

Performance of Minnesota functionals on predicting core-level binding energies of molecules containing main-group elements

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Abstract Here we explored the performance of M06, M06-L, M11, and M11-L Minnesota functionals on predicting core-level 1s binding energies (BEs) and BE shifts (Δ BEs) for a set of 20 organic molecules containing main-group elements C \rightarrow F (39 core levels in total). The broadly used Hartree–Fock (HF) and Becke–Lee–Yang–Parr (B3LYP) methods have also been studied for comparison. A statistical analysis comparing with X-ray photoelectron spectroscopy (XPS) experimental values shows that overall BEs estimations only deviate a small percentage from the experimental values, yet the absolute deviations are generally too large, with the different methods over/underestimating the reported values. However, taking the contribution of relativistic effects of BEs into account leads to larger differences. Overall, the performance of the explored Minnesota functionals is not satisfactory, with errors of up to 1 eV, except for the M06-L meta-GGA functional. In this case, the mean absolute deviation is below 0.1 eV and thus within XPS chemical resolution. Hence, M06-L poses itself as a rather accurate and computational expense-wise method for estimating BEs of organic molecules. Nevertheless, the observed deviations almost cancel when considering Δ BEs with respect to some arbitrary reference, with errors within 0.2–0.3 eV, indicating that these are largely systematic, which in turn implies that the corresponding methods have room for improvement.

Keywords Core-level binding energies · DFT · XPS

1 Introduction

Electron spectroscopy for chemical analysis (ESCA), more commonly referred to as X-ray photoelectron spectroscopy (XPS), is an experimental technique widely used in many materials and surface science laboratories and facilities, either in research or in applied industry. XPS is broadly used for the elemental analysis of bulk materials, especially for surfaces, given its surface sensitivity [1, 2], but it has also been applied to the detection of gas phase molecules [3]. Furthermore, XPS is currently used to in situ observe the evolution of a heterogeneously catalyzed reaction, allowing for the characterization of reactants, intermediates and products, thus serving as a powerful tool to determine reaction mechanisms [4–6].

In part, the XPS usefulness hangs on the elemental analysis by measurements of core-level electron binding energies (BEs). However, the BEs are not only characteristic of a given element, but, more specifically, they are characteristic of a given element in a given chemical environment and electronic state. Thus, BEs provide qualitative information of the elements present in a sample, quantitative information of their concentration, plus qualitative/quantitative information of their different chemical environments and electronic states [1–6]. Such a detailed information enables BEs from XPS experiments to be used as chemical fingerprints in condensed phase systems, reflecting the chemical properties and bonding between the species in it [7]. The small variations for a given element in different chemical environments are often characterized by means of core-level BEs shifts (Δ BEs) and normally allow for distinguishing different structural as well as the oxidation state of a given atom [8].

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The assignment of a given XPS peak to a given chemical element is straightforward and constitutes a useful property to benchmark ab initio methods. In fact, core-level BEs and their Δ BEs have been accurately predicted from ab initio calculations at the well-known Hartree–Fock (HF) level of theory [9–11]. Nevertheless, electron correlation effects are missing in HF, and explicitly correlated methods usually referred to as post-HF rapidly become computationally expensive. On the other hand, electron correlation is implicitly included in density functional theory (DFT)-based methods, which indeed have a better scaling with respect to the number of atoms and electrons than post-HF ones [12]. Not surprisingly, DFT-based methods are becoming the default choice.

The performance of DFT methods in predicting structure and reactivity of molecular systems is well documented [13], but, except for the series of works of Chong et al. [14–17], the information regarding their performance on predicting core-level BEs is missing and, if present, refers mainly to functionals in the lower rungs of Jacob’s ladder of accuracy for DFT functionals. In one of these works, Takahata and Chong [17] studied 35 small organic molecules containing B \rightarrow F atoms and considered a total of 59 1s core electron BEs, tackling the effect of using increasingly large basis sets and a sequence of 21 different DFT exchange–correlation (xc) functionals, either within the local density approximation (LDA) or the generalized gradient approximation (GGA), but also considering some earlier versions of meta-GGA xc functionals. Among all the studied functionals, the Voorhis–Scuseria (VS98) [18], meta-GGA and the Becke–Lee–Yang–Parr (BLYP) [19, 20] GGA were found to be the most accurate for computing BEs, with mean absolute errors (MEA) of \sim 0.2 and \sim 0.3 eV, respectively.

