Adiabatic Corrections to Density Functional Theory Energies and Wave Functions[†]

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The adiabatic finite-nuclear-mass-correction (FNMC) to the electronic energies and wave functions of atoms and molecules is formulated for density-functional theory and implemented in the deMon code. The approach is tested for a series of local and gradient corrected density functionals, using MP2 results and diagonal-Born−Oppenheimer corrections from the literature for comparison. In the evaluation of absolute energy corrections of nonorganic molecules the LDA PZ81 functional works surprisingly better than the others. For organic molecules the GGA BLYP functional has the best performance. FNMC with GGA functionals, mainly BLYP, show a good performance in the evaluation of relative corrections, except for nonorganic molecules containing H atoms. The PW86 functional stands out with the best evaluation of the barrier of linearity of H_2O and the isotopic dipole moment of HDO. In general, DFT functionals display an accuracy superior than the common belief and because the corrections are based on a change of the electronic kinetic energy they are here ranked in a new appropriate way. The approach is applied to obtain the adiabatic correction for full atomization of alcanes C_nH_{2n+2}, $n = 4-10$. The barrier of 1 mHartree is approached for adiabatic corrections, justifying its insertion into DFT.

Introduction

Today, density functional theory (DFT) is an indispensable tool of quantum chemistry for the computation of molecular structures and of reaction energies at very high accuracy. Various density-functionals have been developed for this purpose, and for most molecular systems “chemical accuracy” (1 kcal mol $^{-1} \approx 1$ mHartree or mH) can be achieved.[1,2] Hence, even though the predictive power of density functionals compared to molecular-orbital based calculations is limited, its superior computational performance and its smaller sensitivity to basis set quality made this theory very popular in chemistry.[3,4]

For high-accuracy studies it is immediate to think of small corrections, including those beyond the Born−Oppenheimer approximation (BOA). It is acknowledged that adiabatic corrections are important to attain spectroscopic accuracy (μH) but only recently its importance to thermochemistry has been considered.[5–7] However, the actual appeal of DFT is focused on dynamics and properties of large systems so that in cases the adiabatic correction scales with system size it could become relevant. This is actually the case for some series of molecules. In fact, it has been shown[8] that the absolute finite-nuclear-mass-correction (FNMC)[9,10] for organic molecules follows the approximate prescription of 0.270 mH per electron. A similar result has been recently found for the more established diagonal-Born−Oppenheimer correction (DBOC).[11] For example, in the case of C_2H_6 this prescription gives 0.25 mH as contribution to atomization energy, whereas independent-particle ab initio DBOC predicts 0.22 mH[12] (throughout this work we refer to DBOC and FNMC as different implementations of the adiabatic correction). Having in hands the corrections for isolated atoms C and H [FNMC(H) = 0.272 mH and FNMC(C) = 1.712 mH], we can roughly evaluate the FNMC contribution to full atomization of, for example, $C_{20}H_{42}$ (eicosane) as 1.9 mH and $C_{100}H_{202}$ (centuriane) as 9.6 mH, the last one being 1 order of magnitude above the accepted “chemical accuracy” standard. DBOC contribution, though systematically smaller, will come along with these data. Ab initio computer simulations of the formation of this kind of polymers from the constituent atoms, which seem plausible just within DFT, will involve the same amounts of energy.

Stronger effects on chemical reaction dynamics beyond-BOA are due to nonadiabatic interaction of different electronic states,[13] whose calculation involves small nonadiabatic coupling terms. Further, adiabatic and nonadiabatic corrections have noticeable effects on various molecular properties upon deuteration.[14–16] On the other hand, direct simulation of quantum effects of the nuclei for realistic chemical reactions are unaffordable, both by means of computational power and by the complicated interpretation of the results-as positions of nuclei do not exist in a quantum-mechanical treatment. A simpler, even if less rigorous procedure connected to DFT is desirable. It must be noted that a nonadiabatic DFT theory has already appeared in the literature,[17] but unfortunately it seems to suffer of even stronger computational limitations.

