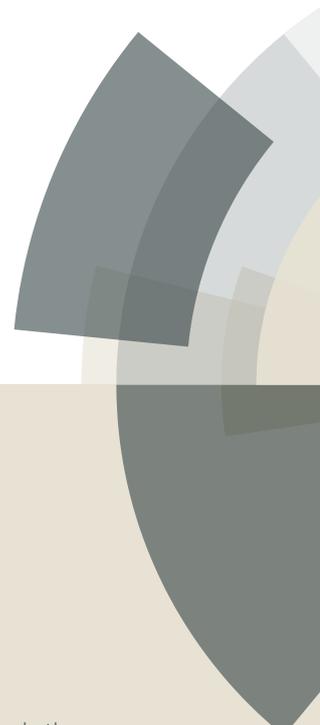


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ARTICLE

In search of the best DFT functional for dealing with organic anionic species

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Abstract: Quantum chemical computational methods are thought to have problems in dealing with unstable organic anions. This work assesses the ability of different Density Functional Theory (DFT) functionals to reproduce electron affinity and reduction potential of organic compounds. The performance of 23 DFT functionals was evaluated computing negative electron affinities (from 0 eV to -3.0 eV) and reduction potentials in acetonitrile (from 0 to -2.7 V). In general, most of the hybrid GGA functionals work fine in the prediction of electron affinities, being BPW91, B3PW91 and M06 the bests on each class of functionals (pure, hybrid and meta-GGA functionals, respectively). On the other hand, the *ab initio* post Hartree-Fock methods, MP2 and coupled-cluster (CCSD(T)), as well as the double hybrid functionals, B2PLYP, mPW2PLYP, usually fail. For compounds with *EAs* lower than -1.75 eV, a method for stabilizing the anion, based on solvation with the IEFPCM model was employed. In this case, BPW91, PBE0 and M06-HF could be the recommended option for a pure, a hybrid and a meta-GGA functional, respectively. The situation improves for the evaluation and prediction of redox potentials. In this case the performance of the DFT functionals is better, in part because the solvent assists in the stabilization of the anions. Nevertheless, there is a systematic bias in the calculations of absolute redox potentials it could be corrected by using a redox partner that helps by a cancellation of errors. In this case, the hybrid and meta-GGA functionals B3PW91, PBE0, TPSSh and M06 are also among the best for computing redox potentials with a mean absolute deviation (MAD) lower than 0.13 V.

Introduction

During the last few decades, density functional theory (DFT)¹ has become the method of choice in quantum chemical studies because of its good performance and comparatively low computational cost. Indeed, many experimental investigations in organic and inorganic chemistry routinely include such calculations, using a popular code, a standard basis, and a standard functional approximation.² It is well known that DFT has provided approximations that work quite well for some problems and fail for others. Hence, a proper recommendation should be to search for the DFT functional that works better within the problem to be studied. Besides, there is a constant search towards a universal all-purpose functional that has produced a zoo of functionals that could be

grouped in any of the rungs of the so-called Jacob's ladder of DFT functionals.³

One field in which DFT may fail is that of radical anions, which sometimes are technically unbound within standard approximations. The ability of a DFT functional for dealing with anions has been already included in the Gn sets (G1,4 G2/97,5 G3/996 and G3/057) usually employed for the evaluation and validation of DFT functionals. However, these data sets contained 63 electron affinities, and 10 proton affinities of monoatomic and diatomic species and small molecules with less than 3 heavy atoms. This situation could be overcome with the appearance of new sets such as the GMTKN248 and GMTKN30,9 however this is not the case. The use of these sets in some cases could produce a strong bias toward an accurate description of small systems relative to bigger molecules, which is not representative for many chemical applications.¹⁰

In organic chemistry, anionic species could be formed by deprotonating a neutral molecule (eq 1) or by an electron transfer to a neutral molecule (eq 2) or to a radical (eq 3). The first process is an acid-base reaction and is directly associated with the acid dissociation constant (*Ka*) or the *pKa*. The last two processes could be related with the electron affinity (*EA*, if the process occurs in gas phase) or with the reduction potential (E_{Red}^0 , in condensed phase or solution) of the species. Consequently, a good DFT functional employed for studying anionic organic species should accurately predict (or compute) at least one of these physical properties.