Unfortunately, this previous study [17] did not include the type of hybrid functionals which are nowadays among the most used and successful main-group element molecules [13]. These functionals incorporate a percentage of HF exchange such as B3LYP [21], probably among the most used methods in molecular quantum chemistry. The success of B3LYP is the significant improvement in the description of the thermochemistry of main-group molecules, relative to GGA and meta-GGA functionals [13]. Another family of meta-GGA and hybrid xc functionals with excellent performance in the thermochemistry of main-group elements is the one developed by Truhlar’s group and often referred to as Minnesota functionals [22].

To assess the performance of these new functionals in predicting 1s core-level BEs of main-group element containing molecules, the present work describes a systematic study for the series of molecules included in the study of Takahata and Chong [17]. In particular, we chose the M06 [23] and M11 [24] hybrids and added the M06-L and

M11-L local meta-GGA functionals [25, 26], given that such xc has proven to deliver an accurate description even in very complex systems [27]. In fact, these methods are able to solve the well-known CO adsorption on Pt(111) puzzle [28]. In addition, their local character and concomitant low computational cost are particularly well suited for periodic DFT calculations [29]. For comparison purposes, HF and B3LYP methods have also been tested.

2 Computational details

Core-level BEs can be rather accurately predicted from ab initio calculations—such as HF- or DFT-based methods—[9–11, 14–17, 31, 32] via the difference between the total energies of the neutral state and the same system with a core–hole configuration generated by subtracting one electron in the desired core level, as shown in Eq. 1.

$$\text{BE} = E(\text{Core hole state}) - E(\text{Neutral state}) \quad (1)$$

A possible way to obtain the energy values in Eq. 1 is to make use of separate self-consistent field (SCF) calculations. The resulting procedure is usually referred as Δ SCF [9, 11], and Eq. 1 is usually rewritten as

$$\text{BE}_i = E_i^{N-1}(\text{SCF}) - E^N(\text{SCF}) \quad (2)$$

where the subindex i in BE_i indicates the ionized core, whereas $E^N(\text{SCF})$ and $E_i^{N-1}(\text{SCF})$ are the variationally optimized energy for the initial system with N electrons and the final systems with $(N-1)$ electrons and the corresponding i core–hole.

The Δ SCF calculations have been performed on the molecular set proposed by Takahata and Chong [17], who assessed the performance of some gradient corrected functionals on a series of organic molecules containing B \rightarrow F elements. Note, however, that here B is not considered, since only BF_3 result is available, and would deliver only one point for B-based molecules, thus not allowing for a statistical analysis. Therefore, only 20 molecules have been contemplated, which involve 39 core levels—see the full list in “Appendix.” The Δ BEs are, for each element C \rightarrow F level, computed with respect to a given simple reference molecule: methane (CH_4), ammonia (NH_3), water (H_2O), and fluoromethane (CH_3F) for C \rightarrow F, respectively.

The calculations have been carried out using a large fully uncontracted basis set near the HF limit, ensuring an accurate and well-defined description of both neutral and ionized states. Specifically, for C \rightarrow F, an uncontracted Partridge (14s,9p) set augmented by a d function taken from the polarized valence triple zeta (pVTZ) set was used. For H atoms, we used an uncontracted basis set (5s) taken from the VTZ basis set augmented with a p function [30]. All

BEs and Δ BEs have been obtained using the M06, M06-L, M11, and M11-L methods, which can be taken as representative of the Minnesota series of functionals, as well as with HF, a well-defined reference method, and B3LYP, one of the most broadly used DFT-based methods. In particular, B3LYP has been recently found to be acutely suited in estimating BEs for a series of N-containing molecules in gas phase [31, 32].

For any of the explored methods, the equilibrium geometry of each molecule is optimized for the neutral molecule. Frequency analyses have been carried out on each studied system, ensuring that they represent a minimum in the corresponding potential energy hypersurface. Note also that Δ SCF calculations aimed to obtain BEs and Δ BEs values are carried out at the geometry of the neutral molecule, i.e., vertical transitions, which is a reasonable choice given the timescale of core-level ionization in the XPS experiments. For the core-hole state, the occupied orbitals are selected using an overlap criterion instead of the usual Aufbau approach. In order to properly account for spin symmetry, calculations at the Hartree-Fock level employ the restricted open-shell (ROHF) formalism. A restricted formalism has also been adopted for the DFT-based calculations, thus avoiding spin contamination and artificial spin polarization in valence electron in the state with a core-hole, the need for spin projection [33] and, at the same time, providing appropriate comparison with those obtained at the HF level. All calculations have been carried out using the GAMESS program [34, 35].