The approach leading to the FNMC[9,10] is a computationally inexpensive way to account for the adiabatic correction to the energy and electronic wave function of molecules. Though reasonable in accuracy, the method allows maintaining the “Born−Oppenheimer world”, both in computational infrastructure and in the way of interpreting results. The combination of FNMC with DFT is therefore an interesting approach to address the adiabatic correction to problems which are computationally unfeasible for higher-level methods.

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This combination is reported in the next sections. As this is the first implementation of FNMC to DFT, we survey carefully the performance of various functionals based in the local density approximation (LDA) and based on gradient-corrected LDA (generalized gradient correction, GGA) and compare these results with benchmark calculations at the Hartree−Fock (HF) and second-order Möller−Plesset (MP2) levels of theory. The GGA functionals are then tested in the evaluation of the adiabatic contribution to the barrier to linearity of the water molecule. The corrections to DFT wave functions are evaluated in the calculation of the isotopic dipole moment of monodeuterated water molecule, HDO. Calculating such small molecular quantities serves to further assess the accuracy of DFT functionals as well as to perform comparison among them in extreme situations. Finally, original results are generated for medium size alkanes for which the adiabatic correction rapidly attains the mark of 1 mH.

Theory

Recently, a simple variational approach to account for the adiabatic correction to molecular energies and wave functions has been developed. To obtain the electronic Hamiltonian, instead of assuming the molecule at rest (the BOA) it assumes that the linear momentum is conserved in each atom (an exact approach would assume it for the whole molecule), when moving from the laboratory reference to the body-fixed frame.[9] This assumption introduces a nuclear-mass-dependent electronic kinetic energy term into the electronic Hamiltonian, which is capable to account for the isotopic effect in any atomic arrangement. The resulting post-HF methodology, especially MP2 and configuration-interaction (CI), has been tested and is available as an upgrade of the Gamess package,[18] called ISOTOPE,[19] and has generated many applications. In one of them, the adiabatic corrections to the energies of 50 molecules have been evaluated at the MP2 level.[8] A single criticism on this scheme appeared in the literature showing that it predicts barrier heights for the $H_2 + H$ reaction that are qualitatively different from those predicted by DBOC.[20] We connect this failure to a probable inadequacy of FNMC to singular points of the potential energy surfaces (the transition-state point in the case cited) where information about the energy derivatives relative to the nuclear coordinates may become important. This is, however, not a crucial point for well isolated ground-state surfaces which are relevant applications to DFT.

In this section we discuss the application of FNMC to Kohn−Sham (KS) Hamiltonians.[21] The FNMC approach is based on the electronic Hamiltonian,[9] given in atomic units (au) as

$$H_{\mathrm{KS}} = \sum_{\mathrm{A}}^{m}\left(-\sum_{i}^{N}\frac{\nabla_i^{\,2}}{2M_{\mathrm{A}}}\delta_{\mathrm{AB}}\right) - \sum_{i}^{N}\frac{\nabla_i^{\,2}}{2} + V_{\mathrm{eff}} \qquad (1)$$

Obviously, only the first term (the sum running over the m nuclei, indexed by A, with mass M_{A}) accounts for the adiabatic corrections to the potential energy surface and also for the isotopic symmetry breaking of the electronic wave function. The δ_{AB} operator acts so that the matrix elements of this term involving different nuclei A and B vanish. The remaining terms are the electronic kinetic energy (N electrons indexed by i) and the effective potential V_{eff}, which are equivalent to those present in the Born−Oppenheimer electronic Kohn−Sham Hamiltonian.

As the KS Hamiltonian is only modified by an additional term added to the core Hamiltonian, all standard expressions to minimize the KS energy $E = E[\rho]$, to calculate energy gradients with respect to the positions of the nuclei, and to calculate any property which is defined by an expectation value of the KS orbitals can be applied also to FNMC. Particularly, dipole moments are obtained in the same way as the BOA, namely

$$\vec{\mu} = \sum_{\mathrm{A}} Z_{\mathrm{A}}\vec{R}_{\mathrm{A}} - \int \rho\vec{r}\, d^3r \qquad (2)$$

in conventional notation.

