Toward reliable density functional methods without adjustable parameters: The PBE0 model

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We present an analysis of the performances of a parameter free density functional model (PBE0) obtained combining the so called PBE generalized gradient functional with a predefined amount of exact exchange. The results obtained for structural, thermodynamic, kinetic and spectroscopic (magnetic, infrared and electronic) properties are satisfactory and not far from those delivered by the most reliable functionals including heavy parameterization. The way in which the functional is derived and the lack of empirical parameters fitted to specific properties make the PBE0 model a widely applicable method for both quantum chemistry and condensed matter physics. © *1999 American Institute of Physics.* [S0021-9606(99)30513-4]

I. INTRODUCTION

Computational models rooted in the density functional (DF) theory [1] are nowadays considered valuable tools for the study of molecular electronic structure. As a matter of fact, for closed shell molecules formed by main row atoms the performances of current DF models using the so called generalized gradient approximations (GGA) are comparable to the results obtained by low-order many body perturbation techniques, such as the second order Möller–Plesset (MP2) approach.[2,3] However, contrary to MP2, DF models deliver essentially the same precision also for open shell systems and for molecules containing atoms belonging to the whole Periodic Table.[4] While DF methods provide *per se* thermochemical data of remarkable accuracy,[5] the reliability of geometries and harmonic force fields is particularly significant since several recent extrapolation procedures (belonging, e.g., to the G2 or CBS families[6–9]) have replaced HF or MP2 geometries and frequencies by DF ones.

Despite these remarkable features, it remains true that the exact density functional is unknown, and approximations must be introduced. In the Kohn–Sham (KS) approach to DF theory, the exact kinetic-energy operator is used together with a density functional for the exchange-correlation energy, E_{xc}.[1] Although strictly speaking exchange and correlation need not be separated in a DF context, it is customary to develop formally separate functionals for E_x and E_c. Since E_c is typically around 10% of E_x, it would seem most important that the exchange functional be accurate.[10] However, since the whole E_{xc} is usually developed and parameterized, there is some error compensation between both partners and combination of E_x and E_c functionals issuing from different sources could be dangerous.

A number of GGA and beyond GGA functionals have been developed in the last years and are being incorporated in several computer codes.[11–33] They are based on some combination of two limiting strategies, namely, (1) fitting of some set of experimental data and (2) fulfillment of a number of well known physical constraints. Although most existing functionals combine both approaches, attention is being shifted to the first aspect with the risk, in our opinion, of overemphasizing the thermochemistry of organic molecules [34] at the expense of other systems and/or properties for which the free electron gas limit and other basic physical constraints could be more important.[35–38] On the other side, Perdew, Burke and Ernzerhof have recently introduced a GGA functional (hereafter referred to as PBE) in which all the parameters (other than those in its local spin density, LSD, component) are fundamental constants.[22] This is obtained using the Perdew–Wang (PW) correlation functional,[13] and a new exchange contribution:

$$E_x^{\text{PBE}} = \frac{bx^2}{1 + ax^2}, \tag{1}$$

with $b = 0.00336$, $a = 0.00449$ and $x = |\nabla\rho|/\rho^{4/3}$, ρ and $\nabla\rho$ being the electron density and its gradient. Due this choice,[39] the PBE functional is expected to provide results of comparable quality for widely different chemical systems.[40]

Several benchmarks have already been published on this functional with remarkable results,[41–45] and some modification of parameters has been suggested to further improve its accuracy.[46] However, a better avenue toward increased reliability is provided, in our opinion, by hybrid HF/DF models.[47,48] These methods are rooted in the adiabatic connection formula:[49]

$$E_{xc} = \int_0^1 d\lambda \, E_{xc,\lambda}, \tag{2}$$

where

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$$E_{xc,\lambda} = \langle \Psi_\lambda | V_{ee} | \Psi_\lambda \rangle - \frac{1}{2} \int d^3r \int d^3r' \frac{\rho(\mathbf{r}) - \rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}, \tag{3}$$

which connects the noninteracting KS reference system ($\lambda = 0$) to the fully interacting real system ($\lambda = 1$), through a continuum of partially interacting real systems, all sharing a common density ρ.[49] Starting from this formula, several hybrid schemes have been proposed, the most widely used (hereafter referred to collectively as ACM3) including three empirical parameters to rule the mixing of HF exchange and DF exchange and correlation:[50–52]

$$E_{xc}^{ACM3} = E_{xc}^{LSD} + a_1(E_x^{HF} - E_x^{LSD}) + a_2 \Delta E_x^{GGA} + a_3 \Delta E_c^{GGA}. \tag{4}$$

More recently, Becke has suggested[53] that just one coefficient is sufficient to rule the HF/DF exchange ratio according to

$$E_{xc}^{ACM1} = E_{xc}^{GGA} + a_1(E_x^{HF} - E_x^{GGA}). \tag{5}$$

These methods (collectively referred to as ACM1) are quite successful,[54–56] and it has been shown that hybrid nonempirical schemes employing a system- and property-dependent mixing coefficient can be approximated quite accurately by Eq. (5).[57]

Perdew and co-workers have next shown that the optimum value of the a_1 coefficient can be fixed *a priori* taking into account that fourth-order perturbation theory is sufficient to get accurate numerical results for molecular systems.[58] This leads to a family of adiabatic connection functionals (hereafter referred to as ACM0) with the same number of adjustable parameters as their GGA's constituents:

$$E_{xc}^{ACM0} = E_{xc}^{GGA} + \frac{1}{4}(E_x^{HF} - E_x^{GGA}). \tag{6}$$

We have recently shown that the B0LYP variant (i.e., Becke exchange and Lee–Yang–Parr correlation functionals[50]) gives results comparable to those of current 3-parameter hybrids like B3LYP,[59,60] whereas the PW0PW model (which uses the Perdew–Wang exchange and correlation functionals[50]) leads to disappointing results. Further studies showed that, starting from the original PW exchange functional,

$$E_x^{PW} = \frac{bx^2 - (b - \beta)x^2 \exp(-cx^2) - 10^{-6}x^d}{1 + 6bx \sinh^{-1} x - \dfrac{10^{-6}x^d}{A_x}} \tag{7}$$

(with $b = 0.0042$, $\beta = 5(36\pi)^{-5/3}$; $c = 1.6455$; $d = 4.0$), optimization of b and d parameters (to $b = 0.0046$, $d = 3.73$; hereafter referred to as mPW) is sufficient to obtain an ACM0 model (mPW0) competitive with the B0LYP approach for the covalent interactions, but characterized by a significantly improved long range behavior.[29] In particular, while both B and PW exchange functionals have a correct asymptotic behavior, this does not apply to the intermediate region characterizing noncovalent interactions. Thus the differential exchange energies (i.e., the exchange energies of dimers minus those of the constituting fragments) provided

by B and PW exchange functionals are quite poor[16] and only purposely tailored functionals behave properly.[16,29,60]

Since the ACM0 models contain, by definition, only the adjustable parameters used in their GGA component, we have thought it interesting to analyze the performances of the ACM0 model issuing from the PBE GGA (hereafter PBE0), which does not contain any adjustable parameter. Since the PW and PBE correlation functionals are very similar, another interesting aspect is whether the PBE exchange functional is closer to the original PW model or to our modified version (mPW). Together with standard organic molecules, we have analyzed also a number of other aspects, including organometallic systems, noncovalent interactions, reactivity, structure and magnetic properties of open shell systems and spectroscopic properties. Furthermore, thermodynamic properties have been evaluated by a fully coherent approach in which geometries, harmonic frequencies and electronic energies are obtained at the same computational level without resorting to HF or MP2 geometries and frequencies. Note that, since the second derivatives of the functional are needed in the evaluation of analytical second derivatives and of excitation energies by the time-dependent density functional (TD-DF) approach, we have derived and implemented both first and second derivatives of the PBE exchange and correlation functionals in a fully self-consistent model.