Note by passing by that relativistic effects, not included in the previously described calculations, are different for distinct core levels and increase with the atomic number of the ionized atom. In order to discuss the accuracy of the different methods in predicting BEs, it is convenient to have a reliable estimate of the contribution of the relativistic effects. To this end, results from relativistic and non-relativistic calculations for the C \rightarrow F isolated atoms at the HF level of theory provided by Bagus [36] have been used. These relativistic calculations were carried out with the DIRAC program [37], and the non-relativistic calculations were carried out with the CLIPS code [38]. The wave functions were based on the average of configurations and do not take into account the multiplet splitting effects for these open-shell atoms [39]. We compared fully relativistic four-component Dirac HF wave functions and energies with non-relativistic HF wave functions and energies for the C \rightarrow F isolated atoms. The basis sets used for these calculations were the same as for the non-relativistic calculations. It is worth pointing out that previous works [31, 32] validated the GAMESS results for the core-hole states by comparing with results obtained with CLIPS.

3 Results and discussion

Let us first analyze the absolute BEs—BE(Δ SCF)—results, which are encompassed in Table 1. At a first glance, any functional explored and also HF are targeting well the experimental BE. Indeed, the statistical analysis, evaluated in terms of mean error (ME), MAE and the mean absolute percentage error (MAPE), consistently shows it. Hence, any functional here explored (also HF) excellently targets the experimental value with a deviation below 0.17 %. When one goes into the fine detail, HF tends to underestimate the experimental BEs by \sim 0.3 eV, due to the neglect of electron correlation which is larger in the ground state than in the core-hole containing cation. Note, however, that B3LYP performs in a similar way even if here correlation effects are accounted for through the xc potential.

A different panorama emerges when analyzing results predicted by the Minnesota functionals. In fact, the M06 hybrid xc is found to underestimate BEs by \sim 0.7 eV and the related meta-GGA M06-L functional also underestimates the BEs by \sim 0.3 eV. Thus, the underestimation seems to be residing in the functional by construction, although relativistic effects must also be considered, as shall be commented below. On the other hand, the M11 and M11-L reformatted xc functionals tend to overestimate the BEs by \sim 0.3 and \sim 0.7 eV, respectively. In any case, it is clear that by adding the corresponding % HF to M06-L or M11-L meta-GGA xc functionals, the BEs lower by \sim 0.45 eV, which is not so easy to interpret. By further analyzing the data using MAE, one can remove sign cancellation errors; in this way, M11 hybrid and M06-L meta-GGA seem to be the best xc functionals to predict absolute BE values, but with a mean error for both near \sim 0.3 eV. Interestingly, this is closely followed by B3LYP, with a mean absolute error of \sim 0.4 eV.

An elemental analysis for BEs of C \rightarrow F is visually presented in Fig. 1, where excellent linear relationships are drawn for calculated BEs versus the experimental ones. Several conclusions can be withdrawn from this analysis. The first one is that C_{1s} are rather accurately described by any of the inspected methods, with just very slight deviations from ideality. Thus, the over/underestimations commented in Table 1 arise from N \rightarrow F elements. Indeed, for N_{1s} orbitals, the BEs of M11-L—the xc functional with the largest overestimation, as seen in Table 1—display a positive offset with respect to the experimental values, whereas HF and M06 display a similar negative offset, which seems to be physically more correct. These deviations seem to be progressively acute when going to O_{1s} and F_{1s} core levels.

Aside, the B3LYP displays a less markedly negative offset, only significant for O_{1s} and F_{1s} . Last but not least, M06-L meta-GGA and M11 hybrid display very little

Table 1 BE(Δ SCF) results for the 1s core orbitals analyzed, in underlined bold font, of the molecules described in the overall set

