

# Exchange functionals with improved long-range behavior and adiabatic connection methods without adjustable parameters: The *mPW* and *mPW1PW* models

Carlo Adamo<sup>a)</sup> and Vincenzo Barone

Dipartimento di Chimica, Università "Federico II," via Mezzocannone 4, I-80134 Napoli, Italy

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Starting from an analysis of the low-density and large gradient regions which dominate van der Waals interactions, we propose a modification of the exchange functional introduced by Perdew and Wang, which significantly enlarges its field of applications. This is obtained without increasing the number of adjustable parameters and retaining all the asymptotic and scaling properties of the original model. Coupling the new exchange functional to the correlation functional also proposed by Perdew and Wang leads to the *mPWPW* model, which represents the most accurate generalized gradient approximation available until now. We next introduce an adiabatic connection method in which the ratio between exact and density functional exchange is determined *a priori* from purely theoretical considerations and no further parameters are present. The resulting *mPW1PW* model allows to obtain remarkable results both for covalent and noncovalent interactions in a quite satisfactory theoretical framework encompassing the free electron gas limit and most of the known scaling conditions. The new functionals have been coded with their derivatives in the Gaussian series of programs, thus allowing fully self-consistent computations of energy and properties together with analytical evaluation of first and second geometry derivatives. © 1998 American Institute of Physics. [S0021-9606(98)03002-5]

## I. INTRODUCTION

Computational models rooted in the density functional (DF) theory are nowadays considered a valuable alternative to conventional Hartree–Fock (HF) and post-HF methods for the study of molecular electronic structure. The appeal of these methods is due to their capacity (at least in principle) of taking into full account many-body effects with computer times characteristic of mean-field approximations. Unfortunately, the exact density functional is unknown, and approximate functionals must be used. In the Kohn–Sham (KS) approach to DFT (density functional theory), the exact kinetic-energy operator is used along with density functionals for the exchange and correlation energies.<sup>1</sup> As the magnitude of the correlation energy is generally less than 10% of the exchange energy, it is most important that the exchange functional be accurate. Furthermore, the available correlation functionals already provide satisfactory numerical results for a wide range of chemical problems.<sup>2</sup>

The simplest DF approach to the exchange energy is the local spin-density approximation (LSD), in which the functional for the uniform electron gas of density  $\rho(\mathbf{r})$  is integrated over the whole space<sup>3</sup>

$$E_X^{\text{LSD}} = A_x \sum_{\sigma} \int \rho_{\sigma}(\mathbf{r})^{4/3} d\mathbf{r} \quad (1)$$

where

<sup>a)</sup>Permanent address: Dipartimento di Chimica, Università della Basilicata, via N. Sauro 85, I-85100 Potenza, Italy.

$$A_x = -\frac{3}{2} \left( \frac{3}{4\pi} \right)^{1/3}, \quad (2)$$

and the index  $\sigma$  denotes either  $\alpha$  or  $\beta$  electron spin. Such an approach underestimates the exchange energy by about 10% (see for instance Ref. 4). Starting from Eq. (1) several corrections for the nonuniformity of atomic and molecular densities have been proposed.<sup>5</sup> In particular, those based on density gradients have received considerable attention due to their simplicity. This approach, referred to as generalized gradient approximation (GGA), is usually expressed in terms of an enhancement factor over the exchange energy of the uniform electron gas, so that the total exchange energy takes the form

$$E_X^{\text{GGA}} = E_X^{\text{LSD}} - \sum_{\sigma} \int F[x_{\sigma}] \rho_{\sigma}(\mathbf{r})^{4/3} d\mathbf{r}, \quad (3)$$

where  $x_{\sigma}$  is the dimensionless reduced gradient for spin  $\sigma$

$$x = \frac{|\nabla \rho_{\sigma}|}{(\rho_{\sigma})^{4/3}}. \quad (4)$$

Semiempirical GGA exchange functionals, which contain parameters obtained by fitting the exchange atomic energies, as well as first-principle GGA functionals, obtained by modeling the Fermi hole, have been proposed.<sup>4,6–15</sup> One of the most used functionals is that published in 1988 by Becke<sup>8</sup> (hereafter B), whose enhancement factor is

$$F[x] = \frac{bx^2}{1 + 6bx \sinh^{-1} x}, \quad (5)$$

where the value of the parameter  $b$  (0.0042) was obtained from a best fitting to the HF exchange energies of the noble gas atoms.<sup>8</sup>

At the same time, several efforts have been made to rationalize the physical conditions that must be satisfied by an exact exchange functional. Among others, three conditions seem to be of particular importance. The first constraint is related to the behavior in the small  $x$  region, where the GGA exchange functional should reduce to  $E_x^{\text{LSD}}$  in order to recover the correct uniform gas limit.<sup>16</sup> The second condition was defined by Perdew and Levy, who showed that some scaling equalities can be satisfied if the asymptotic form of the functional for large  $x$  is  $x^{-\alpha}$ , where  $\alpha \geq 1/2$ .<sup>17</sup> The last condition is the so-called ‘‘Lieb–Oxford bound’’,<sup>18</sup> which, in its ‘‘global’’ version,<sup>10</sup> states that

$$E_x \geq E_{xc} \geq -1.679 \int \rho(\mathbf{r})^{4/3} d\mathbf{r}. \quad (6)$$

Only a few of the available GGA functionals obey the mentioned conditions. In particular, the B functional, despite yielding very useful computational models,<sup>19,20</sup> does not obey neither the Levy condition nor the Lieb–Oxford bound. In this connection, a significant theoretical improvement is represented by the exchange functional proposed by Perdew and Wang (hereafter PW),<sup>9</sup> which is based on the B functional, but is built up to respect all the above mentioned constraints. The enhancement factor of such a functional is<sup>9,14</sup>

$$F[x] = \frac{bx^2 - (b - \beta)x^2 \exp(-cx^2) - 10^{-6}x^d}{1 + 6bx \sinh^{-1} x - \frac{10^{-6}x^d}{A_x}}, \quad (7)$$

where  $\beta = 5(36\pi)^{-5/3}$ ,  $b = 0.0042$ ,  $c = 1.6455$ ,  $d = 4$ , and  $A_x$  is defined in Eq. (2).

The  $x^4$  term causes the functional to respect the Levy scaling inequality and the Lieb–Oxford bound, and the Gaussian term causes the functional to reduce to the gradient expansion with the correct coefficient at small  $x$ . The PW functional has given good results in many atomic, molecular, and solid-state calculations.<sup>21,22</sup>

Recently, Lacks and Gordon carried out a detailed analysis of several exchange functionals,<sup>10</sup> underlining some interesting aspects. In particular, they noted that the arbitrary choice of the coefficient and exponent of the  $x^d$  term in the PW functional does not affect significantly the total atomic exchange energies, but determines the behavior of the exchange functional in low-density and large-gradient regions far from nuclei.<sup>10</sup> This point is of particular physical importance, since a correct long-range behavior of the exchange functional is necessary if DF methods are to be applied to noncovalent interactions, such as H-bond, van der Waals (vdW), and charge transfer (CT) complexes, where weak attractive interactions play an important role. We decided, therefore, to modify the exponent of the  $x^d$  term and the  $b$  constant of the PW functional fitting at the same time the exact exchange energies of isolated atoms and the differential exchange energy ( $E_x^{\text{diff}}$ ) of rare gas dimers ( $\text{He}_2$ ,  $\text{Ne}_2$ ) near their van der Waals minima. The latter quantity is not-

ing else but the difference between the exchange energy of the system at hand minus the sum of the exchange energies of the constituting atoms. Note that, while most of the current functionals give very good total exchange energies, the behavior of differential energies is much more erratic.<sup>10</sup>

Perdew and co-workers argued that their exchange functional is best used in conjunction with the corresponding correlation counterpart<sup>22</sup> (leading to the PWPW functional), since in this case the errors in exchange and correlation contributions tend to cancel out. However, this is not the case for vdW interactions.<sup>10</sup> Furthermore, several papers<sup>2,23,24</sup> have shown that the correlation functional of Lee, Yang, and Parr (LYP),<sup>25</sup> despite not respecting the free electron gas limit, provides improved results especially for thermochemical parameters. Here we will show that replacement of the original PW exchange functional in PWPW by the modified one leads to a model ( $m\text{PWPW}$ ) with significantly improved performances.

