
H	0.000	−0.006	−0.007	0.000	0.000	0.000
He	−0.042	0.000	−0.004	−0.002	−0.005	0.001
Li	−0.045	−0.006	−0.012	−0.008	−0.009	−0.004
Be	−0.094	0.009	0.000	0.000	0.001	0.008
B	−0.125	0.013	0.001	0.000	0.008	0.014
C	−0.156	0.012	−0.002	−0.002	0.008	0.013
N	−0.188	0.009	−0.009	−0.004	0.005	0.008
O	−0.258	0.023	0.001	0.001	0.017	0.020
F	−0.325	0.033	0.006	0.003	0.022	0.023
Ne	−0.391	0.040	0.009	0.007	0.028	0.024
MAE (H–Ne)		0.015	0.005	0.003	0.010	0.012
Na	−0.396	0.024	−0.011	−0.013	0.013	0.005
Mg	−0.438	0.027	−0.012	−0.021	0.013	0.002
Al	−0.470	0.024	−0.019	−0.024	0.012	−0.001
Si	−0.505	0.021	−0.026	−0.024	0.009	−0.006
P	−0.540	0.014	−0.037	−0.026	0.003	−0.014
S	−0.605	0.021	−0.035	−0.023	0.008	−0.009
Cl	−0.666	0.022	−0.038	−0.024	0.007	−0.013
Ar	−0.722	0.016	−0.048	−0.028	−0.001	−0.023
MAE (Na–Ar)		0.021	0.028	0.023	0.008	0.009
Total MAE		0.018	0.015	0.012	0.009	0.011

[a]Reference 35.

A number of different basis sets have been used.[34] In particular, the $6\text{-}311G(d,p)$ basis set of Pople and co-workers has been used to optimize all the molecular structures, since previous experience showed that a polarized valence triple-ζ basis set generally provides nearly converged structural parameters by DFT methods. An extended basis set, namely the $6\text{-}311++G(3df,3pd)$ one, has next been used to evaluate all the energetic parameters (atomization and dissociation energies). Finally, magnetic properties have been evaluated with the EPR-III basis set which has been purposely tailored for this kind of DFT applications.[34]

When necessary for comparison purpose, some computations have been also carried out with standard DFT model, such B3LYP, PBE, or PBE0.[34]

IV. RESULTS AND DISCUSSION

The validation of a functional is still a problematic ground, where some arbitrary (and limited) choices have to be done. As matter of fact, that it is not possible *a priori* to predict the reliability of a chosen functional form in chemical applications and an investigation is then compulsory before routine applications. For instance, the B3LYP functional can be considered as an enlightening example for the large number of papers assessing its validity (see for instance the test cases reported in Ref. 1). Even if a large part of functionals have been tested only on thermochemistry (using the standard G2 molecular data set), some of them have been the subjects of more detailed investigations on large number of already well-known chemical systems or processes.[7,10,11] Following this latter viewpoint, we have tested the quality of results given by the new functionals including KCIS, concerning thermodynamics, geometrical, spectroscopic and magnetic properties on chemical systems including some traditional pathological cases for DFT methods.

A. Atomic correlation energies

The first step to assess the performances of the KCIS functional is to compare the correlation energies of the atoms belonging to the first two rows of the periodic table.[35] As can be seen by the results obtained using HF densities, reported in Table I, the accuracy of KCIS is at the same level as those of the most accurate correlation functionals, such as LYP, PKZB, and PW91. This is a remarkable result, since these last functionals all contain parameters adjusted to atomic data, while this is not the case for the KCIS functional.

Apart from this overall behavior, two points must be stressed. First, it is noteworthy that the larger errors are obtained with atoms having an occupation of *p* orbitals. Indeed, the correlation energy of this kind of electronic configurations often involved contributions from virtual states which should be localized in the gap of the excitation spectrum but which are totally neglected by KCIS.[24] As second point, we notice that although all the functional give similar errors, the mean average error (MAEs) for the atomic correlation energies are different for the first and second rows, the KICIS and the LYP functionals providing a more balanced description between first and second row atoms.

B. Atomization energies

In order to carry out a detailed selection of the numerous models that can be build with KCIS, we have computed for each functional the MAE with respect to experimental values on atomization energies of the molecules belonging to the standard G2-1 (55 molecules) and the extended G2 (148 molecules) sets.[36–38] These sets can be considered as a DFT "classical" test, representatives of covalently bonded systems.[39] Compared to the G2-1 set which contains small saturated molecules, the G2 set includes larger nonsatured molecules.

TABLE II. Mean absolute errors (MAE) and maximal errors (kcal/mol) for the atomization energies of molecules belonging to the G2-1 (55 molecules) and G2 (148 molecules), computed with the $6\text{-}311+G(3df,2p)$ basis set and MP2/6-31G* geometries.