Molecule	BE(Δ SCF)						
	Exp.	HF	B3LYP	M06	M11	M06-L	M11-L
<u>CH₂C(CH₃)₂</u>	289.83	289.56	289.77	289.20	290.12	289.63	290.46
CH ₂ <u>C(CH₃)₂</u>	290.65	290.42	290.63	290.14	290.96	290.61	291.55
CH ₂ C(<u>CH₃)₂</u>	290.69	290.59	290.67	290.16	290.95	290.63	291.40
<u>CH₄</u>	290.91	290.75	290.84	290.29	291.09	290.78	291.45
<u>CH₃COOH</u>	291.55	291.90	291.88	291.31	292.20	291.74	292.38
CH ₃ <u>COOH</u>	295.38	295.99	295.39	294.93	295.91	295.01	295.93
<u>CH₃OH</u>	292.42	292.49	292.50	291.99	292.82	292.38	293.04
CH ₃ <u>CN</u>	292.45	292.86	292.85	292.30	293.24	292.62	293.31
<u>CH₃CN</u>	292.98	292.80	292.74	292.14	293.08	292.58	293.45
<u>HCN</u>	293.40	293.53	293.61	292.98	293.95	293.31	294.06
<u>H₂CO</u>	294.47	294.75	294.66	294.13	294.99	294.40	295.19
<u>HCONH₂</u>	294.95	295.22	294.51	293.99	295.01	294.13	295.01
<u>CO</u>	296.21	296.90	296.59	295.94	296.97	295.91	296.73
<u>CH₂F₂</u>	296.40	296.71	296.41	295.93	296.86	297.47	297.12
<u>CO₂</u>	297.69	299.20	297.89	297.31	298.54	297.23	298.25
<u>CF₄</u>	301.90	302.86	301.90	301.53	302.57	301.35	302.26
N(<u>CH₃)₃</u>	291.26	291.17	291.24	290.78	291.54	291.19	291.98
<u>NH₃</u>	405.56	405.18	405.32	404.76	405.71	405.45	406.24
<u>N(CH₃)₃</u>	404.81	404.12	404.44	404.09	404.96	404.70	405.93
CH ₃ <u>CN</u>	405.64	405.25	405.33	404.74	405.89	405.22	406.14
<u>HCONH₂</u>	406.39	406.17	406.33	405.78	406.83	406.39	407.21
<u>HCN</u>	406.78	406.47	406.66	406.04	407.17	406.58	407.45
<u>NNO</u>	408.71	409.24	408.67	408.04	409.30	408.34	409.32
<u>NNO</u>	412.59	413.98	412.68	412.28	413.63	412.41	413.54
<u>HCONH₂</u>	537.74	536.67	537.03	536.74	537.70	537.35	538.50
CH ₃ <u>COOH</u>	538.33	537.19	537.55	537.21	538.26	537.79	538.83
CH ₃ <u>COQH</u>	540.12	539.53	539.52	539.24	540.24	539.78	541.02
CH ₃ <u>QH</u>	539.11	538.16	538.44	538.19	539.08	538.84	540.04
<u>H₂CO</u>	539.48	538.27	538.86	538.55	539.46	539.27	540.28
<u>H₂O</u>	539.90	539.10	539.30	538.86	539.88	539.53	540.55
<u>CO₂</u>	541.28	540.66	540.83	540.42	541.58	541.01	542.10
<u>NNO</u>	541.42	540.39	541.03	540.69	541.62	541.36	542.44
<u>CO</u>	542.55	541.66	542.10	541.61	542.77	542.29	543.13
CH ₃ <u>F</u>	692.91	691.41	691.75	691.79	692.49	692.36	693.88
CH ₂ <u>F₂</u>	693.65	692.54	692.72	692.72	693.49	694.21	694.09
<u>HF</u>	694.23	693.10	693.32	693.07	694.05	693.65	694.98
<u>CHF₃</u>	694.62	693.59	693.63	693.58	694.46	694.01	695.49
<u>CF₄</u>	695.56	694.58	694.49	694.43	695.38	694.79	696.30
<u>F₂</u>	696.69	695.27	695.69	695.52	696.56	695.92	697.18
ME	–	–0.28	–0.29	–0.71	0.26	–0.26	0.69
MAE	–	0.67	0.39	0.71	0.33	0.33	0.69
MAPE	–	0.15	0.08	0.16	0.09	0.08	0.17

Experimental BE values are also given. A summary of the statistical analysis, ME, MAE, and MAPE, is reported. All values are in eV, except MAPE, in %

deviations with respect to ideality. It is remarkable that for O_{1s} and F_{1s} a trend of underestimation of HF > M06 > B3LYP > M06-L > M11 > M11-L is obtained, regarding

that such underestimation turns to be overestimation in the M11-L case. Last but not least, the above-commented rising of BEs when adding HF exchange to M06-L and M11-L