From another point of view, it is now well established that hybrids of HF and GGA models provide a significant improvement over conventional GGA approaches. The original three-parameter method introduced by Becke<sup>26,27</sup> can be expressed as

$$E_{xc} = a_{x0}E_x^{\text{LSD}} + (1 - a_{x0})E_x^{\text{HF}} + a_{x1}\Delta E_x^{\text{B}} + E_c^{\text{LSD}} + a_c\Delta E_c^{\text{PW}}, \quad (8)$$

with  $a_{x0} = 0.80$ ;  $a_{x1} = 0.72$ ;  $a_c = 0.81$ .

When used in fully self-consistent way this approach has been called simply adiabatic connection method (ACM);<sup>28</sup> however, we will use here the acronym B3PW for reasons of consistency with other functionals. The corresponding model (B3LYP) obtained replacing  $\Delta E_c^{\text{PW}}$  by  $E_c^{\text{LYP}} - E_c^{\text{LSD}}$  has shown improved performances and can be considered the most reliable general purpose functional presently available.<sup>29–31</sup> Here we will show that use of the  $m\text{PW}$  exchange and PW correlation functionals leads to an hybrid model ( $m\text{PW3PW}$ ) with improved performances.

More recently Becke<sup>32</sup> has shown that reduction of the number of optimized parameters to one, does not worsen the results significantly. From a more fundamental point of view, Perdew and co-workers<sup>33</sup> have suggested that the optimum value ruling the exact/DF exchange ratio can be determined by the lowest order of the Gorling–Levy perturbation theory which provides an accurate description of the energy on the coupling parameter  $\lambda$  in the adiabatic connection integral. Since fourth-order perturbation theory usually delivers very accurate results for molecular systems, it can be argued that a true adiabatic connection model (i.e., not involving parameters optimized by fitting experimental data) can be expressed as

$$E_{xc} = 0.25E_x^{\text{HF}} + 0.75(E_x^{\text{LSD}} + \Delta E_x^{\text{GGA}}) + E_c^{\text{LSD}} + \Delta E_c^{\text{GGA}}. \quad (9)$$

In previous work it has been shown that a reliable parameter free ACM (B1LYP) can be obtained only using the LYP correlation functional,<sup>2</sup> whereas the PW correlation functional leads to quite disappointing results, also further optimizing the ratio between HF and DF exchange.<sup>32</sup> Here we

will show that use of the modified exchange functional rectifies all these shortcomings, so that the new *mPW1PW* functional delivers accurate results both for covalent and noncovalent interactions.

We have used as a benchmark for covalent systems a subset of the so-called G2 molecular data set,<sup>34</sup> including all neutral molecules with only first-row atoms plus H<sub>2</sub>. This subset has been previously used to validate other functionals.<sup>35</sup> Next, performances for noncovalent interactions have been tested on rare gas dimers, hydrogen-bonded systems, and charge-transfer complexes. Finally, two representative organic reaction, a proton transfer (PT) process and a *S<sub>N</sub>2* mechanism, have been investigated. These processes have been recently shown to be on the borderline of the applicability of DF methods.<sup>36–39</sup>

## II. COMPUTATIONAL DETAILS

All the DFT computations are based on the KS approach to the DFT<sup>1</sup> as implemented in the development version of the GAUSSIAN package.<sup>40</sup> In this particular implementation, the exchange-correlation energy contribution to the total electronic energy is evaluated using a self-consistent procedure which avoids the computation of the Hessians of the electronic density.<sup>41</sup> 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.<sup>19</sup> 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.

Equations (1), (3), and (7) contain, as particular cases, the B, PW, and *mPW* exchange functionals, which have been coded with their derivatives (see Appendix). Next we have considered both pure DF approaches (BPW, PWPW, and *mPWPW* models) and the more sophisticated adiabatic connection methods (B3PW, *mPW3PW*, B1PW, *mPW1PW*). Some comparison has been done also with models using the LYP correlation functional (BLYP, B1LYP, B3LYP). HF calculations have been carried out in order to evaluate exact exchange energies for atoms and helium and neon dimers. In some cases, starting from HF densities, DFT exchange energies (without any self-consistent procedure) have been also evaluated.

To avoid basis-set convergence problems, two extended sets have been chosen. For He we have used the (8,3,2,1) primitives of the so-called cc-pV5Z basis set,<sup>42(a)</sup> without any contraction. For Ne we have used 15*s* and 9*p* primitives from the corresponding aug-cc-pV5Z set together with 3*d*,2*f*,1*g* polarization functions from the cc-pVQZ set.<sup>42(b)</sup> Only the first 3*s* and 3*p* primitives have been contracted retaining the coefficients of the original basis set. Note that, while the primitive set is sufficient to ensure converged results, the original contraction pattern, optimized for post-HF computations, is not well suited for DF methods. The 6-311G(*d*,*p*) basis set of Pople and co-workers<sup>43</sup> has been used to optimize all the molecular geometries, since previous

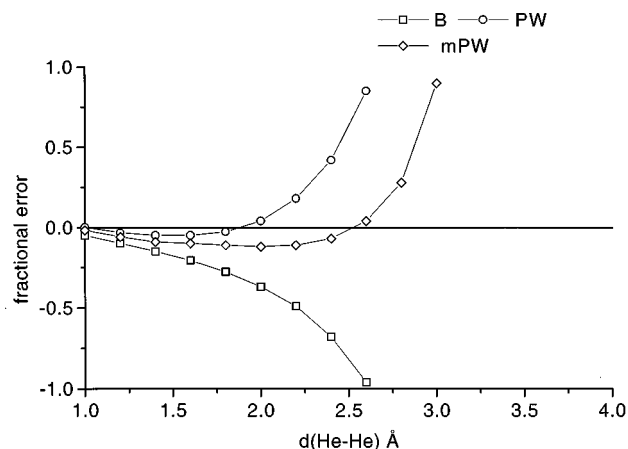


FIG. 1. Fractional errors of several DF approaches with respect to the HF differential exchange energy for the He dimer.

experience show that a polarized valence triple- $\zeta$  basis set generally provides nearly converged structural parameters by DFT methods.<sup>44</sup> Diffuse function on heavy atoms have been added for anionic species. An extended basis set, namely the 6-311++G(3*df*,3*pd*) one,<sup>43</sup> has been next used to evaluate all the energetic parameters and electronic properties at the above geometries.