	G2-1		G2	
	MAE	max.	MAE	max.
PBE	8.2	29.1 (CO_2)	17.2	50.5 (C_2F_2)
PKZB	3.6	11.0 (O_2)	4.5	-37.7 (SiF_4)
PBE0	3.1	-10.7 (SiO)	5.0	-21.7 (SiF_4)
B3LYP	2.4	-9.9 (SO_2)	3.1	-20.2 (SiF_4)
B0LYP	5.1	-20.6 (SO_2)	11.2	-30.1 (SiF_4)
PBEKCIS	11.9	35.2 (CO_2)	24.9	66.5 (C_5H_5N)
PKZBKCIS	4.1	-14.4 (C_2H_6)	9.7	38.8 (SiF_4)
PKZB$_{opt}$KCIS	3.9	13.7 (O_2)	10.0	-23.2 (C_4H_{10})
BKCIS	8.2	25.9 (CO_2)	14.6	39.6 (NO_2)
B0KCIS	3.0	-10.5 (SO_2)	5.3	-28.6 (SiF_4)
B1KCIS	3.0	-9.6 (SiO)	5.4	-28.1 (SiF_4)

The results collected in Table II, show that, among the most common functionals, the reference is the hybrid B3LYP model, with a MAE of 2.4 kcal/mol over the G2-1 set and 3.1 kcal/mol for G2. In contrast, the PBE0 functional, which has no empirical parameters, leads to a relatively small MAE for this kind of system with 3.1 kcal/mol for the G2-1 set. The two most accurate model including the KCIS correlation are the PKZBKCIS and BKCIS with MAEs of 4.1 and 8.2 kcal/mol over the G2-1 and G2 sets, respectively. The optimization of the parameter present in the exchange part of PKZB ($D=0.113$)[18] leads to the PKZB$_{opt}$KCIS functional ($D_{opt}=0.104$) which is not significantly better than the original PKZBKCIS (MAE of 3.9 kcal/mol over the G2-1 set). Furthermore, the introduction of 25% of exact exchange (PKZB0KCIS) only deteriorates the quality of the results (MAE of 6.9 kcal/mol for G2-1). The construction of a more accurate model rather requires hybrid models with the BKCIS functional. In fact, upon introduction of 25% of HF exchange into this functional (leading to the B0KCIS model), the MAE falls to 3.0 kcal/mol for G2-1. The optimization of the percentage of exact exchange over the G2-1 set (B1KCIS with 23.9% of exact exchange) does not induce significant improvements (see last line in Table II). These good performances of B0KCIS, whereas the B0LYP functional is significantly less accurate, are, of course, to be credited to the different correlation.

As last test, we have carried out some computations on the G2 set, without the SCF procedure, using HF or PBE densities and only B0KCIS energy evaluation. This test is particularly interesting, since some recent implementations of exchange–correlation functionals do not include the derivatives need for SCF procedure.[6,18] Our results (not reported in Table II) show that with a PBE density the MAE is 9.1 kcal/mol and it rises up to 11.7 kcal/mol with the HF densities. Both results are really far from the 3.0 kcal/mol obtained with the complete SCF procedure, thus warning about the importance of using an autocoherent procedure.

In the light of these first results, we have decided to study in details the performances of the KCIS functional, and especially those provided by the B0KICS model, which seems to be very accurate for covalent systems, even if it includes only one empirical parameter (in the exchange contribution). The natural reference to compare this model is, in our opinion, the similar B0LYP functional, but, in order to have a more complete picture, we consider also the popular B3LYP and PKZB functionals.

C. Atomic total energies and geometry optimization

As a first step, we have evaluated the total energies of some atoms, H through Ar. The results are collected in Table III and are compared with accurate post-HF values (labeled as "exact" in the table).[33] It is interesting to evaluate the

TABLE III. Exact total atomic energies and differential SCF energies (hartree), computed with the $6\text{-}311+G(3df,3pd)$ basis set.

| Atoms	Exact[a]	PBE	PBE0	B3LYP	B0LYP	PKZB	B0KCIS
H	-0.500	0.000	-0.001	-0.002	0.002	0.004	0.002
He	-2.904	0.014	0.011	-0.009	0.000	0.002	0.003
Li	-7.478	0.018	0.012	-0.012	-0.003	0.004	0.002
Be	-14.667	0.041	0.032	-0.004	0.006	0.019	0.015
B	-24.654	0.045	0.037	-0.009	0.003	0.036	0.017
C	-37.845	0.052	0.042	-0.012	0.000	0.056	0.015
N	-54.589	0.060	0.049	-0.012	0.002	0.083	0.015
O	-75.067	0.062	0.054	-0.024	-0.008	0.110	0.011
F	-99.734	0.073	0.067	-0.028	-0.010	0.147	0.011
Ne	-128.938	0.092	0.087	-0.022	-0.001	0.198	0.018
MAE (H–Ne)		0.046	0.039	0.013	0.004	0.066	0.011
Na	-162.255	0.099	0.085	-0.032	-0.013	0.230	0.006
Mg	-200.053	0.108	0.092	-0.040	-0.023	0.267	0.001
Al	-242.346	0.119	0.098	-0.041	-0.024	0.308	-0.001
Si	-289.359	0.134	0.108	-0.035	-0.020	0.351	-0.001
P	-341.259	0.155	0.124	-0.023	-0.008	0.401	0.005
S	-398.110	0.170	0.135	-0.024	-0.010	0.446	0.005
Cl	-460.148	0.189	0.150	-0.020	-0.006	0.495	0.007
Ar	-527.540	0.209	0.165	-0.014	0.001	0.545	0.007
MAE (Na–Ar)		0.148	0.120	0.029	0.013	0.380	0.004
Total MAE		0.091	0.075	0.020	0.008	0.206	0.008