II. COMPUTATIONAL DETAILS

All the DF computations were carried out within the Kohn–Sham (UKS) formalism, as implemented in the development version of the GAUSSIAN 98 code.[61] In this particular implementation, the exchange-correlation contribution to the total electronic energy is evaluated using a self-consistent procedure which avoids the evaluation of the Hessians of the electronic density.[62] As a consequence, the cost of the exchange-correlation part of the electronic calculation scales linearly with the size of the atomic basis set used in the expansion of the molecular orbitals.[63] Of course, the evaluation of the Hessian of electron density cannot be avoided when computing analytical gradients, or second derivatives. This task is, however, performed only once in each optimization step. We have added the PBE and PBE0 functionals to those already available in the GAUSSIAN package[50] so that all the standard features for geometry optimization, calculation of harmonic frequencies, properties and excitation energies[50] are also available for these methods. Note that, in analogy with our previous implementations,[10,29] the Gaussian keyword for the PBE functional is PBEPBE while both PBE0 and PBE1PBE are recognized for the ACM0 version.[50]

A number of different basis sets have been used. In particular, the 6-311$G(d,p)$ basis set of Pople and co-workers[64] has been used to optimize all the molecular geometries, since previous experience showed that a polarized valence triple-ζ basis set generally provides nearly converged structural parameters by DF methods.[9,65] Diffuse functions on heavy atoms have been added for anionic species. An extended basis set, namely the 6-311++G(3df,3pd) one,[66] has next been used to evaluate all the energetic parameters (atomization and dissociation energies) and electronic properties (dipole moments) at the above geometries. The situation is more

involved for the van der Waals complexes, where, to avoid basis-set converge problems, we have used for He the (8,3,2,1) primitives of the so called cc-PV5Z basis set, without any contraction.[67] For Ne and Ar we have used the (15s,9p) or (20s,12p) primitives from the corresponding aug-cc-pV5Z basis set together with 3d, 2f, 1g polarization functions from the cc-pVQZ basis set.[68] Then general contractions of the first (6s,2p) or (11s,6p) primitives were used for describing inner parts of the core orbitals, whereas all the other primitives were left uncontracted. We have previously verified that these basis sets provides converged results in DF computations.[29] Finally magnetic parameters of the open shell systems have been evaluated with the EPR-III basis set, which has been purposely tailored for the evaluation of magnetic properties in DF computations.[69–72]

All the molecular geometries have been fully optimized and the nature of stationary points has been characterized by computing harmonic wave numbers. When necessary, interaction energies have been corrected for Basis Set Superposition Error (BSSE)[73] and Zero Point Energy (ZPE) effects.

The calculations of NMR chemical shifts were carried out within the gauge-including atomic orbital (GIAO) method.[74,75] We refer the reader to the original paper of Frisch and co-workers[75] for details about the Gaussian implementation. Following previous suggestions,[75] we use the 6-311+G(2d,p) basis set[64] for computing chemical shifts.

Time-dependent DF theory (TD-DF) provides a formally rigorous extension of Hohenberg–Kohn–Sham DF theory, which is time independent, to the situation where a system, initially in its ground stationary state, is subject to a time-dependent perturbation modifying its external potential, ν.[76] A stationary action principle may be derived, analogous to the minimum energy principle of Hohenberg–Kohn theory, and this can be used to derive the time-dependent KS equations.[76] Since the dynamic polarizability describes the response of the dipole moment to a time-dependent electric field, it may be calculated from the response of the charge density obtained from TD-DF. This allows the determinations of the electronic excitation spectrum in the usual dipole approximation, because the poles of the dynamic polarizability determine the excitations energies.[77] Here we follow the TD-DF formalism as reported by Scuseria and co-workers[78] and the 6-31+G(d) basis set of Foresman et al.[79] successfully validated in previous studies.[78,80]

III. RESULTS AND DISCUSSION

In the following we analyze a number of test cases, chosen in order to cover the widest possible class of chemical interesting systems. These systems include typical organic molecules, like those included in the G2 data set, noncovalent interactions, some prototypical organometallic systems, free radicals, hydrogen-bonded and van der Waals (vdW) complexes. A number of molecular properties, other than geometries and frequencies, have been considered in order to make our data set more representative.

The examples analyzed in this work can be roughly divided into two classes: the first class includes all those systems whose properties are accurately described by the MP2

approach (i.e., essentially closed shell organic molecules), whereas the second class is formed by all the other systems and/or properties whose accurate description requires more sophisticated post-HF methods.

Even if a systematic study on the performances of the pure PBE approach has not yet been published, several partial tests have been carried out,[40–45] giving a good definition of the strengths and limits of this functional. So, we do not discuss our results at this level, except to say that we have verified the correctness of our implementation of the functional and its first derivatives, recomputing a number of molecules reported in the above references. Second derivatives of the functional have been then verified by evaluation of harmonic frequencies by both finite differences of analytical gradients and by a completely analytical procedure. We remark that, while the results of both procedures are very close for rigid molecules, analytical second derivatives are much more reliable for flexible systems and allow a significant saving of computer time.

A. Covalent interactions

In Table I are reported the atomization energies for 32 molecules belonging to the G2 data set, computed using the PBE0 model.

This subset has become a standard for the validation of new density functional approaches.[63] A comparison with the mPW0 results well underlines the significant numerical improvement obtained with the PBE0 model. It is also interesting to note that both absolute mean and maximum deviations are smaller at the PBE0 level with respect to the mPW0 results.

In Tables II and III are reported the geometrical parameters of the same molecules, which can be considered quite satisfactory. Zhang and Yang obtained a significant improvement of the atomization energies provided by the PBE functional, relaxing one of the theoretical constraints of the exchange contribution.[46] In contrast, this empirical modification worsens the bond lengths of some model molecules.[39] A comparative analysis of Tables I–III shows that the inclusion of some exact exchange significantly improves at the same time as geometrical parameters and atomization energies, without introducing any additional empirical parameter.

An even better definition of the performance of the PBE0 protocol can be done by a full comparison with some of the most common DF approaches. Table IV collects an error statistic for the most significant molecular properties of the G2 data set, computed at different levels of theory.