## III. SETTING UP OF THE *mPW* EXCHANGE FUNCTIONAL

A recent analysis<sup>10</sup> shows that the B and the PW exchange functionals share a poor behavior in the low-density and large-gradient regions which dominate vdW interactions (see also Figs. 1 and 2). These faults are corrected either by properly-designed exchange functionals, calibrated on such an interaction (see for instance Ref. 10), or by introducing a large amount of HF exchange in pure DF approaches.<sup>38</sup> Unfortunately the former improvement involves a rather complex analytical expression of the exchange functional and the latter significantly worsens atomic and molecular properties.<sup>2,10</sup> A more viable alternative can be obtained, in our opinion, by introducing some modifications in a standard

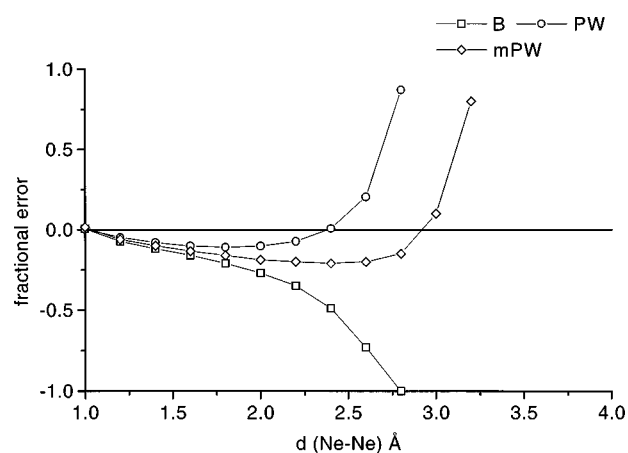


FIG. 2. Fractional errors of several DF approaches with respect to the HF differential exchange energy for the Ne dimer.

TABLE I. Magnitude of the exact exchange energy (Hartrees) and difference between exact exchange energy and various density functionals for the exchange energy, for neutral atoms. All calculations employ Hartree–Fock densities for the computed ground-state configuration and term and the cc-pVQZ basis set (unless explicitly noted).

Atom	HF	$\Delta(\text{LSD})$	$\Delta(\text{B})$	$\Delta(\text{PW})$	$\Delta(m\text{PW})$
H	-0.313	+0.045	+0.003	+0.006	+0.004
He	-1.026	+0.142	+0.001	+0.009	+0.004
Li <sup>a</sup>	-1.781	+0.243	+0.006	+0.018	+0.010
Be <sup>a</sup>	-2.666	+0.354	+0.009	+0.001	+0.013
B	-3.770	+0.474	+0.010	+0.015	+0.013
C	-5.077	+0.590	+0.009	+0.027	+0.013
N	-6.607	+0.706	+0.011	+0.030	+0.018
O	-8.219	+0.835	-0.005	+0.016	-0.001
F	-10.045	+0.956	-0.019	+0.002	-0.017
Ne	-12.110	+1.076	-0.029	+0.006	-0.027
Na <sup>a</sup>	-14.018	+1.234	-0.010	+0.013	+0.010
Mg <sup>a</sup>	-15.992	+1.383	-0.006	+0.016	-0.007
Al	-18.091	+1.541	+0.003	+0.026	0.000
Si	-20.304	+1.696	+0.012	+0.036	+0.008
P	-22.642	+1.849	+0.020	+0.046	+0.016
S	-25.035	+2.012	+0.024	+0.053	+0.020
Cl	-27.545	+2.168	+0.029	+0.057	+0.022
Ar	-30.185	+2.322	+0.031	+0.061	+0.024
abs. aver. error		1.090	0.013	0.025	0.012
max error		2.322	0.031	0.061	0.027

<sup>a</sup>6-311+G(3df,3pd) basis set.

exchange functional, possibly preserving the overall computational performances. For instance, a similar procedure was adopted by Handy and co-workers, who modified and reparametrized the *B* exchange functional for their *Cam* computational model,<sup>23</sup> and by Lembarki and Chermette who reoptimized the PW exchange functional to reproduce either kinetic atomic energies<sup>13</sup> or orbital energies.<sup>45</sup>

Exchange functionals contain a number of parameters which are tuned to reproduce exact atomic exchange energies. For instance, this procedure was adopted by Becke in determining the *b* coefficient of his functional [cf. Eq. (6)].<sup>8</sup> The same parameter is present in the PW functional, which differs from the B one through the introduction of two supplementary terms, namely the  $x^d$  and the Gaussian ones [cf. Eq. (7)]. The choice of the exponent and coefficients of these terms is quite arbitrary.<sup>9</sup> Very recently it has been shown that total atomic exchange energies computed by the PW functional are relatively independent to changes in the exponent of the  $x^d$  term, while the interaction energies for rare-gas atom dimers are extremely sensitive to such changes.<sup>10</sup> So, it is reasonable to presume that a refinement of this parameter to reproduce the long-range behavior, should not modify the performances of this functional in regions significant for the conventional covalent interactions. To this end, we have fitted the differential exchange energies of rare-gas dimers in the region of van der Waals interactions to HF values varying the exponent of the  $x^d$  term in the range  $3.2 \leq d \leq 4.0$ . Without entering the tedious details of the calibration work, we simply state that the best agreement between HF and DF results is obtained with an exponent value

TABLE II. Theoretical and experimental geometries of the biatomic molecules of the G2 data set. Bond distances in angstroms, bond, and dihedral angles in degrees. All theoretical values were obtained with the 6-311G(*d,p*) basis set.

Molecule	Parameter	B1PW	<i>m</i> PW1PW	<i>m</i> PW3PW	Exp. <sup>a</sup>
H <sub>2</sub>	<i>r</i> (HH)	0.744	0.744	0.746	0.742
LiH	<i>r</i> (LiH)	1.600	1.591	1.599	1.595
BeH	<i>r</i> (BeH)	1.349	1.342	1.349	1.343
CH	<i>r</i> (CH)	1.127	1.126	1.129	1.120
NH	<i>r</i> (NH)	1.040	1.043	1.043	1.045
OH	<i>r</i> (OH)	0.971	0.973	0.973	0.971
FH	<i>r</i> (FH)	0.915	0.919	0.918	0.917
Li <sub>2</sub>	<i>r</i> (LiLi)	2.742	2.700	2.731	2.67
LiF	<i>r</i> (LiF)	1.565	1.553	1.560	1.564
CN	<i>r</i> (CN)	1.163	1.163	1.165	1.172
CO	<i>r</i> (CO)	1.125	1.125	1.126	1.128
N <sub>2</sub>	<i>r</i> (NN)	1.093	1.093	1.095	1.098
NO	<i>r</i> (NO)	1.142	1.146	1.145	1.151
O <sub>2</sub>	<i>r</i> (OO)	1.194	1.202	1.198	1.207
F <sub>2</sub>	<i>r</i> (FF)	1.388	1.402	1.395	1.412
avg. abs. error		0.011	0.007	0.009	
max error		0.072(Li <sub>2</sub> )	0.030(Li <sub>2</sub> )	0.061(Li <sub>2</sub> )	

<sup>a</sup>From Ref. 11.

of 3.73. Figures 1 and 2 show the accuracy of the modified functional.