[a]Reference 35.
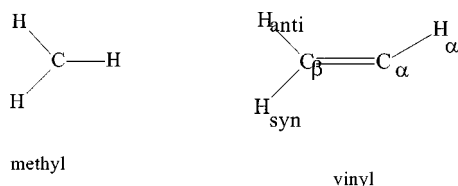
FIG. 1. Schematic structures and atom labeling of the methyl and vinyl radicals.

accuracy of functionals concerning atomic total energies since this property has been recently added to a wide training set used to test and optimize DFT models.[40] Over these 18 atoms, B0KCIS provides a MAE of 0.008 hartrees. This very good result are equaled only by B0LYP containing though four extra fitted parameters in the correlation contribution. We can also notice the astonishing accuracy of B0KCIS over the second row of the periodic table (MAE of 0.004 hartree).

After atomization and atomic energies, we have tested the ability of our new model to reproduce correct molecular geometrical parameters. Figure 1 reports the MAEs over bond lengths of 32 molecules belonging to the G2 set computed with several functionals. With a MAE of 0.008 Å, B0KCIS leads to about the same accuracy of other hybrid models PBE0, B3LYP, and B0LYP. In fact, it is a well-known behavior: the introduction of a fraction of exact exchange in a functional generally leads to very accurate models concerning bond lengths. Indeed, since bond lengths are usually too short at the Hartree–Fock level and too long for GGA functionals, hybrid models benefit from a compensation of errors.[31]

D. Other tests

Even if the exchange–correlation term to be approximated in the KS approach is usually decomposed in well-separated exchange and correlation parts, it is difficult to determine the dependence of molecular properties on just one of these contributions. Few exceptions are represented by the van der Waals interactions and excitations energies, both essentially related to the asymptotic behavior of the exchange functional.[10,41] Here, instead, we focused on more correlation-dependent properties/systems. In this context, small H-bonded dimers are an invaluable test, both for their chemical role and for the difficulty to describe the subtle physical effects (electrostatic, charge transfer, polarization) present. It is therefore interesting to estimate the quality of DFT functionals on these kinds of systems. Table VI collects geometrical parameters and interaction energies of three small H-bond dimers, namely $(H_2O)_2$, $(HCl)_2$, and $(HF)_2$. The computed interaction energies have been corrected for BSSE error which has an order of magnitude of about 0.2 kcal/mol for the first two dimers with the large $6\text{-}311+ +G(3df,3pd)$ basis set, while this error is even lower for $(HF)_2$. For the three systems, only the global energy minimum, of C_s symmetry, has been investigated, even if other stable rearrangements could actually exist.[42]

The water dimer has been studied in considerable detail and the currently accepted values for the binding energy and the OO distance are 5.4 ± 0.7 kcal/mol (not including ZPE corrections) and 2.952 Å, respectively.[43,44] Refined post-HF computations suggest that the interaction energy is close to 4.7 kcal/mol and give a shorter intermolecular distance (2.925 Å).[42,45] As already well documented (see, for instance, Ref. 1), the equilibrium geometry of the water dimer is quite accurately reproduced by standard DFT methods, all the predicted OO distances falling between 2.87 and 2.91 Å, i.e., close to the MP2 estimate.[1] Our results are reported in Table IV, and compared with experimental and post-HF data.[42–44] The most striking feature of these results is the B0KCIS distance, which is slightly longer (2.91 Å) than other DFT values, but closer to the experimental value (2.95 Å).[42] At the same time the binding energy is slightly underestimated (3.8 versus 4.7 kcal/mol for the best *ab initio* value). Interesting both B3LYP and B0LYP provide higher interaction energies and shorter intermolecular distances, thus showing the correlation between these two quantities.

Similar trends are present for all the others two dimers, the B0KCIS providing always lower interactions energies

TABLE IV. Dissociation energies (kcal/mol) and main geometrical parameters (Å) for H-bond dimers. The energies (corrected for BSSE error) have been computed with the $6\text{-}311+ +G(3df,3pd)$ basis set and the $6\text{-}311G(d,p)$ geometries.

	B3LYP	B0LYP	PKZB	B0KCIS	Best *ab initio*[a]	Expt.[b]
$(H_2O)_2$						
d(OO)	2.888	2.892	2.883	2.912	2.925	2.952
d(H–O)	1.926	1.931	2.364	1.952		
ΔE	4.6	4.5	1.9	3.8	4.7	5.4 ± 0.7
$(HF)_2$						
d(FF)	2.707	2.710	2.888	2.734	2.76	2.73/2.74
d(H–F)	1.780	1.786	1.956	1.818		
ΔE	4.7	4.7	3.0	3.8	4.6	4.2
$(HCl)_2$						
d(ClCl)	3.917	3.947	4.387	4.009	3.790	3.75/3.79
d(H–Cl)	2.626	2.657	3.093	2.724		
ΔE	1.2	0.9	0.8	0.8	2.0	1.4/2.0

[a]References 43, 45, and 46.
[b]References 44, 47, and 48.