On the other hand, because the contribution of the present methodology beyond the BO approximation is restricted to a modification of the kinetic energy operator we must consider how it should work within the KS approach to DFT. In fact, the KS kinetic energy operator $\hat{T}$ corresponds to a noninteracting electronic system. The compensation for this approximation is contained in the exchange-correlation energy term in V_{eff}. Therefore, the evaluation of the FNMC approach within DFT requires a systematic study of a series of presently available functionals.

In this work, we concentrate on the adiabatic correction to the energies of molecules in their equilibrium geometries, relative energies, and molecular isotopic dipole moments.

Survey of Adiabatic Corrections within DFT

The development of new functionals in the past 20 years has opened many areas of application to DFT. In chemistry, the reliable calculation of relative energies and reaction energy profiles has been especially relevant. This development is particularly important if larger molecules have to be studied, as DFT shows a superior scaling compared to all methods of the post-Hartree−Fock family.

It is therefore desirable to account for adiabatic corrections for density functional theory. It is not obvious, however, how well FNMC performs for different functionals. Therefore, we calculate the adiabatic corrections for a series of atoms and molecules to check the performances of different exchange correlation functionals. The experimental version of the deMon package[22] has been adapted to account for the adiabatic corrections according to the last section, and a series of local and gradient corrected functionals have been considered in this study. Unfortunately, the variational density-fitting technique[23] does not allow us to perform calculations using hybrid functionals at present. First tests show an uniform behavior of the LDA functionals, namely VWN, PW92 and PZ81, so that we keep just the results for the last one.

The HF- and MP2-DBOC calculations of ref 24 and MP2-FNMC calculations of ref 8 are considered for comparison. The basis sets employed in all calculations are the same used in ref 8, namely the 6-311**.[25–27] FNMC is the difference of the total energy calculated using eq 1 and the Born−Oppenheimer total energy at a given geometry. The molecular equilibrium geometries are taken from the literature[28] and have been reoptimized on the MP2 level.

In the calculation of small quantities it is important to keep control of the accuracy of numerical integration of the exchange-correlation energy and potential. deMon allows four different levels of accuracy in the definition of the numerical integration grids. We worked in general with the default adaptive MEDIUM grid (10^{-5} tolerance). To check the correctness of this procedure, we tested the values of absolute FNMC for hydrogen and benzene molecules with also the FINE and FIXED FINE grids (10^{-6} tolerance). The differences between these choices are as small as 10^{-1} μH for H_2 (the hardest case) and 10^{-2} μH for

TABLE 1: Absolute Adiabatic Correction ($\times 10^{-3}$ au) and DBOC per Electron ε (in Parenthesis in Third Column) for Atoms[a]

atom	HF-DBOC	MP2-DBOC	MP2-FNMC	PZ81	BLYP	PBE	PW91	PW86
H	0.2720	0.2720	0.2720	0.2552	0.2720	0.2706	0.2714	0.2692
C	1.660	1.711 (0.285)	1.709	1.700	1.722	1.719	1.720	1.723
N	2.005	2.070 (0.296)	2.114	2.109	2.131	2.128	2.129	2.132
O	2.366	2.443 (0.305)	2.548	2.545	2.567	2.564	2.566	2.569
F	2.592	2.680 (0.298)	2.856	2.856	2.878	2.875	2.876	2.879
Cl			7.061	7.075	7.103	7.101	7.102	7.107

[a] All DFT data are FNMC.