Since the data reported in this table are sufficiently self-explanatory, we add only a few comments. First, it is not surprising that the pure PBE model performs as well as the PW approach, since both functionals share the same theoretical background. However, both approaches provide deviations that are significantly higher than that obtained with the pure mPW method, especially concerning atomization energies. In contrast, the three functionals give different results when cast in a parameter-free ACM approach. In particular, the absolute average error for the atomization energies is quite high for PW0 (5.0 kcal/mol), while the lowest value is

TABLE I. Theoretical and experimental atomization energies (kcal/mol) of 32 molecules belonging to the reduced G2 data set. All theoretical values were obtained using the $6\text{-}311++G(3df,3pd)$ basis set with $6\text{-}311G(d,p)$ geometries and including ZPE corrections.

Molecule	mPW0	PBE0	exp[a]
H_2	98.7	99.0	103.3
LiH	51.3	51.7	56.0
BeH	53.6	53.7	46.9
CH	78.9	79.6	79.9
$CH_2(^3B_1)$	182.8	183.5	179.6
$CH_2(^1A_1)$	165.8	167.2	170.6
CH_3	289.5	291.0	289.2
CH_4	389.1	391.2	392.5
NH	80.3	81.1	79.0
NH_2	170.7	172.2	170.0
NH_3	272.7	274.7	276.7
OH	100.3	101.1	101.3
OH_2	213.6	214.7	219.3
FH	131.3	131.9	135.2
Li_2	18.8	19.3	24.0
LiF	131.1	131.7	137.6
HCCH	385.5	388.1	388.9
H_2CCH_2	530.0	533.3	531.9
H_3CCH_3	660.6	664.2	666.3
CN	173.5	175.8	176.6
HCN	299.0	301.7	301.8
CO	250.5	253.0	256.2
HCO	271.4	273.4	270.3
H_2CO	355.1	357.3	357.2
H_3COH	477.3	479.7	480.8
N_2	219.2	221.9	225.1
H_2NNH_2	402.8	405.7	405.4
NO	148.7	150.7	150.1
O_2	119.9	121.4	118.0
HOOH	245.8	247.3	252.3
F_2	31.3	32.3	36.9
CO_2	382.7	385.3	381.9
Abs. mean dev.	3.5	2.6	
Max dev.	6.5	5.0	

[a]From Ref. 33.

TABLE II. Theoretical and experimental bond lengths (Å) of the biatomic molecules belonging to the reduced G2 data set. All theoretical values were obtained with the $6\text{-}311G(d,p)$ basis set.

Molecule	PBE	mPW0	PBE0	exp[a]
H_2	0.749	0.744	0.745	0.742
LiH	1.604	1.591	1.597	1.595
BeH	1.355	1.342	1.347	1.343
CH	1.140	1.126	1.126	1.120
NH	1.053	1.043	1.040	1.045
OH	0.983	0.973	0.971	0.971
FH	0.928	0.919	0.916	0.917
Li_2	2.726	2.700	2.705	2.67
LiF	1.569	1.553	1.559	1.564
CN	1.177	1.163	1.163	1.172
CO	1.138	1.125	1.125	1.128
N_2	1.05	1.093	1.093	1.098
NO	1.160	1.146	1.143	1.151
O_2	1.221	1.202	1.194	1.207
F_2	1.420	1.402	1.401	1.412

[a]From Ref. 33.

average error in the frequencies is close to the MP2 value, while the maximum deviation is only half the corresponding MP2 value.

It must be also noted that mPW0 and PBE0 approaches provide close results, whereas conventional DF and ACM3 methods perform quite poorly.[29]

B. Systems containing heavier atoms: NiCO, CuCO and lanthanide halides

The performances of the PBE0 model along the whole periodic table have been checked by considering some small systems containing transition metals and lanthanides.

The NiCO and CuCO molecules were chosen since they represent two limiting bonding situations (covalent and van der Waals, respectively) for an open shell and a closed shell system.[82–91] The essential results on these two systems are summarized in Table VI.

There is a remarkable agreement between the geometrical parameters obtained by ACM0 methods and by the most refined post-HF procedures: actually PBE0 and mPW0 models give very similar values and outperform the B3LYP approach. It must be also pointed out that for CuCO, the MP2 approach predicts a very short Cu–C distance.[88] The same general behavior is also found for the harmonic frequencies, with the PBE0 results close to the post-HF values. The situation is a little more complicated concerning dissociation energies. The value predicted by the PBE0 model for NiCO (31 kcal/mol) is close to that provided by a sophisticated post-HF method (33.0 kcal/mol at the CAS-CI level)[85] or by the B3LYP approach (32.8 kcal/mol)[89] and well within the experimental range (29 ± 15 kcal/mol).[83] In contrast, the CuCO dissociation energy is somewhat overestimated (10.0 kcal/mol at the PBE0 level) with respect the experimental findings (6.0 ± 1.2 kcal/mol).[87] Anyway, this last value is intermediate between CCSD(T) (5.2 kcal/mol) and MP2 (12.5 kcal/mol) results.[88]

Lanthanide trihalides are good candidates for investigating whether the PBE0 approach provides a sufficiently reli-

provided by the PBE0 protocol (2.6 kcal/mol). Anyway, the performances of the PBE0 and mPW0 models are very close to that provided by ACM3 and other ACM0 methods, like B3LYP or B0LYP.[9,29] It must also be noted that the deviation provided by the MP2 method over the same data set is significantly higher.[3]

Since the rationalization discussed in the introduction for the ACM approaches is, in general, not applicable to ionization and electron capture processes, ionization potentials and electron affinities obtained at the PBE0 level are very close to their PBE counterparts. Thus, in order to save space, we do not show these results in detail.

The geometries and harmonic frequencies of the above G2 set are relatively well described by different quantum mechanical methods, and the most discriminating property is the atomization energy. There are, however, well known molecular systems (e.g., ozone, Cr_2) which are much more demanding. Among them, we have selected cis-FONO, which has been recently investigated in detail using several post-HF and DF methods.[81] The results collected in Table V show that the PBE0 model provides results which are comparable to those obtained by the MP2 approach. In particular, the

TABLE III. Theoretical and experimental geometries of the polyatomic molecules belonging to the reduced G2 data set. Bond lengths in Å, angles in degrees. All theoretical values were obtained with the 6-311G(d,p) basis set.