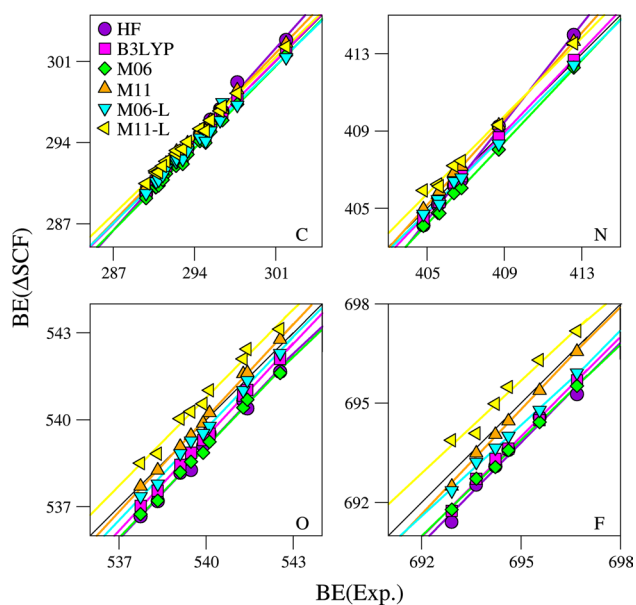


Fig. 1 Calculated, $BE(\Delta SCF)$, versus experimental, $BE(Exp.)$, core-level BEs for C, N, O and F elements. All values are given in eV. Black lines represent the ideal experimental matching

meta-GGAs, i.e., when using M06 and M11, respectively, is clearly seen in $N \rightarrow F$ panels.

Let us pay attention to ΔBEs , listed in Table 2, instead of absolute BE values. The overall statistical analysis reveals that, as expected, the above-commented over/underestimations cancel when comparing BE shifts, and so, the overall deviations for all the tested methods sensibly drop: The Minnesota functionals and B3LYP have MAE values of ~ 0.2 eV, whereas HF displays a larger value of ~ 0.4 eV. Aside the marked underestimation observed for HF, B3LYP, and M06 and M06-L vanish. It is noteworthy how by estimating BE shifts the mean error on DFT xc functionals approach to the XPS chemical accuracy of 0.1 eV. This is a clear indication of systematic errors in the functionals which could in this way be mended.

This agreement is also reflected when plotting, itemized for the different studied elements, the estimated ΔBEs with respect to the experimental ones, as shown in Fig. 2. The agreement between methods is remarkable, and barely one can only highlight a sensibly larger slope for HF, most acute for C_{1s} and O_{1s} cases, slightly followed by M11 and faint value dispersion for F_{1s} cases. Actually, one can inspect the data gained from the linear fittings in this matter, as shown in Table 3. It is clear that linear fitting is excellent for ΔBEs , with R regression coefficients larger than 0.99. One can estimate, for each inspected element and method, the mean offset for the obtained range of ΔBEs . By doing so, it is clear that the larger the slope, i.e., the more deviation with the ideal value of 1.0, the larger the offset, as observed for C_{1s} and N_{1s} ΔBEs , with slopes of 1.12 and 1.27, and offsets

of 0.67 and 0.87 eV, respectively. This is also observed for M11 but to a lower degree, e.g., for N_{1s} , with a slope of 1.11 and an offset of 0.49 eV. Aside from these two cases, the overall offsets range 0–0.2 eV, really close to the ESCA chemical accuracy of 0.1 eV. It is worth highlighting that the lowest offset deviation is found for M06-L meta-GGA, below 0.1 eV regardless of the studied method.

The offset analysis discussed above can also be applied to BEs. Indeed, Table 3 contains the linear fittings for the BEs plots in Fig. 1. Again, the linear adjustments are excellent, with regression coefficients above 0.99. Here, however, the offsets can be larger despite a slope near one, reflecting the over/underestimation of the chosen xc functional or HF. Indeed, the deviations can be as high as 1 eV, as observed for F_{1s} cases.

The analysis of results presented so far refers to non-relativistic calculations. We indeed considered the influence of relativistic effect on the $1s$ BEs on the studied elements. Relativistic (Rel.) and non-relativistic (Non-Rel.) calculations have been carried out for the $C \rightarrow F$ atoms, and the relativistic contributions and the comparison with the non-relativistic ones are given in Table 4. The relativistic change in the final state, including the relaxation of the electrons with a core-hole, Diff., is defined as:

$$\text{Diff} = BE(\Delta SCF, \text{Rel}) - BE(\Delta SCF, \text{Non-Rel}). \quad (3)$$

It has been reported [32] that the relativistic changes on the initial and final states are very close to each other, which means that the relativistic changes are dominant, already at the initial state. Since we want to establish the relativistic contribution to the absolute core-level BEs, the changes were studied for the $BE(\Delta SCF)$ values. The Diff. values in Table 4 show that the relativistic $1s$ core BEs are larger than the non-relativistic values, although the relativistic effects lead to a very small increase in the core-level BEs for these light atoms as expected, from 0.13 eV for B to 0.75 eV for F, thus increasing along the $C \rightarrow F$ series, as expected.