TABLE V. Complexation energies of the ion–molecule complex (ΔE_{comp}), activation energies ($\Delta E^{\#}$) and energetic barriers relative to reagents (ΔE_r) for the considered $S_N 2$ reaction, computed at different levels of approximation. All the energies (kcal/mol) have been computed with the $6\text{-}311++G(3df,3pd)$ base set and the $6\text{-}311+G(d,p)$ geometries.

	G2+(MP2)	B3LYP	B0LYP	PKZB	B0KCIS	Expt.[a]
ΔE_{comp}	10.6	9.8	9.7	9.6	8.4	12.2 ± 2
$\Delta E^{\#}$	13.0	9.1	9.7	9.6	11.9	13.3 ± 2
ΔE_{ovr}	2.5	-0.7	0.0	0.0	3.6	1 ± 1

[a]References 53 and 54.

and higher H-bridge distance than the B3LYP and B0LYP functionals. In the case of the hydrogen fluoride dimer, the combined effects of shorter distance/lower energy results in a better agreement with the experimental data (see Table IV).[47] This is not the case for $(HCl)_2$, where all the methods provide a poor accord with experiments.[48] A detailed comparison with literature data, suggests that more subtle effects, involving either exchange and correlation contributions, are at work in such H-bonded dimers.[7]

The next test is represented by bimolecular nucleophilic substitution reactions ($S_N 2$), which have an important place in organic chemistry. The symmetric Walden inversion, in particular, an excellent well-characterized example[49–54]
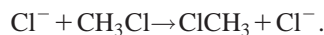
$$Cl^- + CH_3Cl \rightarrow ClCH_3 + Cl^-.$$

This reaction has a double-well energetic profile, with two minima corresponding to the formation of a pre- and a post-reaction ion–molecule complex and a saddle point (SP) with D_{3h} symmetry ($[Cl-CH_3-Cl]^-$). The most significant thermodynamic quantities are the complexation energy of the ion–molecule complex (ΔE_{comp}), the activation energy, i.e., the relative energy of the D_{3h} saddle point with respect to the ion–molecule complex ($\Delta E^{\#}$), and the overall barrier (ΔE_{ovr}), defined as the difference between these two energies. The computed energies are collected in Table V. Apart from PBE0 which leads to a realistic reaction barrier, it is striking to notice that the more popular semiempirical approaches, B3LYP or B0LYP, as well as more theoretically developed functionals, like PBE or PKZB, lead to zero or even negative values for ΔE_{ovr}. Whereas the computation of initial closed-shell reagents does not generate particular difficulties, the determination of the energy of the charged transition state energy $[Cl-CH_3-Cl]^-$ by DFT approaches is more involved.[52] In fact, the majority of functionals are not corrected for the self-interaction error in the exchange part as well as in the correlation part, which implies an exaggerated delocalization of the electron density that overstabilized the transition state.[55] On the contrary, the B0KCIS, which is corrected for self-interaction error in the correlation part, gives a too positive barrier (3.6 kcal/mol) but reproducing the trend of the MP2 computation (2.5 kcal/mol). The comparison between the results given by B0LYP and B0KCIS clearly shows the very strong influence of the correlation contribution for these applications.

Proton transfer mechanisms are often of first importance in chemical or biological processes. In spite of the apparent simplicity of this phenomenon, the theoretical description of proton transfer is a difficult problem for both post-Hartree–Fock methods and DFT approaches. In particular, it is well known that current functionals provide very low activation energies.[56–58] The situation is even more involved when the motion of the proton is coupled with a rearrangement of the π electronic system, as happens in malonaldehyde. In fact, the enol form of this molecule is stabilized by an intramolecular hydrogen bond, and it is possible to switch from a stable form to the other one by a proton transfer mechanism via a transition state of C_{2v} symmetry.[57] Table VI contains the most significant geometrical parameters as well as energetic barriers for the minimum and the saddle point of malonaldehyde. Whereas B0LYP overestimates the energetic barrier with respect to the MP2 computations (3.5 and 2.8 kcal/mol, respectively), B0KCIS gives geometrical and energetic parameters in good agreement with the reference values. Once again, the difference of 1 kcal/mol in the energetic barrier given by B0LYP and B0KCIS shows the importance of the correlation contribution and the better quality of KCIS over LYP for this kind of applications.

Finally, the last difficult playground is represented by one of the physical constant derived from EPR spectroscopy: the isotropic hyperfine coupling constant. The isotropic hyperfine coupling constant of an atom n, related to the interaction of the nuclear spin with an electronic spin by the contact Fermi mechanism depends on the electronic spin density $\rho^s(\mathbf{r}_n)$ at the position of the nucleus $\mathbf{r}_n$:[59]

TABLE VI. Main geometrical parameters (Å) of the H-bond and relative energies (kcal/mol) for the minimum (M) and the saddle point (SP) of malonaldehyde. The energies have been computed with the $6\text{-}311++G(3df3pd)$ basis set and the $6\text{-}311G(dp)$ geometries.