Next we have optimized the *b* term by computing the total exchange energies for the atoms of the first and second row of the periodic table. This set is considered as a common test and standard exchange functionals usually give total atomic exchange energies within 1% of the exact (HF) exchange energies.<sup>8,14,21</sup> The optimized value of 0.0046 is close to the value used in both the B and PW functionals ( $b = 0.0042$ ), but leads to a significant improvement (see Table I). As a matter of fact, the average absolute error for the considered set of atomic exchange energies is 12 mHartrees, i.e., about one half of the PW error (25 mHartrees) and even lower than the B value (13 mHartree). Furthermore the new exchange functional gives the lowest maximum error (27 mHartrees).

Two last remarks are in order about the calibration of the exchange functional. The first is that we have numerically verified that values of the exponent within the range  $3.2 \leq d \leq 4.0$  give functionals respecting, together with the Levy scaling inequality, also the Lieb–Oxford bound. All the advantages of the original PW exchange functional are thus retained. The second remark is that all the functionals obtained by varying the coefficient of the Gaussian term provide atomic exchange energies with an error lower than 1%.

In summary, our modification of the original PW exchange functional is able, without increasing the number of parameters, to give a good representation of total and differential exchange energies over a wide region of density and gradient values. Since, however, total energies have not been considered in the fitting procedure, it remains to be seen whether coupling the modified exchange functional to conventional correlation counterparts leads to an improvement for structural and energetic parameters. Note that, especially

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 are obtained with the 6-311G(*d,p*) basis set. Experimental data are taken from Ref. 11.

Molecule	Parameter	B1PW	<i>m</i> PW1PW	<i>m</i> PW3PW	Exp.
CH <sub>2</sub> ( <sup>3</sup> B <sub>1</sub> )/( <sup>1</sup> A <sub>1</sub> )	<i>r</i> (CH)	1.079/1.115	1.079/1.113	1.080/1.116	1.075/1.107
	<i>a</i> (HCH)	134.3/101.1	134.7/101.2	134.6/100.8	133.9/102.4
CH <sub>3</sub>	<i>r</i> (CH)	1.080	1.079	1.081	1.079
CH <sub>4</sub>	<i>r</i> (CH)	1.090	1.090	1.091	1.086
NH <sub>2</sub>	<i>r</i> (NH)	1.028	1.029	1.030	1.024
	<i>a</i> (HNH)	102.2	102.3	102.1	103.4
NH <sub>3</sub>	<i>r</i> (NH)	1.013	1.015	1.015	1.012
	<i>a</i> (HNH)	106.4	106.5	106.4	106.0
OH <sub>2</sub>	<i>r</i> (OH)	0.958	0.961	0.960	0.957
	<i>a</i> (HOH)	103.9	103.9	103.8	104.5
HCCH	<i>r</i> (CC)	1.198	1.197	1.199	1.203
	<i>r</i> (CH)	1.063	1.063	1.064	1.062
	<i>r</i> (CC)	1.325	1.325	1.326	1.334
H <sub>2</sub> CCH <sub>2</sub>	<i>r</i> (CH)	1.085	1.084	1.086	1.081
	<i>a</i> (HCH)	116.6	116.6	116.6	117.4
H <sub>3</sub> CCH <sub>3</sub>	<i>r</i> (CC)	1.511	1.510	1.516	1.526
	<i>r</i> (CH)	1.095	1.094	1.094	1.088
	<i>a</i> (HCH)	108.2	108.3	108.2	107.4
HCN	<i>r</i> (CN)	1.147	1.147	1.149	1.153
	<i>r</i> (CH)	1.066	1.066	1.067	1.065
	<i>r</i> (CO)	1.174	1.170	1.176	1.175
HCO	<i>r</i> (CH)	1.125	1.124	1.126	1.122
	<i>a</i> (HCO)	124.5	124.4	124.3	124.6
	<i>r</i> (CO)	1.194	1.196	1.198	1.203
H <sub>2</sub> CO	<i>r</i> (CH)	1.107	1.109	1.111	1.099
	<i>a</i> (HCH)	115.6	115.6	115.5	116.4
	<i>r</i> (CO)	1.410	1.409	1.412	1.421
	<i>r</i> (CH <sub><i>a</i></sub> )	1.090	1.090	1.092	1.093
	<i>r</i> (CH <sub><i>b</i></sub> )	1.099	1.098	1.099	1.093
H <sub>3</sub> COH	<i>r</i> (OH)	0.956	0.957	0.959	0.963
	<i>a</i> (OCH <sub><i>a</i></sub> )	107.1	107.1	107.0	107.0
	<i>a</i> (COH)	107.8	107.8	107.7	108.0
	<i>a</i> (H <sub>0</sub> CH <sub>0</sub> )	108.5	108.5	108.4	108.5
	<i>r</i> (NN)	1.420	1.420	1.423	1.447
H <sub>2</sub> NNH <sub>2</sub>	<i>r</i> (NH)	1.012	1.015	1.012	1.008
	<i>a</i> (NNH)	109.5	109.4	109.5	109.2
	<i>a</i> (HNH)	113.5	113.4	113.6	113.3
	<i>d</i> (HNNH)	87.3	87.3	87.6	88.9
	<i>r</i> (OO)	1.431	1.430	1.438	1.475
HOOH	<i>r</i> (OH)	0.961	0.962	0.964	0.950
	<i>a</i> (OOH)	100.6	100.6	100.4	94.8
	<i>d</i> (HOOH)	117.9	118.0	118.3	120.0
CO <sub>2</sub>	<i>r</i> (CO)	1.156	1.156	1.159	1.160

for noncovalent interactions, this would be the case only if the correlation functionals already have a correct long-range behavior.

#### IV. VALIDATION OF THE EXCHANGE FUNCTIONAL

##### A. The G2 data set

In Tables II–V are reported the results obtained for the geometric and thermodynamic parameters of 32 molecules belonging to the G2 data set. This subset has become a standard for the validation of new density functional approaches.<sup>19</sup> In Tables II and III are compared the geometries obtained by the *m*PW1PW and *m*PW3PW models with the corresponding B1PW results. In this connection, it is remarkable that on this set of covalently bonded molecules

both the *m*PW1PW and *m*PW3PW approaches give geometries which are close to those obtained by the B1PW method. On the other hand, the *m*PW1PW atomization energies (Table V) are significantly better than those obtained by the B1PW model. In particular, the average absolute error is 3.5 kcal/mol for the *m*PW1PW model and 5.4 kcal/mol for the B1PW one. Furthermore, the *m*PW1PW results are more precise, the maximum deviation being 6.5 kcal/mol. Even better results are obtained at the *m*PW3PW level, the average absolute error being 2.7 kcal/mol.