When properly accounting for the relativistic effects on $1s$ core orbitals, a clear distinction in between HF and the other xc meta-GGA and hybrid functionals pops up. HF overestimates C_{1s} and N_{1s} levels by ~ 0.65 eV, whereas it underestimates O_{1s} and F_{1s} by ~ 0.45 eV. Such trend behavior is mimicked by B3LYP, but with smaller values of around 0.2 eV, implying that this functional seems to efficiently capture the correlation effects missing in HF. When dealing with Minnesota xc hybrid functionals, M06 is consistently, for $C \rightarrow F$ elements, underestimating BEs by ~ 0.3 to 0.4 eV, while M11 consistently overestimates by ~ 0.6 to 0.8 eV. The meta-GGA M11-L xc functional only worsens the situation, with an overestimation of more than 1 eV. However, despite the overall poor description of Minnesota functionals in estimating $1s$ core-level BEs, the M06-L meta-GGA performs excellently. By including the relativistic contributions to properly

Table 2 $\Delta BE(\Delta SCF)$ results for the analyzed $1s$ core orbitals of atoms in molecules described in the overall set and highlighted in underscored bold font

Molecule	$\Delta BE(\Delta SCF)$						
	Exp.	HF	B3LYP	M06	M11	M06-L	M11-L
<u>CH</u> ₂ C(CH ₃) ₂	-1.08	-1.19	-1.07	-1.09	-0.97	-1.15	-1.00
CH ₂ <u>C</u> (CH ₃) ₂	-0.26	-0.33	-0.20	-0.15	-0.13	-0.17	0.09
CH ₂ C(<u>CH</u>) ₂	-0.22	-0.16	-0.17	-0.12	-0.14	-0.15	-0.05
<u>CH</u> ₄	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<u>CH</u> ₃ COOH	0.64	1.15	1.04	1.02	1.11	0.96	0.93
CH ₃ <u>C</u> OOH	4.47	5.24	4.56	4.64	4.82	4.23	4.48
<u>CH</u> ₃ OH	1.51	1.75	1.67	1.70	1.73	1.60	1.59
CH ₃ <u>C</u> N	1.54	2.12	2.01	2.01	2.16	1.84	1.86
<u>CH</u> ₃ CN	2.07	2.06	1.91	1.85	1.99	1.80	2.00
<u>H</u> CN	2.49	2.78	2.77	2.70	2.86	2.53	2.61
H ₂ <u>C</u> O	3.56	4.00	3.82	3.85	3.91	3.62	3.73
<u>H</u> CONH ₂	4.04	4.48	3.68	3.70	3.92	3.35	3.56
<u>C</u> O	5.30	6.16	5.75	5.65	5.88	5.13	5.27
<u>CH</u> ₂ F ₂	5.49	5.97	5.58	5.64	5.77	6.69	5.67
<u>C</u> O ₂	6.78	8.45	7.06	7.02	7.46	6.45	6.80
<u>C</u> F ₄	10.99	12.11	11.07	11.24	11.48	10.57	10.81
N(<u>CH</u>) ₃	0.35	0.43	0.40	0.49	0.45	0.41	0.53
<u>N</u> H ₃	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<u>N</u> (CH ₃) ₃	-0.75	-1.06	-0.87	-0.67	-0.76	-0.75	-0.31
CH ₃ <u>C</u> N	0.08	0.07	0.01	-0.01	0.18	-0.22	-0.10
<u>H</u> CONH ₂	0.83	0.99	1.01	1.02	1.12	0.94	0.97
<u>H</u> CN	1.22	1.29	1.34	1.28	1.46	1.14	1.21
<u>N</u> NO	3.15	4.06	3.36	3.28	3.59	2.90	3.07
<u>N</u> NO	7.03	8.80	7.36	7.52	7.91	6.96	7.30
<u>H</u> CONH ₂	-2.16	-2.43	-2.28	-2.12	-2.18	-2.19	-2.04
CH ₃ <u>C</u> OOH	-1.57	-1.91	-1.75	-1.65	-1.61	-1.75	-1.72
CH ₃ <u>C</u> OOH	0.22	0.42	0.22	0.38	0.36	0.25	0.47
CH ₃ <u>O</u> H	-0.79	-0.94	-0.86	-0.67	-0.80	-0.69	-0.51
H ₂ <u>C</u> O	-0.42	-0.83	-0.45	-0.31	-0.42	-0.27	-0.27
H ₂ <u>O</u>	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<u>C</u> O ₂	1.38	1.56	1.52	1.55	1.70	1.48	1.55
<u>N</u> NO	1.52	1.29	1.73	1.83	1.74	1.82	1.89
<u>C</u> O	2.65	2.56	2.80	2.75	2.89	2.76	2.58
CH ₃ <u>F</u>	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CH ₂ <u>F</u> ₂	0.74	1.12	0.97	0.93	1.01	0.86	0.21
<u>H</u> F	1.32	1.69	1.58	1.28	1.56	1.29	1.10
<u>C</u> HF ₃	1.71	2.17	1.88	1.79	1.98	1.65	1.62
<u>C</u> F ₄	2.65	3.17	2.75	2.64	2.90	2.43	2.42
<u>F</u> ₂	3.78	3.86	3.94	3.73	4.07	3.56	3.30
ME	-	0.27	0.10	0.11	0.22	-0.01	0.03
MAE	-	0.38	0.16	0.16	0.24	0.18	0.18