TABLE 2: Absolute Adiabatic Correction ($\times 10^{-3}$ au) for Some Molecules, Mostly Inorganic[a]

molecule	HF-DBOC	MP2-DBOC	MP2-FNMC	PZ81	BLYP	PBE	PW91	PW86
H_2	0.4608	0.5101	0.461	0.433	0.454	0.450	0.451	0.451
N_2	3.982	4.137	4.203	4.189	4.233	4.228	4.230	4.236
O_2	4.713	4.884	5.100	5.093	5.139	5.132	5.135	5.142
F_2	5.175	5.358	5.711	5.711	5.756	5.749	5.752	5.760
Cl_2			14.123	14.153	14.209	14.205	14.208	14.218
NH_3	2.610	2.719	2.775	2.730	2.801	2.786	2.789	2.796
NO	4.554	4.555 (4.503[a])	4.652	4.643	4.689	4.682	4.685	4.691
CO_2	6.315	6.545	6.755	6.741	6.808	6.799	6.803	6.812
H_2O	2.711	2.826	3.003	2.978	3.027	3.021	3.022	3.026
H_2O_2	5.079	5.283	5.552	5.522	5.596	5.586	5.589	5.597
HF	2.736	2.846	3.077	3.069	3.102	3.098	3.100	3.102
HCl			7.297	7.296	7.340	7.333	7.335	7.342
HCN	3.820	3.978	3.999	3.974	4.037	4.026	4.029	4.037
C_2H_2	3.674	3.833	3.807	3.788	3.860	3.851	3.854	3.856
C_4H_6	7.949	8.271	8.161	8.027	8.243	8.188	8.198	8.222
C_6H_6	11.217	11.656	11.554	11.407	11.656	11.605	11.617	11.639

[a] This result corresponds to a coupled-cluster calculation from ref 24. All DFT data are FNMC.

benzene, so that we are confident that our results are not affected by numerical errors.

Table 1 shows the absolute adiabatic correction for atoms present in the following molecular applications. The DFT calculations, both LDA and GGA, show good agreement with the MP2 references. The only large deviation is observed in the LDA calculation for H, which shows a large error (6% from MP2-DBOC or -FNMC). The results are not too dependent on the functionals; within the LDA parametrization and the four GGAs involved in this study only minor differences are detected. With these observations we are confident that also hybrid functionals will perform similarly well for the computation of the adiabatic correction in atoms.

Table 2 displays the absolute adiabatic corrections for some small molecules for which DBOC values are available. With the exceptions of H_2 and organic molecules, the corrections increase in the sequence: HF-DBOC, MP2-DBOC, PZ81, MP2 and GGA-FNMC. The error bars of the gradient corrected functionals relative to MP2-FNMC are well below 1%. Relative to the MP2-DBOCs the FNMCs differ less than 10% in general, with a surprisingly better performance of the LDA functional for nonorganic molecules. For organic molecules the advantage turns to the GGA functionals and it can be observed that BLYP overcomes MP2-FNMC as compared to MP2-DBOC. A singular case is H_2, whose FNMC result show the largest relative departure from MP2-DBOC. For NO, the only case that presents decreasing values of DBOC as electron correlation is introduced, we included in the table also the coupled-cluster result from ref 24.

Table 3 displays results for a set of other organic molecules which can be used to calculate corrections relative to many breaking processes. The performances of the GGA functionals are almost equivalent. We found no DBOC calculations for these molecules but we can identify an analogous pattern to the previous table (for organic molecules) so that we guess that the BLYP values are the best ones.

TABLE 3: Absolute Adiabatic Correction FNMC ($\times 10^{-3}$ au) for Some Organic Molecules Not Included in Table 2