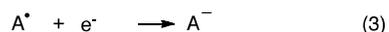
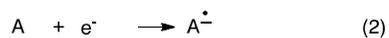
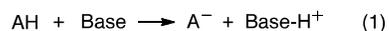
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Electronic Supplementary Information (ESI) available: Charts and tables with the structures and references of the experimental data of the studied compounds, references of the DFT and *ab initio* methods employed, tables, figures and graphics with additional information is available. See DOI: 10.1039/x0xx00000x



Several authors have assessed the abilities of DFT for predicting or estimating pKa values as summarized in reviews by Coote *et al.*^{11, 12} The methods could be differentiated by the use of continuum solvation models,^{13, 14} the inclusion of discrete solvent molecules,^{15, 16} or the use of QM/MM molecular dynamics simulations with explicit solvation,¹⁷ among others. It should be noted that chemical accuracy in pKa calculations is difficult to achieve, because an error of 1.36 kcal/mol in the free energy change for deprotonation results in an error of 1 pKa unit.¹⁸

Regarding EA, two scenarios could be found. For those compounds where the anion is more stable than the neutral molecule (positive EA) DFT methods work fine, as reviewed by Rienstra-Kiracofe *et al.*¹⁹ On the other side, many neutral molecules have negative experimental EA, meaning that the energy of the anion is above that of the neutral. The characterization of these temporary anions, unstable with respect to electron loss, represents a challenge for the experimental²⁰ and theoretical methods.²¹ Formal theoreticians claimed that standard DFT does not apply to negative species.²² However, despite that argument, from a practical point of view useful results could be obtained for many organic small molecules.^{19, 23} Even though, considerable care must be taken when conventional electronic structure codes are employed for studying such states. This question was recently revisited,²⁴ bibliographic references reviewing this controversy can be found in references²³ and²⁴.

When dealing with temporary anions, Vera *et al.*²³ distinguished two possible kind of anions: (i) valence type (V), the EA can be reproduced accurately; (ii) non-valence (N), i.e. with the unpaired electron in a diffuse orbital around the molecule. In this case, the EA is not comparable to that of the lowest valence state, generally obtained from electron transmission spectroscopy (ETS),²⁰ and what is more, it is not the expected state in organic or biological reactions in solution. Four factors increase the probability of getting an N anion:

- (i) EAs lower than -1.0 eV²³
- (ii) high dipolar moment and/or strong local dipoles that help to form a dipole bound anion^{23, 25}
- (iii) augmented basis sets²³
- (iv) exchange functionals without a component of Hartree-Fock exchange.²⁶

Latter on, two practical methods for solving the problem of the EA of N anions were published.^{27, 28, 29} One alternative to overcome this problem is the use of solvents of different polarities (ϵ) for getting the V anion and then extrapolating the energies of the "solvated" V anions to the limiting gas phase value of $\epsilon=1$. The other approach uses the TDDFT approximation for correcting the energy of the anion affording good results even for species of EAs lower than -2.5 eV up to a

limit value of -3.5 eV.²⁷ In these studies only B3LYP, PBE0 and PW91 functionals were evaluated being B3LYP the best.

When changing from gas phase (EA) to solution, the key task is the computation of the reduction potential (E_{Red}^0). Due to the importance of electron transfer reactions in biological processes, in solar energy conversion and in organic synthesis, among others, the knowledge of E_{Red}^0 is relevant in many fields of chemistry. In most cases experimental values of E_{Red}^0 could be determined,³⁰ with cyclic voltammetry or even with pulse radiolysis, with low errors of 0.01 to 0.02 V.³¹ However, for unstable or reactive species, like organic radicals, it can be very difficult to measure, and hence a good method is necessary to get an estimation or prediction of E^0 . This is the reason why much effort has been made to prove the efficiency of theoretical methods for the prediction of redox potentials of organic species.^{32, 33} Within this context we should differentiate oxidation reactions (with the participation of cations, or radical cations)^{34, 35} from reduction reactions, which could be more difficult to compute due to the participation of anionic species. A general idea is that the method works really well within compounds of a family or class (i.e. quinones,³⁶ anthraquinones,³⁷ amines,³⁸ nitrobenzene,³⁹ poli-aromatic compounds⁴⁰), that is, a correlation of the computed E_{Red}^0 with experimental values should be calculated before the prediction of the potential of new members of the family.⁴¹ This is true indeed, however a really good prediction could also be done without a special calibration, with a global correlation, showing the robustness of DFT for the prediction of E_{Red}^0 .⁴²