Experimental ΔBE values are taken from an arbitrary reference; CH₄, NH₃, H₂O, and CH₃F for C, N, O, and F. A summary of the statistical analysis, ME and MAE, is reported. All values are given in eV

compare with experiment, the deviation with respect to the experimental values is, in average terms, below 0.1 eV, and this is within the XPS chemical accuracy. Thus, M06-L, known to be a rather accurate xc meta-GGA functional,

even suited to simulate particularly complicated systems [27, 28], is here reinforced in the sense that is also well suited in obtaining an excellent description of $1s$ core electron energies of main-group elements.

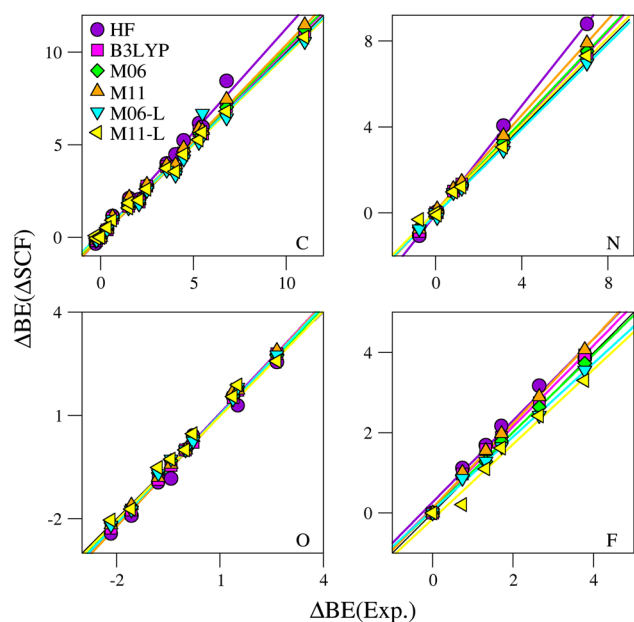


Fig. 2 Calculated, $\Delta\text{BE}(\Delta\text{SCF})$, versus experimental, $\Delta\text{BE}(\text{Exp.})$, core-level ΔBEs for C, N, O, and F elements in the molecular data set. All values are given in eV. *Black lines* represent the ideal experimental matching

In light of the above-presented discussion, the obtained results for the six explored methods, with and without relativistic corrections, are overall good when computing ΔBEs of main-group organic molecules, and predict absolute core-level BEs with a small percentage deviation. However, when relativistic effects are considered, the meta-GGA M06-L xc functional stands out in between its fellows, showing chemical accuracy in both BEs and ΔBEs , with the concomitant advantage of being computationally more affordable than other tested hybrid functionals, and so poses itself as excellent for describing at the same time the thermochemistry of organic molecules and their core state energies as well as its capability to be used in periodic DFT calculations with plane wave basis sets [29].

4 Conclusions

Here we have explored the performance of M06, M06-L, M11 and M11-L Minnesota functionals in predicting $1s$ core-level BEs of a set of 20 molecules (39 core levels explored in total) extracted from a previous study [17] containing samples of molecules containing C \rightarrow F main-group elements. Results for HF and B3LYP have been included for comparison. The obtained results using ΔSCF

Table 3 Summary of the regression adjustments of the $1s$ core-level BEs and ΔBEs for each element and the overall set for the different explored methods, including the slope and the linear equation regression coefficient, R