Molecule	Parameter	PBE	mPW0	PBE0	exp
CH$_2$	d(CH)	1.086/1.126	1.079/1.113	1.079/1.114	1.075/1.107
(^{3}B$_1$/^{1}A$_1$)	a(HCH)	135.1/99.7	134.7/101.2	134.5/100.9	133.9/102.4
CH$_3$	d(CH)	1.087	1.079	1.080	1.079
CH$_4$	d(CH)	1.097	1.090	1.089	1.086
NH$_2$	d(NH)	1.040	1.029	1.028	1.024
	a(HNH)	101.2	102.3	102.2	103.4
NH$_3$	d(NH)	1.023	1.015	1.013	1.012
	a(HNH)	105.6	106.5	106.4	106.0
H$_2$O	d(OH)	0.970	0.961	0.958	0.957
	a(HOH)	102.9	103.9	103.8	104.5
HCCH	d(CC)	1.208	1.197	1.198	1.203
	d(CH)	1.070	1.063	1.063	1.062
H$_2$CCH$_2$	d(CC)	1.334	1.325	1.325	1.334
	d(CH)	1.092	1.084	1.085	1.081
	a(HCH)	116.5	116.6	116.6	117.4
H$_3$CCH$_3$	d(CC)	1.519	1.510	1.510	1.526
	d(CH)	1.102	1.094	1.095	1.088
	a(HCH)	108.1	108.3	108.2	107.4
HCN	d(CN)	1.160	1.147	1.147	1.153
	d(CH)	1.074	1.066	1.067	1.065
HCO	d(CO)	1.184	1.170	1.171	1.175
	d(CH)	1.138	1.124	1.125	1.122
	a(HCO)	123.6	124.4	124.4	124.6
H$_2$CO	d(CO)	1.209	1.196	1.197	1.203
	d(CH)	1.120	1.109	1.109	1.099
	a(HCH)	115.3	115.6	115.6	116.4
H$_3$COH	d(CO)	1.426	1.409	1.410	1.421
	d(CH$_a$)	1.099	1.090	1.091	1.093
	d(CH$_b$)	1.107	1.098	1.098	1.093
	d(OH)	0.969	0.957	0.957	0.963
	a(OCH$_a$)	106.7	107.1	107.0	107.0
	a(COH)	107.8	107.8	107.7	108.0
	a(H$_a$CH$_b$)	108.4	108.5	108.5	108.5
H$_2$NNH$_2$	d(NN)	1.442	1.420	1.419	1.447
	d(NH)	1.023	1.015	1.012	1.008
	a(NNH)	109.2	109.4	109.3	109.2
	a(HNH)	107.0	113.4	113.4	113.3
	d(HNNH)	85.3	87.3	87.7	88.9
HOOH	d(OO)	1.473	1.430	1.431	1.475
	d(OH)	0.975	0.962	0.962	0.950
	a(OOH)	99.2	100.6	100.7	94.8
	d(HOOH)	120.4	118.0	118.5	120.0
CO$_2$	d(CO)	1.165	1.156	1.157	1.160

[a]From Ref. 33.

TABLE IV. Absolute mean deviations obtained by different methods for some properties of 32 molecules of the G2 data set. Bond lengths, bond angles, and harmonic frequencies are computed using the 6-311G(d,p) basis set, while atomization energies and dipole moments are evaluated by the 6-311++G(3df,3pd) extended basis set.

Method	Bond lengths (Å)	D_0 (kcal/mol)	Dip. mom. (D)	Harm. freq (cm^{-1})
PW	0.012	9.5	0.12	66
PBE	0.012	9.5	0.12	66
mPW	0.012	6.7	0.11	65
PW0	0.011	5.0	0.10	52
PBE0	0.010	2.6	0.10	42
mPW0	0.010	3.5	0.10	39

TABLE V. Geometrical parameters (bond lengths in Å and valence angles in degrees) and harmonic frequencies (cm^{-1}) computed for cis-FONO by different methods.

	CCSD[T][a,b]	MP2[a,b]	mPW0	PBE0
FO	1.433	1.414	1.417	1.419
ON	1.445	1.488	1.371	1.39
NO	1.162	1.155	1.157	1.157
FON	110.4	108.4	113.0	113.1
ONO	115.8	114.6	118.0	118.0
$\omega_1(a')$	1747	1744	1805	1802
$\omega_2(a')$	933	977	968	961
$\omega_3(a')$	787	799	847	840
$\omega_4(a')$	441	329	485	470
$\omega_5(a')$	381	366	447	440
$\omega_6(a')$	277	267	267	255
Abs. mean dev.		33	46	41
Max dev.		112	66	59

[a]TZ2P basis set.
[b]Reference 81.

TABLE VI. Bond lengths (Å), valence angles (degrees), harmonic wave numbers (cm^{-1}) and dissociation energies (kcal/mol) for NiCo and CuCO.

Method	d(M–C)	d(C–O)	Angle	D_0[a]	ϖ(CO)
NiCO					
exp				41.6±6[b]	2028[d]
				29±15[c]	
CAS-CI[e]	1.698	1.158	180.0	33.0	2010
B3LYP[f]	1.666	1.152	180.0	32.8	2073
mPW0	1.675	1.147	180.0	30.0	2119
PBE0	1.675	1.148	180.0	30.9	2118
CuCO					
exp.				6.0±1.2[g]	2042[h]
MP2[i]	1.783	1.137	180.0	12.5	2103
CCSD(T)[i]	1.910	1.140	152.5	5.2	2094
B3LYP[f]	1.957	1.142	138.8	8.4	2036
mPW0	1.945	1.140	140.2	9.7	2084
PBE0	1.948	1.140	140.3	10.0	2085

[a]Dissociation energy including ZPE corrections.
[b]Reference 82.
[c]Reference 83.
[d]Reference 84 corrected for anharmonicity and matrix effects (+32 cm^{-1}).
[e]Reference 85.
[f]Reference 86.
[g]Reference 87.
[h]Reference 84 corrected for anharmonicity and matrix effects (+32 cm^{-1}).
[i]Reference 88.

able description of bonding in very heavy-transition metal compounds since they have been the subject of a number of theoretical[92–96] and experimental investigations.[96–99] In particular, we have focused our attention on the trichloride compounds, namely LaCl$_3$, GdCl$_3$ and LuCl$_3$, which do not exhibit first-order spin–orbit coupling. Following previous DF studies,[2,96] our computations have been carried out using the relativistic effective core potentials (RECP) of Cundari and Stevens.[100,101] Table VII collects the PBE0 results, together with other DF and post-HF values.

The structures and properties provided by the PBE0 model are in good agreement with the experimental findings.

TABLE VII. Bond lengths (Å), harmonic wave numbers (cm^{-1}) and atomization energies (eV) for the LnCl$_3$ series.

	CISD+Q[a]	MCSCF[b]	MP2[c]	B3LYP[d]	mPW0	PBE0	exp[e]
LaCl$_3$							
d(LaCl)	2.612	2.643	2.65	2.634	2.611	2.609	2.62
ΔE	13.80			15.18	15.25	15.23	15.88
ν_2		323	294	317	3.29	332	335
ν_2		26	16	43	28	26	51
ν_3		301	317	316	311	312	300
ν_4		72	67	76	76	75	72
GdCl$_3$							
d(GdCl)	2.511	2.528	2.53	2.519	2.501	2.498	2.528
ΔE	13.24			15.97	15.85	15.83	15.14
ν_2		336	304	333	332	335	338
ν_2		45	35	43	40	42	56
ν_3		314	328	331	331	329	326
ν_4		77	66	77	75	76	84
LuCl$_3$							
d(LuCl)	2.428	2.440	2.43	2.447	2.429	2.429	2.417
ΔE				16.02	15.88	15.79	15.10
ν_2			305	341	338	339	342
ν_2			60	75	71	70	60
ν_3			327	318	325	326	331
ν_4			80	78	87	80	88

[a]Reference 92.
[b]Reference 93.
[c]Reference 95.
[d]Reference 94.
[e]References 97–99.