A full comparison with the most common DF approaches is reported in Table VI, which collects an error statistics for the most significant molecular properties of the G2 data set. Since the data reported in this table are suffi-

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

Molecule	B1PW	<i>m</i> PW1PW	<i>m</i> PW3PW	Exp. <sup>a</sup>
H <sub>2</sub>	99.0	98.7	100.8	103.3
LiH	50.8	51.3	53.2	56.0
BeH	53.5	53.6	54.3	46.9
CH	78.4	78.9	80.0	79.9
CH <sub>2</sub> ( <sup>3</sup> B <sub>1</sub> )	181.6	182.8	184.5	179.6
CH <sub>2</sub> ( <sup>1</sup> A <sub>1</sub> )	165.1	165.8	168.8	170.6
CH <sub>3</sub>	290.8	289.5	293.1	289.2
CH <sub>4</sub>	386.5	389.1	393.9	392.5
NH	79.8	80.3	80.8	79.0
NH <sub>2</sub>	169.3	170.7	174.1	170.0
NH <sub>3</sub>	270.3	272.7	277.9	276.7
OH	99.6	100.3	102.5	101.3
OH <sub>2</sub>	211.9	213.6	218.0	219.3
FH	131.8	131.3	133.9	135.2
Li <sub>2</sub>	17.3	18.8	19.5	24.0
LiF	130.2	131.1	134.3	137.6
HCCH	381.9	385.5	388.7	388.9
H <sub>2</sub> CCH <sub>2</sub>	525.5	530.0	535.7	531.9
H <sub>3</sub> CCH <sub>3</sub>	654.8	660.6	668.0	666.3
CN	171.5	173.5	177.7	176.6
HCN	296.2	299.0	303.4	301.8
CO	249.1	250.5	255.2	256.2
HCO	268.7	271.4	276.6	270.3
H <sub>2</sub> CO	351.7	355.1	356.6	357.2
H <sub>3</sub> COH	472.0	477.3	484.7	480.8
N <sub>2</sub>	216.9	219.2	223.8	225.1
H <sub>2</sub> NNH <sub>2</sub>	397.1	402.8	411.4	405.4
NO	146.5	148.7	153.4	150.1
O <sub>2</sub>	117.8	119.9	124.6	118.0
HOOH	241.7	245.8	253.5	252.3
F <sub>2</sub>	22.6	31.3	35.4	36.9
CO <sub>2</sub>	369.1	382.7	389.1	381.9
mean aver. dev.	5.4	3.5	2.7	
max dev.	11.5	6.5	6.6	

<sup>a</sup>From Ref. 35.

ciently self-explanatory, we add only a few comments. First, from these results it is quite apparent that the *m*PW1PW protocol performs better than all the other functional containing either the original PW exchange or the PW correlation functionals. A more significant comparison is that with the results obtained by the B1LYP approach, our parameter free ACM protocol performing as well as the popular B3LYP method over a wide class of chemical systems, including the G2 data set.<sup>2</sup> A detailed comparison with these reference data show that the *m*PW1PW model gives results close to those provided by the B1LYP model, whereas the *m*PW3PW protocol provides thermochemical data with an accuracy approaching the B3LYP method. It is also interesting to note the different behavior of the two considered correlation functionals. From the one hand, the performances of the LYP functional are very close in a three-parameter scheme (e.g., B3LYP) and in a parameter-free protocol (e.g., B1LYP) irrespective of the exchange functional used. On the other hand, the PW correlation functional gives results for the G2 set which are significantly better in the former scheme than in the second one when using exchange functionals different

TABLE V. Mean absolute 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, while atomization energies and dipole moments are evaluated by the 6-311++G(3df,3pd) extended basis set.

Methods	Bond lengths (Å)	<i>D</i> <sub>0</sub> (kcal mol <sup>-1</sup> )	Dip. mom. (D)	Harm. freq. (cm <sup>-1</sup> )
HF <sup>a,b</sup>	0.022	82.0	0.29	144
MP2 <sup>c,b</sup>	0.014	23.7	0.28	99
CCSD[T] <sup>a,b</sup>	0.005	11.5	0.10	31
LSD <sup>a,d</sup>	0.017	43.5	(0.25) <sup>c,d</sup>	(75) <sup>c,d</sup>
BPW	0.014	6.0	0.11	69
PWPW	0.012	8.6	0.12	66
BLYP	0.014	9.6	0.10	59
<i>m</i> PWPW	0.012	6.7	0.11	65
B3LYP	0.004	2.4	0.08	31
B3PW	0.008	4.8	0.08	45
<i>m</i> PW3PW	0.008	2.7	0.08	37
B1LYP	0.005	3.1	0.08	33
B1PW	0.010	5.4	0.10	48
<i>m</i> PW1PW	0.010	3.5	0.10	39

<sup>a</sup>Basis set of triple- $\zeta$  quality+double polarization func.

<sup>b</sup>Ref. 35.

<sup>c</sup>6-31G(*d,p*) basis set.

<sup>d</sup>Ref. 23.

from *m*PW.<sup>2,32</sup> Furthermore, *m*PW1PW behaves even better than *m*PW3PW when other, and more stringent, tests are considered (see below). So, due to its particularly appealing theoretical foundation, we prefer in the following to discuss only the results obtained by the *m*PW1PW method. The results obtained by the *m*PW3PW approach are, anyway, reported in all the considered tests for the sake of completeness.

## B. Noncovalent interactions

We turn next to noncovalent interactions in van der Waals, H-bonded or CT complexes, where the spread of results obtained by different functionals is particularly signifi-

TABLE VI. Bond lengths and interaction energies for He<sub>2</sub> and Ne<sub>2</sub>. All values are computed using the modified cc-pV5Z basis set and are corrected for BSSE effect (see text for details).

Dimer	Method	<i>d</i> (Å)	<i>D</i> <sub>int</sub> (eV)
He <sub>2</sub>	BPW, BLYP, B1LYP, B3LYP	Unbound	
	PWPW	2.78	0.010
	<i>m</i> PWPW	3.14	0.003
	<i>m</i> PW3PW	2.97	0.002
	<i>m</i> PW1PW	3.11	0.002
	exact <sup>a</sup>	2.97	0.001
Ne <sub>2</sub>	BPW, BLYP, B1LYP, B3LYP	Unbound	
	PWPW	2.94	0.014
	<i>m</i> PWPW	3.25	0.004
	<i>m</i> PW3PW	3.16	0.003
	<i>m</i> PW1PW	3.23	0.003
	exact <sup>a</sup>	3.09	0.004

<sup>a</sup>Reference 47.

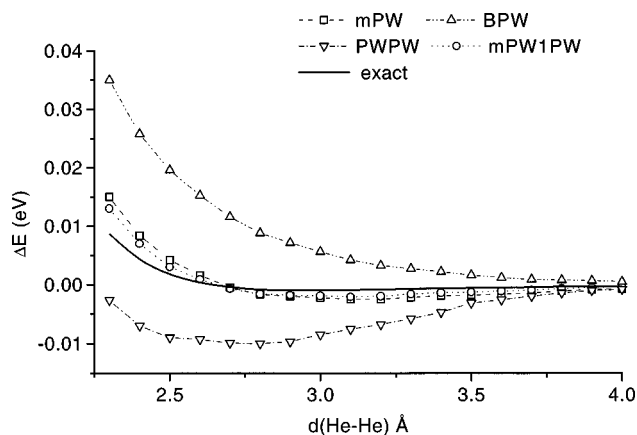


FIG. 3. Potential-energy curves for the interaction of the two He atoms. The curve labelled "exact" has been computed using the analytical expression of Ref. 47.

cant. We have chosen a few prototypical systems, namely the He, Ne, and water dimers, and the CT complex formed by  $\text{Cl}_2$  with  $\text{C}_2\text{H}_4$ .