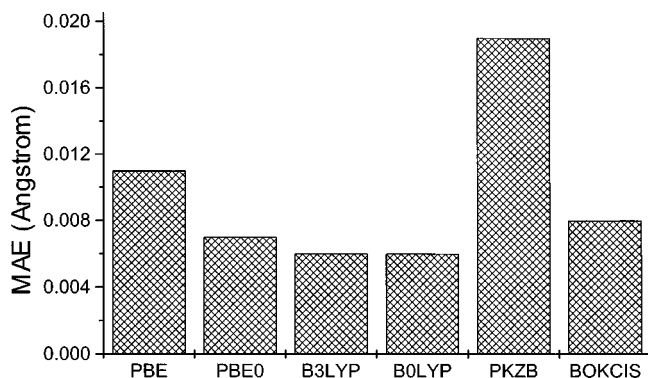|	MP2		B3LYP		B0LYP		B0KCIS	
	M	SP	M	SP	M	SP	M	SP
$d(OO)$	2.581	2.355	2.580	2.367	2.593	2.363	2.564	2.356
$d(H-O)$	1.678	1.197	1.687	1.208	1.711	1.207	1.666	1.202
$d(OH)$	0.991	1.197	0.999	1.208	0.992	1.207	0.996	1.202
ΔE		2.8		3.0		3.5		2.5

FIG. 2. Mean absolute errors (MAEs, Å) for the bond lengths of 32 molecules belonging to the G2 set. Computed with the 6-311G(d,p) basis set.

$$a_n = \frac{8\pi}{3h} g_e \beta_e g_n \beta_n \rho^s(\mathbf{r}_n), \qquad (6)$$

where β_e, β_n are the electronic and nuclear magnetons, g_e, g_n the electronic and nuclear g-factors, and h is the Planck's constant. The spin density can be easily obtained from density matrices of electrons α and β, $P_{\mu,\nu}^\alpha$ and $P_{\mu,\nu}^\beta$, and from the basis atomic orbitals $\{\varphi_\mu\}$,

$$\rho^s(\mathbf{r}_n) = \sum_{\mu,\nu} (P_{\mu,\nu}^\alpha - P_{\mu,\nu}^\beta) \varphi_\mu^*(\mathbf{r}_n) \varphi_\nu(\mathbf{r}_n). \qquad (7)$$

This spin density on the nucleus can have two origins. The first direct origin is simply provided by a unpaired electron in an orbital which has a nonzero density at the position of the nucleus. The second indirect origin is due to spin polarization of paired electrons, which have a nonzero presence probability on the nucleus, caused by the interaction with the unpaired electron under the effect of electronic correlation which acts differently depending whether the electrons have the same spin or opposite ones.[60]

In order to test B0KCIS, we have performed computations on the methyl and vinyl radicals (see Fig. 2). These radicals can be considered as prototype of π and σ organic radicals, respectively. The computed values of hyperfine coupling constants are collected in Table VII.

First of all, it is striking to notice that for this property, DFT approaches are globally more accurate than very refined correlation *ab initio* methods like CCSD (coupled-cluster single double).[61] For the methyl radical, the unpaired elec-

tron being in a p orbital of zero density on the carbon atom, the hyperfine coupling constants originate exclusively from spin polarization of electrons of the $2s$ orbital for C or the $1s$ orbital for H. Concerning electrons of same spin, this interaction can only be treated properly with an accurate exchange functional like in PBE0.[62] On the contrary, when a less accurate exchange functional is used like B, results strongly depend on error compensation with the correlation part. As a consequence, B0LYP overestimates the hyperfine coupling constant of C in the methyl radical whereas B0KCIS underestimates it.

The case of nonsaturated σ radicals like the vinyl radical is more complicated to treat by DFT approaches as well as by post-HF methods since it involves both direct and indirect contributions to hyperfine coupling constants.[60] Nevertheless, it is striking to notice the excellent value of hyperfine coupling constant of C_α, dominated by the direct contribution of the unpaired electron in a σ orbital of nonzero density on the nucleus, given by B0KCIS. The comparison of the results given by B0LYP and B0KCIS functionals suggests the importance of the correlation contribution for this application.

V. CONCLUSIONS

In this work, we have tested the new meta-GGA parameter-free correlation functional KCIS. Concerning atomic correlation energies, this functional is globally more accurate than other theoretical or semiempirical correlation functionals like the correlation part of PBE or LYP, respectively. The search for the best exchange functional which can been coupled to KCIS has lead us to a new hybrid model with the Becke 88 (B) exchange functional: B0KCIS. This model, including 25% of exact exchange and containing only one parameter in the exchange part, has been tested over a varied set of physicochemical properties and have turned out to have performances better or at least equivalent to those provided by semiempirical exchange–correlation functionals like B3LYP. In details, the use of B0KCIS instead of B0LYP brings a significant improvement for properties where the correlation contribution plays an important role like for atomization energies, energetic reaction barriers and magnetic properties.

While, in the present study we have searched for the best suitable exchange functional, among those already available

TABLE VII. Isotropic hyperfine coupling constants (a, Gauss) for the methyl and vinyl radical computed with the EPR-III basis set.

		B3LYP	B0LYP	B0KCIS	CCSD(T)[a]	Expt.[a]
Methyl	$a(C)$	29.8	31.7	24.9	27.8	28.4
	$a(H)$	−23.3	−24.3	−26.2	−24.6	−25.1
Vinyl	$a(C_\alpha)$	113.1	112.7	107.6	121	107.6
	$a(C_\beta)$	−5.8	−5.8	−5.2	−8	−8.6
	$a(H_\alpha)$	17.8	17.7	12.3	9	13.3
	$a(H_{anti})$	41.9	41.9	40.7	28	34.2
	$a(H_{syn})$	65.6	65.5	62.2	48	68.5
MAE		3.8	3.9	3.3	6.6	

[a]From Ref. 60.