molecule	MP2	PZ81	BLYP	PBE	PW91	PW86
CH_4	2.614	2.535	2.641	2.610	2.615	2.627
C_2H_4	4.308	4.235	4.356	4.325	4.330	4.344
C_2H_6	4.792	4.668	4.844	4.792	4.800	4.821
CH_3CCH	5.978	5.898	6.043	6.010	6.017	6.029
CH_2CCH_2	5.977	5.897	6.041	6.005	6.011	6.030
C_3H_4	6.007	5.922	6.065	6.033	6.039	6.053
CH_2CHCH_3	6.469	6.348	6.541	6.489	6.498	6.523
C_3H_6	6.453	6.322	6.519	6.464	6.473	6.497
C_3H_8	6.957	6.789	7.035	6.962	6.973	7.004
$CHCCH_2CH_3$	8.149	8.017	8.231	8.178	8.188	8.210
$CH_2CHCH_2CH_3$	8.636	8.466	8.729	8.657	8.669	8.700
$CH_2CCH_3CH_3$	8.628	8.461	8.724	8.651	8.663	8.695
$CH_3CH_2CH_2CH_3$	9.124	8.911	9.228	9.134	9.148	9.189
COH_2	4.745	4.706	4.787	4.770	4.773	4.784
HCOOH	7.228	7.190	7.289	7.273	7.277	7.290
CH_3OH	5.200	5.125	5.247	5.217	5.222	5.237
CH_3CH_2OH	7.361	7.243	7.435	7.384	7.392	7.417
CH_3COOH	9.352	9.268	9.438	9.400	9.408	9.430
C_3H_7OH	9.529	9.364	9.626	9.555	9.565	9.600
CH_3COCH_3	8.979	8.850	9.071	9.013	9.023	9.051
CH_3NH_2	4.971	4.876	5.020	4.982	4.988	5.006
$CH_3CH_2NH_2$	7.131	6.988	7.202	7.144	7.153	7.181
NH_2CONH_2	9.286	9.215	9.371	9.342	9.347	9.368

The absolute adiabatic correction can influence static properties at the equilibrium geometry of a molecule. As the total energy, it is almost proportional to the number of electrons in an atom or a molecule. Similarly, it is not an observable quantity itself, but the difference of the adiabatic correction of reactants and products, particularly the atomization of a molecule, is. In a recent paper, one of us argued that for multielectron molecules, DBOCs behave closely like atomic ones, with their values being strongly dominated by internal electrons.[11] As a consequence, DBOCs become a bulk molecular property described by its value per electron, ε. Another consequence is that, although this

TABLE 4: Relative Adiabatic Corrections ($\times 10^{-3}$ au) of Products and Reactants for Some Dissociation Processes[a]

process	HF-DBOC	MP2-DBOC	MP2-FNMC	BLYP	PBE	PW86
$CO_2 \rightarrow C + 2O$	0.077	0.052	0.050	0.048	0.048	0.049
$F_2 \rightarrow 2F$	0.009	0.002	0.001	0.000	0.001	−0.002
$Cl_2 \rightarrow 2Cl$			−0.001	−0.003	−0.003	−0.004
$NO \rightarrow N + O$	−0.183	−0.042 (0.006[a])	0.010	0.009	0.010	0.010
$C_2H_2 \rightarrow 2C + 2H$	0.190	0.133	0.155	0.128	0.128	0.128
$C_4H_6 \rightarrow 4C + 6H$	0.323	0.205	0.307	0.277	0.311	0.285
$C_6H_6 \rightarrow 6C + 6H$	0.375	0.242	0.332	0.308	0.333	0.314
$C_6H_6 \rightarrow C_4H_6 + 2C$	0.052	0.037	0.025	0.031	0.021	0.028
$H_2O \rightarrow O + 2H$	0.200	0.161	0.089	0.084	0.060	0.081

[a] This result correponds to a coupled-cluster calculation from ref 24. All DFT data are FNMC.

argument fails in the presence of H atoms in nonorganic molecules (particularly for H_2), the closeness of the DBOC for H, namely 0.272 au, to the DBOC per electron for the carbon atom (see Table 1), $\varepsilon = 0.285$ au extend fortunately this property to organic molecules. At this point the atomic character of FNMC becomes relevant as a mean to turn this argument operative in the calculation of relative adiabatic corrections. In the following, we evaluate the adiabatic contribution to dissociation energies, namely [FNMC(products) − FNMC(reactants)], displayed in Table 4. We consider some representative dissociation processes described by MP2-FNMC and the more promising GGA functionals, BLYP, PBE and PW86 (the LDA functional performs badly in this case) and compare the results with HF- and MP2-DBOC. Further results can be readily obtained from the previous tables of absolute adiabatic corrections.