Van der Waals complexes, such as the dimers of rare-gas atoms, are very difficult to handle in the framework of DF methods.<sup>10,38,46</sup> In particular, standard methods, including ACM approaches, significantly underestimate the interaction strength in such complexes. The numerical values for the energy minima of He and Ne dimers obtained by several functionals and corrected for basis set superposition error (BSSE) effects<sup>47</sup> are collected in Table VI, while the overall trends of different functionals are shown in Figs. 3 and 4. Two limiting situations are evidenced by these data. From the one hand, all the protocols using the B exchange functional predict a vanishing interaction between He atoms, while, from the other hand, a strong interaction is found at the PWPW level. This last functional predicts a short equilibrium distance ( $d=2.78$  Å) and a high interaction energy ( $D_{\text{int}}=0.010$  eV). Between these two extremes, the *mPWPW* conventional DF approach gives much improved results ( $d=3.14$  Å and  $D_{\text{int}}=0.003$  eV) and an even better

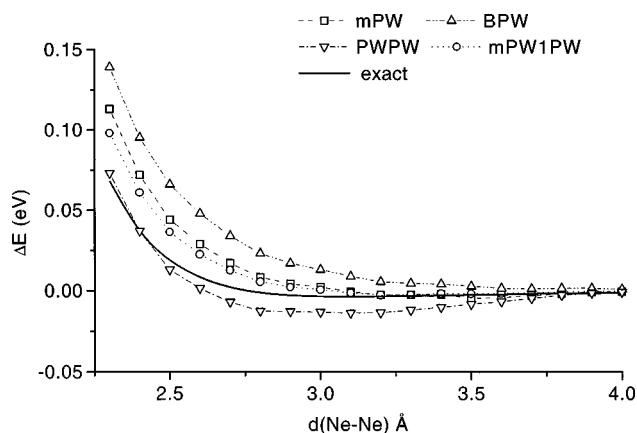


FIG. 4. Potential-energy curves for the interaction of the two Ne atoms. The curve labelled "exact" has been computed using the analytical expression of Ref. 47.

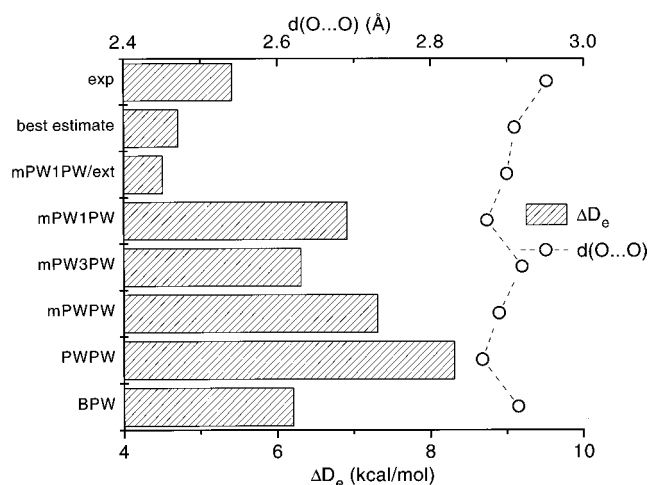


FIG. 5. Intramolecular O...O distance and binding energy of the water dimer obtained by different methods. The geometrical parameters are computed using the 6-311G(*d,p*) basis set, while binding energies are evaluated on these geometries with the 6-311++G(3*df*,3*pd*) basis set.

agreement with the exact values ( $d=2.97$  Å and  $D_{\text{int}}=0.001$  eV)<sup>48</sup> is obtained at the *mPW1PW* ( $d=3.11$  Å,  $D_{\text{int}}=0.002$  eV) and *mPW3PW* ( $d=2.97$  Å,  $D_{\text{int}}=0.002$  eV) levels. Analogous trends are obtained for the  $\text{Ne}_2$  system. In this connection, it is noteworthy that our PWPW results are essentially identical to those obtained by Patton *et al.*<sup>15(b)</sup> using a different extended basis set. The trends are well evidenced in the graphs of Figs. 3 and 4, which represent the potential-energy profiles for the He-He and Ne-Ne interactions, computed with several DF methods. All the curves fall between the BPW repulsive curve and the strongly attractive curve obtained at the PWPW level. In the middle, and close to the exact profile, we find both the *mPWPW* and the *mPW1PW* plots. In this connection, it must be remembered that also the standard ACM approaches, such as the popular B3LYP model, are not able to localize an energy minimum for such vdW complexes.<sup>38,49</sup> A similar behavior is obtained for the Ne dimer, where a variety of situations is predicted by standard pure DF approaches, while a good agreement with the "exact" data<sup>48</sup> is obtained by all the models which include *mPW* exchange and by the very recent functional proposed by Perdew *et al.*<sup>15</sup>

Let us consider now the water dimer. We do not want to make a complete review of the huge amount of results available for this system, but we refer, instead, to more detailed discussions and references included in previous works.<sup>20,50</sup> Even if this system has been studied in detail,<sup>50</sup> some problems still remain, especially concerning the experimental determination of the binding energy. The currently accepted value is  $5.44 \pm 0.7$  kcal/mol,<sup>51</sup> even if refined post-HF computations suggest that the interaction energy is close to 4.7 kcal/mol (see discussion in Ref. 50). Similarly, the main geometrical parameter, i.e., the O-O 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,<sup>52</sup> whereas a shorter

TABLE VII. Some relevant geometrical parameters (Å), harmonic stretching Cl–Cl frequencies ( $\text{cm}^{-1}$ ) and complexation energies (kJ/mol) for the  $\text{C}_2\text{H}_4 \cdots \text{Cl}_2$  complex. The energies are computed at the 6-311++G(3df,3pd) level, using 6-311G(d,p) geometries and are corrected for BSSE and ZPE effects.

	MP2 <sup>a</sup>	BPW	PWPW	<i>m</i> PWPW	<i>m</i> PW1PW	B3PW	B1LYP	<i>m</i> PW3PW	Exp. <sup>b</sup>
$d(\text{Cl} \cdots \text{plane})$	3.003	2.650	2.599	2.627	2.834	2.811	2.890	2.792	3.128
$d(\text{ClCl})$	2.044	2.147	2.151	2.149	2.062	2.070	2.093	2.079	
$\nu(\text{Cl–Cl})$	506	380	390	379	467	420	450	450	527
$\Delta E_{\text{comp}}$	–6.7	–15.9	–23.2	–13.3	–5.9	–8.5	–5.0	–11.7	–7.1/–11.3

<sup>a</sup>Reference 60.

<sup>b</sup>References 62–64.

intermolecular distance (2.910 Å) is predicted by refined post-HF methods.<sup>53</sup>

In Fig. 5 are reported the computed O $\cdots$ O intermolecular distances and the corresponding binding energies. These latter have been corrected both for zero-point energy (ZPE) and BSSE.<sup>47</sup> As already described in the literature,<sup>36,54–56</sup> the equilibrium geometry of the water dimer is quite accurately reproduced by standard DF methods, all the predicted O $\cdots$ O distances falling between 2.87 and 2.92 Å, i.e., close to the MP2 estimate. In particular, the results predicted by all the methods which incorporate the *m*PW exchange are close to 2.87 Å. As expected,<sup>20,57</sup> a large basis set [the 6-311++G(3df,3pd) one] increases the intermolecular distance, further improving the agreement with the post-HF data (2.90 vs 2.91 Å for the *m*PW1PW and MP2 approaches, respectively).

Binding energies are more sensitive to the choice of the exchange functional. In particular the PWPW functional predicts a very strong interaction (8.3 kcal/mol), while the BPW functional gives a value about 2 kcal/mol lower (6.1 kcal/mol). In the middle, there are the results obtained by the *m*PW1PW functional, which predicts a binding energy (BE) of 7.0 kcal/mol. Once again, extension of the basis set plays a not negligible role, the BE being 4.5 kcal/mol at the *m*PW1PW/6-311++G(3df,3pd) level. This last result is close to the best theoretical estimate<sup>53</sup> and in the range of the experimental determinations.