"on the market," to be used with KCIS, we believe that it would be interesting to develop a new exchange functional entirely adapted to KCIS in order to obtain an even more accurate model. Work is in progress in such a direction.

ACKNOWLEDGMENT

APPENDIX: THE ANALYTICAL EXPRESSION OF THE KCIS FUNCTIONAL

This appendix contains the complete expression of the KCIS correlation functional. The following seven variables are involved in this meta-GGA functional: ρ_α, ρ_β, $\gamma_\alpha = g_\alpha^2 = |\nabla \rho_\alpha|^2$, $\gamma_\beta = g_\beta^2 = |\nabla \rho_\beta|^2$, $\gamma_{\alpha\beta} = \nabla \rho_\alpha \cdot \nabla \rho_\beta$, τ_α, and τ_β,

$$E_c^{\text{KCIS}}[\rho_\alpha, \rho_\beta] = \int F(\rho_\alpha, \rho_\beta, \gamma_\alpha, \gamma_\beta, \gamma_{\alpha\beta}, \tau_\alpha, \tau_\beta) d\mathbf{r}, \tag{A1}$$

where F,

$$F = \rho \varepsilon_c^{\text{GGAGAP}}(\rho_\alpha, \rho_\beta, g, \zeta)$$
$$- \sum_{\sigma=\alpha,\beta} \frac{\tau_\sigma^W(\rho_\sigma, g_\sigma)}{\tau_\sigma} \rho_\sigma \varepsilon_c^{\text{GGAGAP}}(\rho_\sigma, 0, g_\sigma, \zeta = 1) \tag{A2}$$

with $\rho = \rho_\alpha + \rho_\beta$, $g = |\nabla \rho| = (\gamma_\alpha + \gamma_\beta + 2\gamma_{\alpha\beta})^{1/2}$, $\zeta = (\rho_\alpha - \rho_\beta)/\rho$, and $\tau_\sigma^W = g_\sigma^2/8\rho_\sigma$.

$\varepsilon_c^{\text{GGAGAP}}$ is the correlation energy per particle of a uniform electron gas with a gap, including gradient corrections. It can be obtained for any spin polarization ζ by the formula

$$\varepsilon_c^{\text{GGAGAP}}(\rho_\alpha, \rho_\beta, g, \zeta)$$
$$= \varepsilon_c^{\text{GAP,unp}}(\rho, g) + f(\zeta)[\varepsilon_c^{\text{GAP,pol}}(\rho, g) - \varepsilon_c^{\text{GAP,unp}}(\rho, g)] \tag{A3}$$

with the polarization function

$$f(\zeta) = \frac{(1+\zeta)^{4/3} + (1-\zeta)^{4/3} - 2}{2(2^{1/3}-1)} \tag{A4}$$

and the correlation energies of the unpolarized and polarized electron gas,

$$\varepsilon_c^{\text{GAP,unp}}(\rho, g)$$
$$= \frac{\varepsilon_c^{\text{GGA,unp}}(r_s, g) + c_{1,\text{unp}}(r_s)G(\rho, g)}{1 + c_{2,\text{unp}}(r_s)G(\rho, g) + c_{3,\text{unp}}(r_s)G(\rho, g)^2},$$
$$\varepsilon_c^{\text{GAP,pol}}(\rho, g)$$
$$= \frac{\varepsilon_c^{\text{GGA,pol}}(r_s, g) + c_{1,\text{pol}}(r_s)G(\rho, g)}{1 + c_{2,\text{pol}}(r_s)G(\rho, g) + c_{3,\text{pol}}(r_s)G(\rho, g)^2}, \tag{A5}$$

where the Seitz local radius $r_s = (3/4\pi\rho)^{1/3}$ and the gap, $G(\rho, g) = g^2/8\rho^2$, have been introduced.

The coefficients $c_{1,\text{unp}}(r_s)$, $c_{2,\text{unp}}(r_s)$, and $c_{3,\text{unp}}(r_s)$ have been determined by a fitting procedure, starting from a model of uniform electron gas with a gap G:

$$c_{1,\text{unp}} = C \frac{2(\varepsilon_c')^2 - \varepsilon_c^0 \varepsilon_c''}{2(C\varepsilon_c' - \varepsilon_c^{0^2})},$$
$$c_{2,\text{unp}} = \frac{2\varepsilon_c^0 \varepsilon_c' - C\varepsilon_c''}{2(C\varepsilon_c' - \varepsilon_c^{0^2})}, \tag{A6}$$
$$c_{3,\text{unp}} = -\frac{2(\varepsilon_c')^2 - \varepsilon_c^0 \varepsilon_c''}{2(C\varepsilon_c' - \varepsilon_c^{0^2})}$$

with $C = 0.064\,83 k_F^2$ obtained from second-order perturbation theory, and the Fermi wave vector $k_F = (9\pi/4)^{1/3} (1/r_s) = (3\pi^2\rho)^{1/3}$.