TABLE VIII. Bond lengths and interaction energies for He$_2$, Ne$_2$ and Ar$_2$ computed by different methods using the modified cc basis sets discussed in the main text and corrected for BSSE effects.

Dimer	Method	d (Å)	D_{int} (eV)
He$_2$	PW	2.78	0.010
	PBE	2.73	0.003
	mPW	3.14	0.003
	mPW0	3.11	0.002
	PBE0	2.78	0.002
	exact[a]	2.97	0.001
Ne$_2$	PW	2.94	0.014
	PBE	3.13	0.005
	mPW	3.25	0.004
	mPW0	3.23	0.003
	PBE0	3.04	0.003
	exact[a]	3.09	0.004
Ar$_2$	PW	3.90	0.014
	PBE	4.00	0.007
	mPW	4.45	0.005
	mPW0	4.42	0.003
	PBE0	4.04	0.006
	exact[a]	3.76	0.012

[a]Reference 104.

In particular, the errors on bond lengths (<0.02 Å) and on harmonic frequencies (<14 cm^{-1}) are very small. Furthermore, the PBE0 model performs slightly better than the MP2 approach when using similar RECP.[95] The larger error found for the atomization energies might be due to the not-complete inclusion of relativistic effects by RECP.[96] In this connection, it is noteworthy that CI/RECP computations provide an even larger error.[92] The better performances of PBE0 with respect to B3LYP are also remarkable since they confirm that functionals respecting the free electron gas limit provide more reliable results for heavy metals[96] and that the performances of the PBE0 model should be very close over a wide range of electronic densities.

C. Noncovalent interactions

We turn next to noncovalent interactions, where the spread of results obtained by different functionals is particularly significant. We have chosen different prototypical systems, namely the He, Ne, Ar, hydrogen fluoride, and water dimers, representative of very weak van der Waals and of hydrogen–bond interactions.

van der Waals complexes are very difficult to handle in the framework of the DF approach. In particular, the most common DF methods, including some hybrid HF/DF approaches, significantly underestimate the stability of these complexes,[102,103] whereas the PW model has just the opposite behavior.[29,41,42] Only the mPW0 approach provides accurate results for both He$_2$ and Ne$_2$ complexes due to the optimization of parameters shortly described in the Introduction.[29]

The numerical values for the energy minima of He, Ne and Ar dimers obtained by several functionals and corrected for BSSE effects are collected in Table VIII, while the overall trends of different functional are shown in Figs. 1 and 2 for He$_2$ and Ne$_2$.
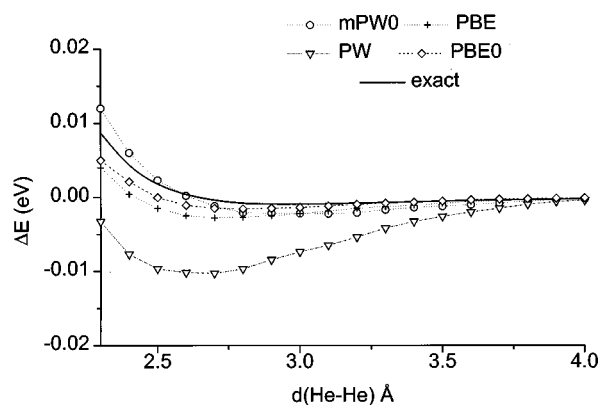

FIG. 1. Potential-energy curves for the interaction of two He atoms. The curve labeled ''exact'' has been computed using the analytical expression of Ref. 104.

From these data it is quite apparent that both the PBE and PBE0 models predict interaction energies and equilibrium distances which are sufficiently close to the experimental values.[104] In particular, the PBE0 functional gives an interatomic distance for the He dimer (2.78 Å) which is slightly lower than the experimental value (2.97 Å), while the interaction energy is overestimated (0.002 vs 0.001 eV). Anyway, similar small errors are found by the mPW0 protocol, which has been specifically parameterized to reproduce long-range interactions.[29]

The situation is even better for Ne and Ar dimers, where the PBE0 model significantly outperforms the mPW0 one. It must be noted, anyway, that the PBE0 results for Ne$_2$ are in very good agreement with experiment, whereas for Ar$_2$ the interatomic distance is slightly overestimated and the interaction energy is about one half of the experimental value (see Table VIII).

Let us next consider the water dimer. It is behind the scope of this paper to make a complete review of the huge amount of results available for this system, but we refer, instead, to a more detailed discussion and references included in previous works.[105,106] Even if this system has been studied in considerable detail, some problems still remain,
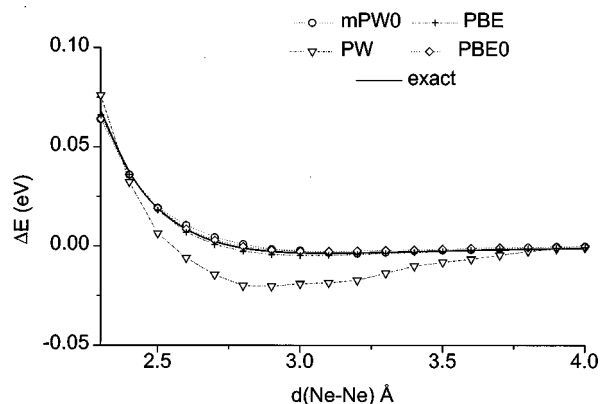

FIG. 2. Potential-energy curves for the interaction of two Ne atoms. The curve labeled ''exact'' has been computed using the analytical expression of Ref. 104.
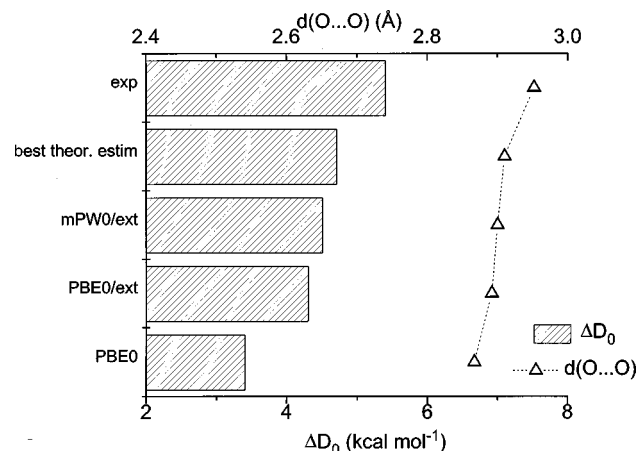
FIG. 3. The intermolecular O···O distance and binding energy of the water dimer obtained by different methods. All values have been corrected for BSSE and ZPE effects (see the text for details).
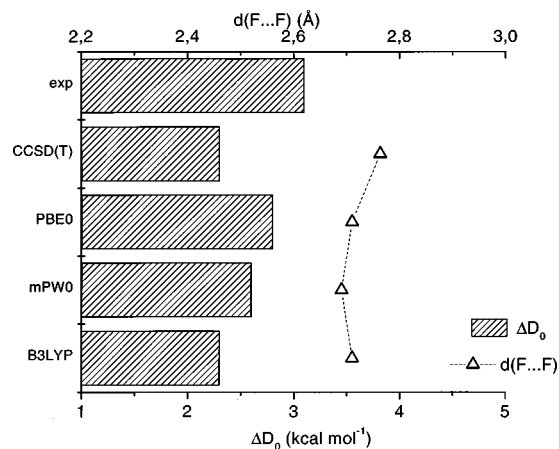