Judging from both the energy and the geometry results, the *m*PW1PW scheme seems to give, among the functionals considered, a slightly better description of the water dimer.

An even more stringent test is represented by CT complexes, and in particular those arising from a  $\pi$ – $\sigma$  type interaction, such as that of ethylene with a halogen molecule. These systems are very difficult to describe either at the post-HF<sup>58,59</sup> or DF<sup>37,60</sup> levels. In particular, the most com-

mon DF methods, including some ACM approaches, predict too short intermolecular distances and too high interaction energies.<sup>60</sup> Among the well characterized CT systems, we have focused our attention on the simple ethylene–chlorine complex. Furthermore, even if several different molecular arrangements are possible, the axial-perpendicular structure is the most stable one.<sup>61</sup> So we have limited our attention only to this arrangement, whose main molecular parameters are reported in Table VII. The most striking features in the calculations by the different methods are the chlorine–ethylene distances, which are directly related to the interaction strengths. In this connection, GGA methods provide very short intermolecular distances, even if the *m*PWPW result (2.63 Å) can be considered a significant improvement over the original PWPW value (2.45 Å). The inclusion of some HF exchange increases the distance up to 2.83 Å for the *m*PW1PW model. This last value is very close to the B3LYP estimate (2.84 Å),<sup>60</sup> but it is not accurate enough to describe this parameter properly, the experimental value being 3.13 Å. In contrast, it must be noted that all the methods provide geometries for the free molecules (not reported in Table VII) which are in good agreement with experimental results.<sup>62–64</sup>

The trend in the geometrical parameters is reflected in the harmonic frequencies and, in particular, in the stretching of the Cl–Cl bond. In this complex, the intermolecular distance is directly related to the  $\sigma$ – $\pi$  electron donation from chlorine to ethylene, which weakens the Cl–Cl bond. As a consequence an overestimation of this interaction induces a very low Cl–Cl stretching frequency. This is the case for the conventional DF approaches, which predict harmonic wave numbers significantly lower than the experimental estimate. A better agreement is found at the *m*PW1PW level, whose value is close to the MP2 prediction (467 vs

TABLE VIII. Main H-bond geometrical parameters (Å) and relative energies (kJ/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 the 6-311G(d,p) geometries.

	MP2		BPW		<i>m</i> PWPW		<i>m</i> PW1PW		B3PW		<i>m</i> PW3PW	
	M	SP	M	SP	M	SP	M	SP	M	SP	M	SP
$d(\text{O} \cdots \text{O})$	2.581	2.355	2.526	2.389	2.518	2.387	2.539	2.353	2.541	2.360	2.534	2.359
$d(\text{H} \cdots \text{O})$	1.678	1.197	1.571	1.218	1.561	1.217	1.632	1.200	1.629	1.204	1.620	1.203
$d(\text{OH})$	0.991	1.197	1.031	1.218	1.034	1.217	1.001	1.200	1.005	1.204	1.006	1.203
$\Delta E$	0.0	11.7	0.0	4.0	0.0	3.8	0.0	12.0	0.0	8.5	0.0	8.2



TABLE IX. Main geometrical parameters of the ion-complex  $\text{Cl}^- \cdots \text{CH}_3\text{Cl}$  and the corresponding saddle point for the Walden inversion. All values are computed at the 6-311+G(*d,p*) level.

Parameter	MP2	BPW	<i>m</i> PWPW	<i>m</i> PW1PW	B3PW	<i>m</i> PW3PW
			ion-complex			
<i>d</i> (C $\cdots$ Cl)	3.270	3.133	3.108	3.157	3.167	3.160
<i>d</i> (CCl)	1.810	1.870	1.870	1.828	1.836	1.835
<i>d</i> (CH)	1.085	1.090	1.089	1.083	1.084	1.084
<i>a</i> (ClCH)	108.8	107.9	107.9	108.5	108.4	108.4
			SP			
<i>d</i> (CCl)	2.317	2.366	2.362	2.328	2.339	2.336
<i>d</i> (CH)	1.073	1.079	1.079	1.072	1.073	1.073

506  $\text{cm}^{-1}$ , respectively), which is, in turn, slightly lower than the experimental value of 527  $\text{cm}^{-1}$ .<sup>62</sup>

In the same table are reported the interaction energies, corrected for both ZPE and BSSE effects (about 4 and 1 kJ/mol, respectively, for all DF methods). As expected, these energies are related to the intermolecular distances predicted by the different methods. Thus, the BPW model predicts a strong  $\text{Cl}-\text{C}_2\text{H}_4$  interaction ( $-15.9$  kJ/mol), which is reduced to  $-5.9$  kJ/mol at the *m*PW1PW level. This last value is only slightly lower than the MP2 estimate ( $-6.7$  kJ/mol) or the experimental findings (between  $-7.1$  and  $-11.3$  kJ/mol).<sup>64</sup>

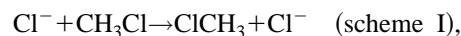
### C. Proton transfer in malonaldehyde

Several authors have explored the applicability of DF methods in the study of proton transfer (PT) reactions showing that standard DF approaches provide very low activation energies.<sup>20,36,54,55,65,66</sup> The situation is even more involved when the motion of the proton is coupled with a rearrangement of the  $\pi$  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.<sup>44</sup> In order to correctly reproduce these effects, large basis sets must be used in the framework of DF approaches. The results obtained by the *m*PW functional are reported in Table VIII. Pure DF approaches, i.e., BPW and *m*PWPW, give a poor description of the PT reaction, providing very low energy barriers. It is interesting that different exchange functionals provide similar results, the barrier being 4.9 and 4.6 kJ/mol for the for the

BPW and *m*PWPW method, respectively. A significant improvement is obtained at the *m*PW1PW level (12.0 kJ/mol), this effect being strictly related to the computed O $\cdots$ O distance (see Table VIII). For instance, the *m*PWPW method predicts a distance of 2.518 Å, significantly shorter than the MP2 value (2.581 Å), while the *m*PW1PW model performs slightly better (2.539 Å), but without reaching the post-HF values. In contrast, the other geometrical parameters obtained by MP2 and *m*PW1PW models are very close to each other. The short H-bridge distance found in the minimum energy structure is due to an excessive degree of conjugation, which, in turn, significantly destabilizes the minimum energy structure with respect to the saddle point, leading to a low energy barrier. ACM methods, through the introduction of HF exchange, significantly reduce this fault, reaching at least the accuracy of MP2 calculations.<sup>44</sup>

### D. The Walden inversion

As a last significant test, we have chosen a  $S_N2$  reaction, whose importance in organic chemistry is well evidenced by the accumulation of a large body of experimental and theoretical data.<sup>39,67-69</sup> From a theoretical point of view, several studies have shown these reactions to be extremely sensitive to the theoretical model used.<sup>68,69</sup> Already the thermodynamics of the simple Walden inversion



is difficult to describe by quantum-mechanical methods. This is particularly true at the DF level, where most of the available approaches, including the B3LYP protocol, fail in predicting some thermodynamic quantities.<sup>39</sup> A good agreement

TABLE X. Complexation energies of the ion-molecule complex ( $\Delta E_{\text{comp}}$ ), activation energy ( $\Delta E^\ddagger$ ) and overall activation energy relative to reactants ( $\Delta E_{\text{ovr}}$ ) for the Walden inversion, computed at various computational levels. All values are in kJ/mol and include BSSE and ZPE corrections.