ε_c^0 is the correlation energy per particle of the unpolarized uniform electron gas at $G = 0$, computed using the local part of the Perdew–Wang 91 (PW91) correlation functional

$$\varepsilon_c^0 = \varepsilon_c^{\text{PW91}Lc}(r_s, \zeta = 0), \tag{A7}$$

ε_c' and ε_c'' are, respectively, the first and second derivatives of ε_c with respect to G at $G = 0$, and can be calculated by the expressions

$$\varepsilon_c' \approx \frac{a_1 r_s^{3/2}}{1 + a_2 r_s^{1/2} + a_3 r_s + a_1 r_s^{3/2}} \tag{A8}$$

and

$$\varepsilon_c'' \approx \sum_{i=3}^{7} b_i r_s^i \tag{A9}$$

with $a_1 = 0.049\,53$, $a_2 = 1.079\,24$, $a_3 = 0.079\,28$, $b_3 = -0.025\,04$, $b_4 = 0.007\,026$, $b_5 = -0.001\,268$, $b_6 = 0.000\,1136$, $b_7 = -0.000\,003\,8421$.

The coefficients $c_{1,\text{pol}}(r_s)$, $c_{2,\text{pol}}(r_s)$, and $c_{3,\text{pol}}(r_s)$ for the polarized case are simply evaluated from the coefficients of the unpolarized case

$$c_{1,\text{pol}}(r_s) = 0,7 c_{1,\text{unp}}(r_s),$$
$$c_{2,\text{pol}}(r_s) = 1,5 c_{2,\text{unp}}(r_s), \tag{A10}$$
$$c_{3,\text{pol}}(r_s) = 2,59 c_{3,\text{unp}}(r_s).$$

The gradient correction in the correlation energies per particle of the unpolarized and polarized electron gas, $\varepsilon_c^{\text{GGA,unp}}$ and $\varepsilon_c^{\text{GGA,pol}}$, is introduced by the expressions

$$\varepsilon_c^{\text{GGA,unp}}(r_s, g) = \frac{\varepsilon_c^0}{1 + \beta \ln\left(1 + \frac{t(r_s, g)^2}{|\varepsilon_c^0|}\right)},$$
$$\varepsilon_c^{\text{GGA,pol}}(r_s, g) = \frac{\varepsilon_c^1}{1 + \beta \ln\left(1 + 2^{-1/3} \frac{t(r_s, g)^2}{|\varepsilon_c^1|}\right)}, \tag{A11}$$

where $\beta = 0.066\,725$ is determined so as to satisfy the slowly varying limit, $t(r_s, g) = (\pi^{4/3}/3)(\frac{2}{3})^{1/3} r_s^{7/2} g$ and ε_c^1 is analogous to ε_c^0 for the polarized uniform electron gas

$$\varepsilon_c^1 = \varepsilon_c^{\text{PW91}Lc}(r_s, \zeta = 1). \tag{A12}$$

[1] W. Koch and M. C. Holthausen, *A Chemist's Guide to Density Functional Theory* (Wiley-VCH, Weinheim, 2000).
[2] R. G. Parr and W. Yang, *Density Functional Theory of Atoms and Molecules* (Oxford University Press, New York, 1989).
[3] K. Burke, J. P. Perdew, and Y. Wang, in *Electronic Density Functional*

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Theory: Recent Progress and New Derivations, edited by J. F. Dobson, G. Vignale, and M. P. Das (Plenum, New York, 1997).

[4] C. Adamo, A. di Matteo, and V. Barone, Adv. Quantum Chem. **36**, 4 (1999).

[5] S. Kurth, J.P. Perdew, and P. Blaha, Int. J. Quantum Chem. **75**, 889 (1999).

[6] J. Tao, J. Chem. Phys. **116**, 2335 (2002).

[7] C. Adamo and V. Barone, J. Chem. Phys. **116**, 5933 (2002).

[8] A. D. Becke, J. Chem. Phys. **85**, 7184 (1986).

[9] A. D. Becke, Phys. Rev. A **38**, 3098 (1988).

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

[11] W. M. Hoe, A. J. Cohen, and N. C. Handy, Chem. Phys. Lett. **341**, 319 (2001).

[12] T. Tsuneda and K. Hirao, Phys. Rev. B **62**, 15527 (2000).

[13] J. P. Perdew and Y. Wang, Phys. Rev. B **33**, 8800 (1986).

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

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

[16] T. van Voorhis and G. E. Scuseria, J. Chem. Phys. **109**, 400 (1998).

[17] H. L. Schmider and A. D. Becke, J. Chem. Phys. **109**, 8188 (1998).

[18] J. P. Perdew, S. Kurth, A. Zupan, and P. Blaha, Phys. Rev. Lett. **82**, 2544 (1999).

[19] E. Proynov, H. Chermette, and D. R. Salahub, J. Chem. Phys. **113**, 10013 (2000).

[20] R. Colle and O. Salvetti, Theor. Chim. Acta **37**, 329 (1975).

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

[22] T. Tsuneda, T. Suzumura, and K. Hirao, J. Chem. Phys. **110**, 10664 (1999).

[23] Y. Imamura, G. E. Scuseria, and R. M. Martin, J. Chem. Phys. **116**, 6458 (2002).

[24] J. B. Krieger, J. Chen, G. J. Iafrate, and A. Savin, in *Electron Correlations and Materials Properties*, edited by A. Gonis and N. Kioussis (Plenum, New York, 1999).