FIG. 4. The intermolecular F···F distance and binding energy of the hydrogen fluoride dimer obtained by different methods. All values have been corrected for BSSE and ZPE effects (see the text for details).

especially concerning the experimental determination of the binding energy. The currently accepted value is 5.4 ± 0.7 kcal/mol,[107] even if refined post-HF computations suggest that the interaction energy is close to 4.7 kcal/mol (see, for instance, the discussion in Ref. 106). At the same time, the most important geometrical parameter, namely the OO distance, is influenced by strong effects of anharmonicity, which obscure the precise experimental estimate of the equilibrium geometry. The current experimental value, taking into account anharmonicity effects in a model fashion, is 2.952 Å,[108] whereas a shorter distance, 2.910 Å is predicted by refined post-HF methods.[109] In Fig. 3 are reported the computed OO intermolecular distances and the corresponding binding energies corrected for both ZPE and BSSE effects.

As is already well documented,[110–112] the equilibrium geometry of the water dimer is quite accurately reproduced by standard DF methods, all the predicted OO distances falling between 2.87 and 2.92 Å, i.e., close to the MP2 estimate.[110–112] Also, the PBE distance (2.88 Å) falls in the same range and, as already found for the van der Waals dimers, this value is negligibly modified by the inclusion of exact exchange (the PBE0 value is 2.88 Å). In contrast, a significant difference is found for the binding energy between the PBE (2.9 kcal/mol) and the PBE0 (3.4 kcal/mol) results. An extension of the basis set plays a not negligible role, the binding energy being 4.3 kcal/mol at the PBE0/6-311++G($3df$,$3pd$) level. This last result is close to the mPW0 value (4.5 kcal/mol), to the best theoretical estimate (4.7 kcal/mol), and is also in the range of experimental determinations.

An even more difficult test is represented by the hydrogen fluoride dimer, a molecule studied for many years by both experimentalists and theoreticians.[113–116] The best current estimate of the experimental dissociation energy is 3.06 ± 0.01 kcal/mol,[113,114] while the best theoretical value is 2.3 kcal/mol (including ZPE and BSSE corrections), obtained at the CCSD(T) level by Racine and Davidson[115] (see Fig. 4).

There is a significant basis set effect on the geometrical

parameters of (HF)$_2$. In particular, up to the 6-311G(d,p) level all the KS methods, including PBE0, predict an energy minimum characterized by an antiparallel disposition of the two HF moieties. In contrast, the energy minimum obtained at the PBE0/6-311++G($3df$,$3pd$) level is characterized by a C_s symmetry with an almost linear F–H–F arrangement. Furthermore, the geometrical parameters are now quite close to those of the reference structure of Racine and Davidson.[115] For instance, the F–F distance is 2.56 Å at the PBE0/6-311G(d,p) level and increases up to 2.71 Å with the extended 6-311++G(d,p) basis set, not far from the best theoretical estimate of 2.76 Å.[115]

The binding energy is significantly underestimated by the PBE functional (1.2 kcal/mol), and also the inclusion of some exact HF exchange does not introduce a significant improvement, the PBE0 value being 1.4 kcal/mol. In contrast, the effect of basis set extension is more significant than in a water dimer, the binding energy increasing up to 2.8 kcal/mol at the PBE0/6-311++G($3df$,$3pd$) level (including BSSE and ZPE corrections). This last result is close to the mPW0 estimate (2.6 kcal/mol) and close to the experimental value (3.06 kcal/mol).

In summary, judging from both energy and geometry results, the nonempirical PBE0 approach seems to perform as well as the purposely tailored mPW0 model over such a difficult playground represented by noncovalent interactions.

D. Reactivity: Walden inversion and proton transfer in malonaldehyde

As a further significant test, we have chosen a SN_2 reaction, whose importance in organic chemistry is well evidenced by the accumulation of a large body of experimental and theoretical data.[117–122] From a theoretical point of view, several studies have shown that these reactions are extremely sensitive to the theoretical model used.[119,120] Already the thermodynamics of the simple Walden inversion:
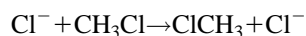
$$Cl^- + CH_3Cl \rightarrow ClCH_3 + Cl^-$$

TABLE IX. Complexation energies of the ion–molecule complex (ΔH_{comp}), activation energy ($\Delta H^{\#}$) and overall activation energy relative to reactants (ΔH_{ovr}) for the Walden inversion, computed at various computational levels. All energies are in kcal/mol and include BSSE and ZPE corrections.

	G2+(MP2)[a]	B3LYP[a]	mPW0	PBE0	exp[b]
ΔH_{comp}	10.6	9.4	10.0	9.6	12.2±2
$\Delta H^{\#}$	13.0	8.2	10.5	10.2	13.3±2
ΔH_{ovr}	2.5	−1.2	0.5	0.6	1±1

[a]Reference 106.
[b]References 108, 109.

is difficult to describe by quantum mechanical methods. This is particularly true at the DF level, where all the methods, including the B3LYP protocol, fail in predicting some thermodynamic quantities.[120] This reaction is characterized, in the gas-phase, by a double-well energetic profile, with two minima corresponding to the formation of a pre- and a post-reaction ion–molecule complex (Cl⁻...CH_3Cl) and a saddle point (SP) with D_{3h} symmetry (ClCH$_3$Cl⁻). The most significant thermodynamic quantities are the complexation energy of the ion–molecule complex (ΔH_{comp}), the activation energy, i.e., the relative energy of the D_{3h} saddle point with respect to the ion–molecule complex ($\Delta H^{\sharp}$) and the overall barrier ($\Delta H^{\sharp}_{ovr}$), defined as the difference between these two energies. The computed energies collected in Table IX show a good agreement between MP2 and the PBE0 results concerning both ΔH_{comp} and $\Delta H^{\sharp}$, even if this latter barrier is slightly underestimated. Anyway, all the computed PBE0 values fall in the range of the experimental estimation.[121,122]

The situation is more involved for the overall barrier, because standard DF methods, including the popular B3LYP approach, give a negative energy. This effect is probably related to the overstabilization of compact (saddle point, SP) with respect to looser (minimum) structures by current DF methods.[60] The right trend can be restored only using functionals with a correct long-range behavior, like the mPW0 one.[29] So, it is reassuring that the PBE0 predictions are very close to the results obtained with this functional (0.6 vs 0.5 kcal/mol).