Method	R	Slope	Offset	Rel-Offset
C_{1s}				
BE				
HF	0.997	1.12	0.53	0.66
B3LYP	0.998	1.00	0.07	0.20
M06	0.998	1.01	-0.45	-0.32
M11	0.998	1.04	0.53	0.66
M06-L	0.992	0.97	-0.19	-0.06
M11-L	0.998	0.97	0.55	0.68
ΔBE				
HF	0.997	1.12	0.67	-
B3LYP	0.998	1.01	0.12	-
M06	0.998	1.01	0.17	-
M11	0.998	1.04	0.20	-
M06-L	0.992	0.97	0.04	-
M11-L	0.998	0.97	-0.04	-
N_{1s}				
BE				
HF	1.000	1.27	0.39	0.64
B3LYP	1.000	1.05	-0.07	0.18
M06	0.999	1.06	-0.59	-0.34
M11	1.000	1.12	0.60	0.85
M06-L	0.998	0.99	-0.21	0.04
M11-L	0.997	1.01	0.78	1.03
ΔBE				
HF	1.000	1.27	0.87	-
B3LYP	1.000	1.05	0.19	-
M06	0.999	1.06	0.24	-
M11	1.000	1.11	0.49	-
M06-L	0.998	0.99	-0.10	-
M11-L	0.997	1.01	0.10	-
O_{1s}				
BE				
HF	0.993	1.06	-0.91	-0.46
B3LYP	1.000	1.08	-0.57	-0.12
M06	0.998	1.04	-0.93	-0.48
M11	0.999	1.08	0.09	0.54
M06-L	0.998	1.05	-0.29	0.16
M11-L	0.994	1.01	0.78	1.23
ΔBE				
HF	0.993	1.06	0.02	-
B3LYP	1.000	1.08	-0.03	-
M06	0.998	1.04	-0.03	-
M11	0.999	1.08	-0.05	-
M06-L	0.998	1.06	-0.02	-
M11-L	0.994	1.01	-0.02	-

Table 3 continued

Method	R	Slope	Offset	Rel-Offset
F_{1s}				
BE				
HF	0.988	1.02	-1.19	-0.44
B3LYP	0.998	1.01	-1.01	-0.26
M06	0.998	0.97	-1.10	-0.35
M11	0.998	1.05	-0.20	0.55
M06-L	0.999	0.92	-0.64	0.11
M11-L	0.989	0.93	0.70	1.45
Δ BE				
HF	0.989	1.02	0.31	-
B3LYP	0.998	1.01	0.16	-
M06	0.998	0.97	0.02	-
M11	0.998	1.05	0.23	-
M06-L	0.999	0.92	-0.08	-
M11-L	0.989	0.93	-0.27	-

Aside, offsets for BEs are given, in eV, as well as the offsets corrected for the relativistic contributions, Rel-Offset, as corrected by the values reported in Table 3

Table 4 Relativistic contributions (Rel.) and non-relativistic (Non-Rel.) results for BE(Δ SCF) B \rightarrow F calculations

Atom	BE(Δ SCF)		
	Rel.	Non-Rel.	Diff.
C	297.08	296.95	0.13
N	412.04	411.79	0.25
O	545.85	545.40	0.45
F	698.36	697.62	0.75

The difference (Diff.) between Rel. and Non-Rel. is also given. All values are given in eV

methodology have been compared to the reported experimental references. This has been carried out in a non-relativistic fashion, yet the relativistic effects have been explicitly considered on isolated atoms and since are known to be independent of the particular chemical environment, added a posteriori on the obtained estimates.

The analysis yields that computed absolute core-level BEs are overall, and regardless of the method, close to the reported experimental values, with small percentage deviations, but sensible when considered in an absolute deviation, due to the inherent different construction of the explored functionals and methods. The BEs values have also been analyzed in terms of shifts, Δ BEs, where such building differences are cancelled, showing in overall terms a good performance; actually B3LYP and M06 hybrids, or M06-L and M11-L meta-GGAs are recommended for

Δ BEs since their deviations, of the order of 0.2–0.3 eV, are close to the XPS chemical resolution of 0.1 eV.

However, when relativistic effects are included, all methods show strong over/underestimations of the BEs, which can be as large as 1 eV. There is, however, one exception to this unexpected behavior. The M06-L meta-GGA Minnesota xc functional, which after applying the pertinent relativistic corrections, displays an overall mean deviation of the estimated BEs with respect to the experimental measurements below 0.1 eV, and this is well within the XPS chemical resolution and so, poses itself as an excellent choice when modeling core-level BEs of main-group organic molecules, plus being computationally less demanding than hybrid functionals, which in turn display a lower accuracy in BEs.

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Appendix

See Table 5.

Table 5 List of the studied molecules conforming the dataset

1. 1,1-Dimethylethane
2. Methane
3. Acetic Acid
4. Methanol
5. Acetonitrile
6. Hydrogen cyanide
7. Formaldehyde
8. Amine formaldehyde
9. Carbon monoxide
10. Difluoromethane
11. Carbon dioxide
12. Tetrafluoromethane
13. Trimethylamine
14. Ammonia
15. Nitrous oxide
16. Water
17. Fluoromethane
18. Hydrofluoric acid
19. Trifluoromethane
20. Fluorine

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