[25] J. Rey and A. Savin, Int. J. Quantum Chem. **69**, 581 (1998).

[26] J. B. Krieger, J. Chen, and S. Kurth, in *Density Functional Theory and Its Applications to materials*, edited by V. van Doren, C. van Alsenoy, and P. Geerlings, AIP Conf. Proc. **577**, 48 (2001).

[27] A. D. Becke, J. Chem. Phys. **98**, 5648 (1993).

[28] A. D. Becke, J. Chem. Phys. **109**, 2092 (1998).

[29] J. P. Perdew, in *Proceeding of the 21st Annual International Symposium on the Electronic Structure of Solids*, edited by P. Ziesche and H. Eschrig (Akademie Verlag, Berlin, 1991).

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

[31] C. Adamo and V. Barone, Chem. Phys. Lett. **272**, 242 (1997).

[32] A. D. Becke, J. Chem. Phys. **98**, 5648 (1993).

[33] M. J. Frisch, G. W. Trucks, H. B. Schlegel *et al.*, GAUSSIAN 99 Development version (Revision B.05), Gaussian, Inc., Pittsburgh, PA, 1999.

[34] A. E. Frisch and M. J. Frisch, GAUSSIAN 98 *User's Reference*, Gaussian, Inc., Pittsburgh, PA, 1998, and reference therein.

[35] S. J. Chakravorty, S. R. Gwaltney, E. R. Davidson, F. A. Parpia, and C. F. Froese Fischer, Phys. Rev. A **47**, 3649 (1993).

[36] J. A. Pople, M. Head-Gordon, D. J. Fox, K. Raghavachari, and L. A. Curtiss, J. Chem. Phys. **90**, 5622 (1989).

[37] L. A. Curtiss, C. Jones, G. W. Trucks, K. Raghavachari, and J. A. Pople, J. Chem. Phys. **93**, 2537 (1990).

[38] L. A. Curtiss, K. Raghavachari, P. C. Redfern, and J. A. Pople, J. Chem. Phys. **106**, 1063 (1997).

[39] B. G. Johnson, P. M. W. Gill, and J. A. Pople, J. Chem. Phys. **98**, 5612 (1993).

[40] G. Kin-Lic Chan and N. C. Handy, J. Chem. Phys. **112**, 5639 (2000).

[41] J. M. Pérez-Jordà and A. D. Becke, Chem. Phys. Lett. **233**, 134 (1995).

[42] A. K. Rappé and E. R. Bernstein, J. Phys. Chem. A **104**, 6117 (2000).

[43] L. A. Curtis, D. J. Frurip, and M. Blander, J. Chem. Phys. **71**, 2703 (1979).

[44] J. A. Odutola and T. R. Dyke, J. Chem. Phys. **72**, 5062 (1980).

[45] M. J. Frisch, J. E. Del Bene, J. S. Binkley, and H. F. Schaefer III, J. Chem. Phys. **84**, 2279 (1986).

[46] C. Tuma, A. D. Boese, and N. C. Handy, Phys. Chem. Chem. Phys. **1**, 3939 (1999).

[47] A. S. Pine and B. Howard, J. Chem. Phys. **84**, 590 (1986).

[48] M. Quack and M. A. Suhm, Theor. Chim. Acta **93**, 61 (1996), and references therein.

[49] S. S. Shaik, H. B. Schlegel, and S. Wolfe, *Theoretical Aspects of Physical Organic Chemistry. The SN$_2$ Mechanism* (Wiley, New York, 1992).

[50] T. N. Truong and E. V. Stefanovich, J. Phys. Chem. **99**, 14700 (1995).

[51] M. N. Glukhovtsev, A. Pross, and L. Radom, J. Am. Chem. Soc. **117**, 2024 (1995).

[52] M. N. Glukhovtsev, R. D. Bach, A. Pross, and L. Radom, Chem. Phys. Lett. **260**, 558 (1996).

[53] J. W. Larson and T. B. McMahon, J. Am. Chem. Soc. **106**, 517 (1984).

[54] S. E. Barlow, J. M. van Doren, and V. M. Bierbaum, J. Am. Chem. Soc. **116**, 10645 (1994).

[55] S. Patchkovskii and T. Ziegler, J. Chem. Phys. **116**, 7806 (2002).

[56] V. Barone, L. Orlandini, and C. Adamo, Chem. Phys. Lett. **231**, 295 (1994).

[57] V. Barone and C. Adamo, J. Chem. Phys. **105**, 11007 (1996).

[58] S. Sadhukhan, D. Munoz, C. Adamo, and G.E. Scuseria, Chem. Phys. Lett. **306**, 83 (1999).

[59] W. Weltner, Jr., *Magnetic Atoms and Molecules* (Dover, New York, 1989).

[60] C. Adamo, V. Barone, and A. Fortunelli, J. Chem. Phys. **102**, 384 (1995).

[61] V. Barone, in *Recent Advances in Density Functional Methods, Part 1*, edited by D.P. Chong (World Scientific, Singapore, 1995), p. 287.

[62] C. Adamo, M. Cossi, and V. Barone, J. Mol. Struct.: THEOCHEM **493**, 145 (1999).