As a second representative organic reaction, we have chosen the proton transfer (PT), which, despite its apparent simplicity, represents a severe challenge both for post-HF and DF approaches. In particular, several authors have explored the applicability of DF methods to the study of PT processes,

showing that standard DF approaches provide very low activation energies.[9,123–129] 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 this case, the underestimation of the PT activation energy by DF methods is augmented by the overestimation of correlation energy which produces an excessive degree of conjugation in the molecular backbone.[9] The results obtained by the PBE0 functional are reported in Table X.

From these data it is quite apparent that the PBE0 protocol underestimates the activation energy, the computed value being 2.1 kcal/mol, very close to the mPW0 result (2.2 kcal/mol). The reference MP2 value is 0.7 kcal/mol higher, while the more parameterized B3LYP functional predicts an even larger value (3.0 kcal/mol).[9]

As concerns the H-bond geometrical parameters, subtle effects rule the relationship between the O–O distance and energy barrier, so that a direct connection between these two factors cannot be drawn. For instance, the O–O distance in the SP is very similar at the PBE0 (2.354 Å) and at the MP2 (2.355 Å) levels, whereas the barrier height is significantly different. In contrast, this distance is underestimated in the minimum structure (2.534 Å) with respect to the MP2 result (2.581 Å).

E. Open shell systems: methyl and vinyl radicals

Free radicals are generally short-lived, highly reactive species, usually characterized by an experimental point of view only by their magnetic properties (especially isotropic hyperfine splittings, hfs).[69] Thus a successful theoretical approach must be able to provide at the same time reliable structural and magnetic properties.

The methyl radical is well characterized by both experimental and theoretical points of view (e.g., Refs. 130–132) thus providing the most natural benchmark for the study of π-radicals. Some results are shown in Table XI. It is quite apparent that all the ACM approaches are remarkably accurate and this is also the case for the MP2 method. Note, however, that conventional density functionals provide comparable hyperfine splittings for the hydrogen atom, but disappointing results for carbon.[69]

As is always the case for unsaturated σ radicals, the theoretical reproduction of the hyperfine structure of vinyl radical[133,134] is particularly demanding.[69,135] It provides, therefore, a significant benchmark for new computational

TABLE X. Main H-bond geometrical parameters (Å) and relative energies (kcal/mol) for the minimum (M) and saddle point (SP) of malonaldehyde. The relative energies are computed at the 6-311++G(3df,3pd) level using 6-311G(d,p) geometries.

	MP2[a]		B3LYP[b]		mPW0		PBE0	
	M	SP	M	SP	M	SP	M	SP
d(OO)	2.581	2.355	2.559	2.370	2.537	2.353	2.534	2.354
d(H..O)	1.678	1.197	1.656	1.207	1.631	1.200	1.662	1.200
d(OH)	0.991	1.197	0.969	1.211	1.001	1.200	1.003	1.200
ΔE	0.0	2.8	0.0	3.0	0.0	2.2	0.0	2.1

[a]From Ref. 9.
[b]Reference 60.

TABLE XI. Geometrical parameter (Å) and isotropic hyperfine coupling constants (a, in G) computed for the methyl radical by different methods. Density functional methods have been carried out using the EPR-III basis set.

Parameter	CCSD[T][a]	B3LYP	mPW0	PBE0	exp[b,c]
d(CH)	1.079	1.079	1.078	1.078	1.079
a(C)	27.8	29.8	26.9	29.2	28.4
a(H)	−24.6	−23.3	−26.9	−26.1	−25.1

[a]Reference 132.
[b]Reference 130.
[c]Reference 131.

models. As shown in Table XII, the ACM0 and MP2 geometrical parameters are quite close and not far from those obtained by the much more expensive CCSD model.

The difficulties met by standard methods for the computation of isotropic hfs in unsaturated σ radicals are well reflected by the data of Table XII. For instance, the UMP2 coupling constant of C_β has the wrong sign (14 vs −8.6) and the hfs of H_{syn} is about 30 G below the experimental value. Even the very refined coupled cluster methods are not completely accurate for these systems. On the other hand, ACM3 and ACM0 models provide remarkable results, the difference between different implementations being only marginal. Note that conventional DFT models and all the ACM implementations including the original PW functional[136,137] are much less successful for nonhydrogen atoms.

The limits of conventional post-HF methods for open shell systems are reflected, of course, also on the prediction of kinetic parameters. Therefore it is particularly significant to develop a relatively cheap model for treating these systems. As an example of the performances of the PBE0 model in this connection we have considered the isomerization of the formaldehyde radical cation $H_2C=O^+$ (FRC) to its distonic form $HCOH^+$ (HMRC). It is well known that the MP2 method incorrectly predicts that the FRMC/HMRC isomerization is endothermic (by about 2 kcal/mol) and significantly underestimates the activation energy (about 40 kcal/mol).[69] On the other hand, the PBE0 model restores the correct stability order and gives reaction energies (6.4 vs 6.6 kcal/mol) and activation energies (48.2 vs 49.0 kcal/mol) very close to those provided by the much more expensive coupled cluster (CCSD) approach.[69] Also the geometrical structures and vibration frequencies obtained at the PBE0 and CCSD levels are very close, thus further confirming the reliability of this ACM0 approach.[138]

F. Molecular properties: NMR chemical shifts

A number of DF based methods for the computation of NMR properties have been developed and implemented recently.[139–144] Among others, the GIAO method seems to be particularly effective.[74,75] Anyway, it has been recently pointed out that the MP2 method predicts chemical shifts which are closer to experiment than those obtained using DF approaches, including the ACM3 method.[75] It is so natural to include, as a stringent test, the computation of chemical shieldings. In particular, we have selected some examples representative of the different possible hybridization of carbon atoms. We have next added the ozone molecule, which is a particularly difficult test for NMR properties.[143,145] The results are collected in Table XIII.

Let us first analyze the results for ^{13}C. From the data reported in the table, it is apparent that all the computational methods provide reliable results for chemical shieldings of sp^3 carbons. For instance the PBE0 value for the methyl carbon of formaldehyde is 156 PPM, whereas the MP2 value is 163 PPM, both values being close to the experimental finding (153 PPM). In going to sp^2 carbon atoms, like the

TABLE XII. Geometrical parameter (Å) and isotropic hyperfine coupling constants (a, in G) computed for the vinyl radical by different methods. Density functional methods have been carried out using the EPR-III basis set.