Results in Table 4 start with molecules without H atoms. The atomization of CO_2 shows an impressive accordance of FNMC with MP2-DBOC at any level and for all DFT functionals. Because adiabatic corrections are mostly atomic properties, their relative values for atomization of homonuclear molecules must be zero or very small. This is exactly what is observed for F_2 and Cl_2. Another important account is found in the NO case, the only in ref 24 for which the electronic correlation contributes a negative value for DBOC, which appears just on the coupled-cluster level. We see in the table that this effect is already accounted for with FNMC. Although differing 30−40% from the coupled-cluster value, all MP2 and DFT-FNMC values for NO represent a large improvement over the HF- and even the MP2-DBOC. For atomization or partial breaking of organic molecules, the general behavior is that all FNMC calculations represent an improvement from the HF-DBOC toward MP2-DBOC. In this case, like for the absolute corrections, the BLYP performance results better than all others including MP2-FNMC. The table ends with an illustration for the water molecule of the predicted worse behavior of FNMC in nonorganic molecules containing H atoms; the corrections fall to about half of the MP2-DBOC ones. A final observation is that if larger atoms are involved (Ge, As, Se, etc.), the relative adiabatic correction may become too small to be assessed by DFT so that the dispersion of the results becomes too large. Even though, an observed superior behavior of PW86 for the cases in which the atomization contribution is found to be larger than 0.00003 au (about 10% deviation from MP2) would recommend this functional for applications in the studies of metal or semiconductor surface reactions.

Small differences of the MP2 adiabatic corrections shown here from those displayed in ref 8 are due to different versions of ISOTOPE and possibly, in the cases of molecules, to small geometry differences, because they have been reoptimized. On the other hand, as we recalculate the MP2 corrections we found an input error for the Benzene molecule in ref 8 so that the correct value is the one displayed here.

TABLE 5: MP2- and GGA-FNMC Contributions to the Barrier to Linearity of Water (in cm $^{-1}$)

MP2	BLYP	PW91	PBE	PW86	DBOC[29]
−13.7	−8.0	−8.7	−8.3	−13.1	-14 ± 1

Applications

Barrier to Linearity of the Water Molecule. The DBOC contribution to the barrier to linearity of the H_2O molecule has been recently evaluated by Valeev and Sherrill with various methods and basis sets, resulting in an estimate of -14 ± 1 cm^{-1}.[29] We perform MP2 and GGA evaluations of this contribution with the aug-cc-pVQZ basis set. As shown in Table 5, our MP2 value is inside the error bar of ref 29. All functionals reasonably reach more than 70% of the MP2 value, whereas PW86 practically recovers it, with a deviation of just 4%.

Isotopic Dipole Moment of HDO. In BOA based approaches, the adiabatic correction is commonly obtained just for potential energy surfaces, not for the electronic wave functions. This feature limits the examples of post-BOA molecular properties to just a few.[16,30,31]

The asymmetries yielded by isotopic substitution in molecules are able to create small but measurable[32,33] isotopic dipole moments. Particularly important in laboratory is the substitution of an H atom by its heavier isotope D (deuterium). The simplest case, HD, is not the easiest one for calculations, because the isotopic dipole moment points in the direction of the chemical bond. Shrinking and stretching the bond implies modifications in the physics of the system that are strong enough to difficult calculations of this small quantity with a fixed atomic-centered basis set. In the HDO isotopologue of water, on the other hand, there is no bond between H and D so the variation of this property against the bond angle, for example, is much more stable. In this molecule, a small isotopic dipole appears pointing from D to H (the X direction here), almost orthogonal to the principal dipole moment of the water molecule. Generalized calculations of this quantity by the present approach, using eq 2, became available with the development of a specially designed basis set for H and D, leading to the evaluation of the isotopic dipole moment of HDO in its equilibrium geometry as $\mu_X = 1.5 \times 10^{-3}$ Debye, at the MP2 level as well.[16] This quantity is now used as a standard to assess the quality of DFT functionals in its evaluation. μ_X is then obtained for a set of bond angles between the O−H and O−D bonds. The output is presented in Figure 1, with shows the dipole moment curves for MP2 and for the GGA functionals. The LDA curves not shown in the figure have been found between the PBE and BLYP ones and display the same pattern. All functionals yield a qualitative correct behavior up to 120°. From this angle on they start departing from the MP2 curve. Here again the PW86 functional shows an outstanding performance, agreeing almost exactly with MP2 for a large range of angles around equilibrium