	G2+(MP2) <sup>a</sup>	BPW91	<i>m</i> PWPW	<i>m</i> PW1PW	B1LYP	B3PW	<i>m</i> PW3PW	Exp. <sup>b</sup>
$\Delta E_{\text{comp}}$	44.3	39.2	43.8	42.0	40.8	39.2	39.8	51.0 $\pm$ 8.4
$\Delta E^\ddagger$	10.3	26.6	26.2	43.7	37.6	40.4	40.4	55.8 $\pm$ 8.4
$\Delta E_{\text{ovr}}$	54.6	-12.6	-17.6	1.7	-3.2	1.2	0.6	4.2 $\pm$ 4.2

<sup>a</sup>Reference 39.

<sup>b</sup>References 71 and 72.

with the experimental results has been obtained only by using the half and half ACM method.<sup>68</sup> This reaction is characterized, in the gas-phase, by a double-well energy profile, with two minima corresponding to the formation of a pre- and post-reaction ion–molecule complex ( $\text{Cl}\cdots\text{CH}_3\text{Cl}$ ) and with a saddle point (SP) of  $D_{3h}$  symmetry ( $\text{ClCH}_3\text{Cl}^-$ ). The most significant thermodynamic quantities are the complexation energy of the ion–molecule adduct ( $\Delta E_{\text{comp}}$ ), the activation energy, i.e., the relative energy of the  $D_{3h}$  saddle point with respect to the ion–molecule complex ( $\Delta E^\ddagger$ ) and the overall barrier ( $\Delta E_{\text{ovr}}$ ), defined as the difference between these two energies.<sup>70,71</sup> The geometrical parameters of the ion–molecule complex and the SP are collected in Table IX, while the corresponding energetic quantities are plotted in Fig. 5. The key parameter in rationalizing the behavior of the different functionals is the distance between the chloride anion and the carbon atom of the methyl chloride. Once again, the MP2 results can be considered as the reference data, the distance being 3.270 and 2.317 Å for the ionic-complex and for the SP, respectively. The BPW model leads to a too short distance for the ion–molecule complex (3.133 Å) and a too long bond length (2.366 Å) for the Cl–Cl bond in the SP. Similar values are obtained at the *mPWPW* level, whereas a longer Cl–Cl bond (2.328 Å) is found with the *mPW1PW* protocol for a similar value of  $\text{Cl}\cdots\text{C}$  (3.157 Å). These geometrical trends are reflected in the computed energetical parameters (see Table X). In particular, an increasing of the Cl–C distance induces a significant stabilization of the SP structure with respect to the minimum. The effect may be so relevant to induce a negative value for  $\Delta E_{\text{ovr}}$ . This is true for all the pure DF methods considered in the present paper, as well as all other standard functional (cf. Table X and Ref. 68). In particular, the B3LYP method predicts an overall barrier of  $-7.7$  kJ/mol.<sup>37</sup> In contrast, the *mPW1PW* approach predicts a positive, albeit small, value for  $\Delta E_{\text{ovr}}$ , restoring the right trend. As concerns all the other energetical quantities, we found that complexation energies are relatively well reproduced by all the DF methods, as already found for the water dimer. A larger sensitivity to the model used in the computations is found for  $\Delta E^\ddagger$ , whose value ranges between 26.2 (*mPWPW*) and 43.7 (*mPW1PW*) kJ/mol. Once again the *mPW1PW* result is within the range of the experimental values.<sup>71</sup>

## V. CONCLUDING REMARKS

Among the most common exchange functionals, the original PW model is the only one showing the correct behavior for a number of asymptotic limits. This functional has been developed starting from the B formulation and improving the theoretical representation. Unfortunately, this improved behavior has been obtained at the expense of the chemical accuracy, the overall performances of the B exchange functional being better than those obtained by the PW one.<sup>14,57</sup> The simple modification which we propose in the present paper significantly improves the long-range behavior, retaining all the asymptotic characteristics of the par-

ent PW functional. Even if this modification has been especially tuned on vdW interactions, we have found that this improved formulation makes the modified exchange functional competitive with the parent B functional also for covalent interactions. Furthermore, when coupled with the corresponding correlation counterpart (leading to the *mPWPW* complete functional) it gives numerical results of a very good quality. Finally, even better results are obtained by including such a functional in a particular ACM scheme, which does not contain optimized parameters for the mixing of HF exchange (the *mPW1PW* protocol).<sup>2</sup> In the field of ACM approaches, the touchstone is the so-called B3LYP model, whose strengths and limits have been well evidenced in a series of papers.<sup>20,36,39,44,60,65</sup> In this connection we have found that the *mPW1PW* protocol generally provides results which are close or even better than those obtained by the B3LYP method. The most striking example is the Walden inversion, where the B3LYP model fails to capture not only the numerical value but also the right trend of the overall activation energy. In contrast, the *mPW1PW* protocol gives an estimate of this energy which falls in the experimental range. The situation is more involved for CT complexes, whose binding characteristics are described quite poorly by all of the considered DF methods, thus suggesting that further developments are needed.

Finally, the test over the G2 molecular data set assures that all the improvements are not merely due to a fortuitous compensation of errors and are uniform over a wide class of molecular properties, including geometrical, one-electron, and thermochemical data. This is not a less important point, since some ACM's, and the half and half method in particular, provide good results for "difficult cases," such as CT interactions and PT activation energies, but performs quite poorly for the G2 set.<sup>2</sup>

On the basis of the tests reported in the present paper, we can conclude that the *mPWPW* functional should be considered among the best-performing pure DF approaches. Furthermore, the corresponding ACM schemes provide results of a quality comparable to that of the B3LYP protocol.

## APPENDIX

All the exchange functionals considered in the present paper (B,PW,*mPW*) have the form given in Eq. (7) with different values of the parameters  $b$ ,  $c$ , and  $d$ . The relevant first derivatives are

$$\frac{\partial F}{\partial \rho_\sigma} = \frac{4}{3} \rho_\sigma^{1/3} [F(x) - xF'(x)], \quad (\text{A1})$$

$$\frac{\partial F}{\partial \nabla \rho_\sigma} = \frac{1}{2} \Delta \rho_\sigma^{-1/2} F(x), \quad (\text{A2})$$

and

$$F'(x) = - \frac{\left( 2bx^2 - \frac{(b-\beta)x^2}{\exp(cx^2)} - 10^{-6}x^d \right) \left( \frac{-10^{-6}ax^{d-1}}{A_x} + \frac{6bx}{(1+x^2)^{1/2}} + 6b \sinh^{-1} x \right)}{1 + 6bx \sinh^{-1} x - \frac{10^{-6}x^d}{A_x}} + \frac{\left( 2bx - \frac{2(b-\beta)x}{\exp(cx^2)} - 10^{-6}dx^{d-1} + \frac{2c(b-\beta)x^3}{\exp(cx^2)} \right)}{1 + 6bx \sinh^{-1} x - \frac{10^{-6}x^d}{A_x}}, \quad (\text{A3})$$

where  $x$ , defined in Eq. (4), can refer either to  $\alpha$  or  $\beta$  spin.

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