Parameter	MP2	CCSD(T)	B3LYP	mPW0	PBE0	exp[a]
$C^\beta C^\alpha$	1.299	1.330	1.302	1.301	1.301	
$C^\alpha H^\alpha$	1.086	1.087	1.077	1.078	1.078	
$C^\beta H_{syn}$	1.090	1.090	1.084	1.085	1.086	
$C^\beta H_{anti}$	1.095	1.094	1.089	1.090	1.091	
$H_{anti}C^\beta H_{syn}$	116.9	117.3	116.1	116.3	116.2	
$H_{anti}C^\beta C^\alpha$	121.1	121.0	121.7	121.6	121.7	
$H^a C^\alpha C^\beta$	135.8	135.3	138.3	138.1	138.2	
$a(C^\alpha)$	115	121	113.1	108.6	110.2	107.6
$a(C^\beta)$	14	−8	−5.8	−7.0	−6.9	−8.6
$a(H^\alpha)$	23	9	17.8	12.9	13.3	13.3
$a(H^\beta_{anti})$	19	28	41.9	40.2	40.2	34.2
$a(H^\beta_{syn})$	40	48	65.6	62.3	62.2	68.5

[a]References 133, 134.

TABLE XIII. Absolute isotropic NMR shielding constant (ppm) for carbon atoms computed for different molecules. All the values are computed using the 6-311+G(2d,2p) basis set and the PBE0/6-311G(d,p) geometries.

Molecule	Atom	HF	MP2	B3LYP	mPW0	PBE0	exp[b]
O_3	$O_{central}$	-2767[a]	2875[a]	-1010	-1046	-1040	-724
	$O_{terminal}$	-2861[a]	1248[a]	-1426	-1459	-1453	-1290
CH_3CHO	CH_3	162	163	148	154	156	153
	$C=O$	-15	1	-27	-14	-13	-14
CH_2CO	CH_2	177	190	174	189	189	188
	$C=O$	-38	-11	-38	-10	-13	-8
CH_3CH_2OH	CH_2	174	178	164	170	171	170
	CH_2	136	134	118	127	128	132

[a]Reference 140.
[b]Reference 143; the chemical shifts have been converted to absolute shieldings using $\sigma(^{17}O, \text{liq } H_2O)$ =307.9 ppm and $\sigma(^{13}C, CH_4)$=344.0 ppm.

carboxylic one in the same molecule, a dramatic change is observed. In particular, both MP2 and B3LYP methods fail in predicting the shielding constants, the computed values being 1 and -27 PPM, respectively. In contrast, both the mPW0 and PBE0 approaches give results close to the experimental value. Finally, the chemical shifts of the *sp* carbon, in CH_2CO, is well reproduced by the PBE0 model (-13 PPM), which gives values close to MP2 (-11 PPM) and to experiment (-8 PPM). In contrast a dramatic difference is observed for the B3LYP value (-38 PPM).

It must be noted that for chemical shifts of first-row nuclei, and carbon in particular, the inclusion of HF exchange has a small effect. For instance GIAO-BLYP and GIAO-B3LYP chemical shifts have been shown to differ by few PPM.[75,144] So the differences found in the present study can be attributed to the underlying GGA functional, rather than to the quantity of exact exchange.[148]

A more stringent test is represented by ozone, since correlation effects play a huge role both on the structure and on the NMR properties of such a molecule. The results obtained by our PBE0 model are compared in Table XIII to those obtained by HF and MP2 methods.[145] The most striking feature of these data is the poor performance of the MP2 approach in predicting the shielding constants of both oxygen atoms, giving high values and the wrong signs.[146,147] In contrast, all the ACM methods, including the PBE0 one, give the right trend, even if the absolute values are significantly underestimated with respect to experimental data. It must be emphasized, anyway, that quantitative accuracy cannot be expected from single-reference calculations, as the DF ones, in the case of ozone, where the preferred choice is repre-

sented by multiconfiguration methods.[145] Furthermore, the role played in this case by the neglected current dependency of the exchange correlation functional[139] could be particularly significant.

G. Electronic excitation energies

There is a growing interest in the application of TD-DF to the calculation of adiabatic excitation energies.[77–79,149,150] The results obtained for low excitation energies are usually superior to the those obtained by HF-based methods, like the Random Phase Approximation (RPA),[151] or the Configuration Interaction Singles (CIS) approach.[79,149,152] In addition, given that the time-dependent HF (TDHF) scheme can be derived along the same lines as TDDF, Bauernschmitt and Ahlrichs[79] have also included the ACM3 model in the calculation of energies, showing that the B3LYP functional represents a further improvement over conventional DF methods. In this connection, it has been suggested that the numerical performances of the different functionals strongly depend on their ability to predict reliable molecular ionization potentials (IP).[77] This points out that, like in ground-state computations, the domain of applicability of TDDF rests on the development and validation of suitable functionals. We expect that the PBE0 functional gives results at least comparable with those provided by ACM3 approaches, because it provides comparable IP's, but has an improved long-range behavior.

In Table XIV are collected our PBE0 and mPW0 results together with HF-based and experimental data from Ref. 79. The chosen molecular set, even if quite limited, is in our

TABLE XIV. Vertical excitation energies (eV), computed at different theoretical levels using the 6-31+G(d,p) basis set and 6-31G(d,p) geometries.

Molecule	transition		CIS[a]	RPA[a]	B3LYP	mPW0	PBE0	exp
N_2	$^1\Pi_g$	$\sigma_g \to \pi_g$	10.02	9.77	9.36	9.35	9.31	9.3
H_2CO	$^1A_2$	$n \to \pi^*$	4.55	4.37	4.12	4.13	4.08	4.1
C_2H_4	$^1B_{1u}$	$\pi \to \pi^*$	7.71	7.75	8.51	8.54	8.38	8.0
C_5H_5N	$^1B_2$	$\pi \to \pi^*$	6.10	5.85	5.07	5.15	4.99	5.0
	$^1A_2$	$n \to \pi^*$	6.79	6.79	5.26	5.38	5.31	5.4

[a]Reference 144.

opinion quite representative, since it includes $\pi \rightarrow \pi^*$, $\sigma \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions.

The remarkable quality of PBE0 results is quite apparent since this model is slightly more reliable than B3LYP, and both methods represent a significant improvement over CIS or RPA approaches. It is interesting to note that the largest deviation is found for C_2H_4 (+0.38 eV at the PBE0 level), whose IP is one of the less accurately predicted by PBE0, the error being -0.22 eV.

IV. CONCLUDING REMARKS

In the present work we have explored the behavior of a parameter free density functional approach (PBE0) using the PBE functional and HF exchange with predefined coefficients. The results obtained for a number of systems are satisfactory and at least competitive with those delivered by the parent mPW0 functional, which includes parameters specifically optimized for improving its long range behavior. Under such circumstances the PBE0 model is probably the best functional currently available which couples a good accuracy for molecular structures and properties along the whole periodic table to a direct connection to physical principles. The same functional can be used in the adiabatic approximation of time-dependent DF theory to obtain remarkable excitation energies. From a computational point of view, the availability of linear scaling implementations of this model allows the study of very large systems, whereas very accurate energetic predictions for relatively small molecules can be obtained by extrapolation techniques (e.g., G2 or CBS) using geometries and vibration frequencies computed at the PBE0 level. The whole computational protocol is or will be shortly available to other researchers in the field through a standard quantum chemical package.

After completion of this work we became aware of an independent implementation of the PBE and PBE0 functionals by Ernzerhof and Scuseria.[153]

ACKNOWLEDGMENT

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