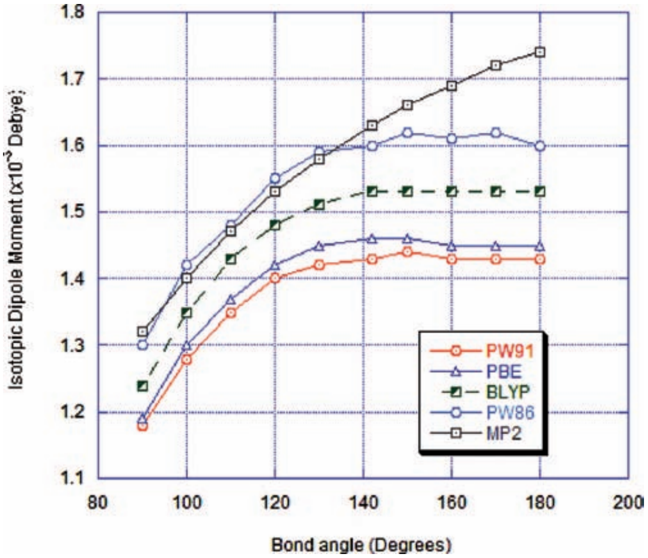

Figure 1. Isotopic dipole moment of HDO versus bond angle for MP2 and GGA functionals. The last point of all curves is obtained at 179.99°.

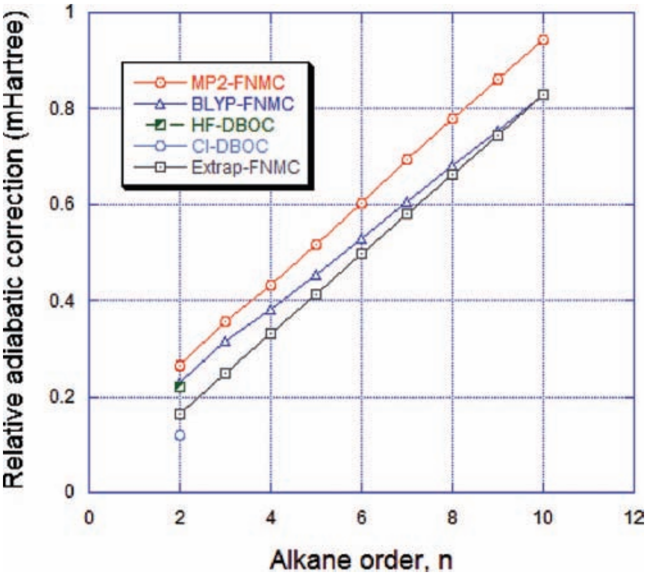

Figure 2. Adiabatic correction to atomization of alkanes versus the alkane order *n*; HF and CI calculations from ref 12. For the meaning of Extrap-FNMC see text.

(104°). In fact, PW86 results also start differing from MP2 in the same point all other functionals change their behavior. A possible explanation is the too strong electron delocalization of DFT, which might shift the isotopic dipole moments to lower values if the molecular geometry approaches linearity.

Corrections to the Atomization Energy of Alkanes. In the Introduction we argue that the insertion of adiabatic correction to present days DFT calculations could be worth because particularly for organic molecules it could overcome 1 mH. The approximate recipe of a constant contribution per electron leaded us to propose that in medium size alkanes the correction would readily attain this value. A connected feature is the observed quasi-linear behavior of the contribution of adiabatic corrections to full molecule atomization against the number of atoms in series of organic molecules.[24]

To check these points, we perform calculations to the alkane series C_nH_{2n+2}. The basis sets are the same as given in the Survey section, but optimized geometries were not found for most alkanes so that we optimized them on the MP2 level. This application is particularly interesting here because the relative number of C electrons to the number of H electrons in the series starts at 2 for C_2H_6 and converges to 3 as *n* increases. The "excess" of H atoms in the first molecules of the series worsens the FNMC results, which are, however, expected to get progressively better with increasing *n*. In fact, Figure 2 shows DBOCs for C_2H_6 from ref 12 on the HF (0.22 mH) and CI (0.12 mH) levels and FNMCs on the MP2 (0.265 mH) and BLYP (0.232 mH), which are a little worse than HF. This case corresponds to $\varepsilon_{\mathrm{BLYP}} = 0.270$ au. As we move to $C_{10}H_{22}$, for example, we get $\varepsilon_{\mathrm{BLYP}} = 0.272$ au. Assuming this converged value as holding for all *n* and recalculating the atomization correction as [$N\varepsilon$-FNMC(reactants)] we obtain the curve Extrap-FNMC, which extrapolates the BLYP results from $C_{10}H_{22}$ to C_2H_6, yielding a very reasonable value of 0.165 mH, again improving the HF-DBOC toward CI-DBOC. The conclusion is that the BLYP-FNMC values rapidly attain a better performance than HF as *n* increases from 2. Another important observation is that, one more time, BLYP-FNMC overcomes MP2-FNMC in the calculation of adiabatic contribution of atomization energies. Finally, it is interesting to note that extrapolation of the BLYP curve to higher values of *n* predicts attainment of the mark of 1 mH correction already for $C_{12}H_{26}$, according to our prediction in the introduction and showing that the inclusion of adiabatic corrections into DFT codes can be relevant.

Discussion and Remarks

We report applications of DFT to the calculation of some small molecular quantities and functional ranking based on the output. For calculations of absolute adiabatic correction our results recommend the use of an LDA functional for nonorganic molecules and a GGA functional, especially BLYP, for organic molecules, as they show the closest performances to benchmark MP2 results. In the calculation of relative adiabatic corrections to light nonorganic molecules without H atoms, the GGA functionals work very well, with a performance equivalent to MP2-DBOC. This means a larger accuracy capability of DFT than the common belief because the relative corrections are about 1 order of magnitude at least lower than 1 kcal. mol $^{-1}$. Systematically, MP2 and DFT absolute FNMC values are larger than DBOC ones but the relative values behave properly for the systems cited above.

Organic molecules are potentially the most important kind of applications. For them, as well as for other kinds of molecules, HF usually overestimates the relative adiabatic correction. In this case we observe that DFT becomes a nice alternative to evaluate corrections displaying a reasonable amount of correlation (see Table 4), without the computational burden that makes post-HF applications unfeasible. For these molecules, we nicely observe that BLYP-FNMC performs better than MP2-FNMC.

Although FNMC gets less accurate than HF-DBOC in the atomization of nonorganic molecules containing H atoms, like H_2O, it works well for the evaluation of the barrier to linearity of this molecule, with an outstanding performance of PW86. This means that the problem with H atoms that affects atomization is not present in the calculation of corrections when there is no bonding breaking (e.g., from reactants to a transition state).

A major advantage of FNMC over the common adiabatic approaches (e.g., DBOC) is that it affects also the electronic wave function, allowing the calculation of corrections to molecular properties other than energy. In the calculation of the isotopic dipole moment of HDO, the results reinforce the impression that PW86 has a larger overall capability to assess small molecular quantities, no matter whether they are energies or properties. This point links our functional ranking to the very competitive field of functional development. In view of the definition of FNMC, it seems that the better ranked functionals have a superior ability to account for correlation effects affecting the electronic kinetic energy, this characteristic being the actual source of the different performances. It appears that this point should be considered for the development of new functionals. A more uniform behavior for reactants and products that would admit similar performances in calculating absolute and relative corrections is another quite important goal.

Finally, a few more words are due about the meaning of assessing such small corrections with DFT. The computationally simple FNMC approach nicely complements BO-DFT. The adiabatic corrections can grow with system size, and the inclusion of these effects will have a measurable effect within the error bars of DFT (few kcal/mol). Further improvement of functionals will push the DFT performance even closer to chemical accuracy, and motivate adiabatic corrections to the Hamiltonian even stronger.

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