In the present study we addressed the overall performance of 23 different DFT functionals, from different rungs in the so called Jacobs ladder³ and the *ab initio* methods MP2 and coupled-cluster (CCSD(T)) to find the best method. In order to evaluate its scope and limitations, EA and E_{Red}^0 were computed. For calculating the EA, a wide set of 60 molecules was employed,⁴³ all of them with known experimental EAs in the range of ~0 to -3.4 eV, with the lowest anionic state experimentally found as V type. Besides, 62 compounds with different functional groups were selected for the computation of the E_{Red}^0 , in acetonitrile as solvent, ranging from -2.71 V to 0.06 V (vs. standard hydrogen electrode, SHE).

Methodology

Direct EA computation

The procedure followed has been previously described.^{23, 27, 28} The EAs were computed as the energy difference between the anionic and the neutral species. In the case of vertical EAs (VEA) the energy of the anion was calculated at the frozen geometry of the neutral, (eq. 4a); whereas for adiabatic EAs (AEA) the anion was also optimized and the zero point energy corrections were included in the calculation of the EA, (eq. 4b).

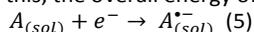
$$\text{VEA} = E_{(\text{optimized neutral})} - E_{(\text{anion on the geometry of the neutral})} \quad (4a)$$

$$\text{AEA} = E_{(\text{optimized neutral})} - E_{(\text{optimized anion})} + \Delta ZPE_{(\text{neutral-anion})} \quad (4b)$$

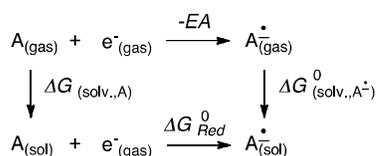
As previously stated, the EA obtained by this procedure is close to the experimental one when the anion is of V type, for those cases where the anion obtained is of N type the EA was evaluated by extrapolation.²⁸

EA obtained by extrapolation

When studying anions and radical anions we observed that due to the effect of slightly polar solvents the V, instead of the N, state of the anion becomes the ground state. This fact could be used to overcome the impossibility of calculating EAs by eq. 4a-b. According to this, the overall energy of the process



could be related to the EA through the thermodynamic cycle of scheme 1 where the reduction reactions in gas phase and in solution are presented:



scheme 1

The energy difference of the process relates the ΔG_{Red} with the EA according to eq. 6

$$\Delta E = \Delta G_{(Red)}^0 = -EA + \Delta \Delta G_{(Solv)}^0 \quad (6)$$

On these bases, ΔE is related to the solvation energy, hence varies with the solvent and could be treated as a function of the solvent polarity or its dielectric constant (ϵ). ΔE should tend to the actual value of the EA as ϵ tends to 1 (vacuum or gas phase), eq. 7:

$$EA = \lim_{\epsilon \rightarrow 1} \Delta E(\epsilon) \quad (7)$$

In order to extrapolate eq. (7), $\Delta E(\epsilon)$ is computed within a set of 10 solvents of decreasing polarity. For convenience, ΔE is plotted against $1/\epsilon$ yielding a plot that varies from 0.012 (water) to 0.44 (benzene). The EA can be readily obtained from a plot of ΔE vs. $1/\epsilon$ using eqn (8).²⁸

$$EA = \lim_{\epsilon \rightarrow 1} \Delta E_{(1/\epsilon)} \quad (8)$$

Redox potential calculations

The overall calculated reaction is presented in the thermodynamic cycle shown in scheme 1 and eq. 6. In previous works, this equation has been employed for the calculation of reduction^{36, 41, 42, 44} and oxidation potentials,⁴⁵ when replacing the EA for the ionization energy (IE). In some cases the $\Delta \Delta G_{(Solv)}^0$ was calculated over the gas phase geometries, in other cases different solvent models were employed to improve its quality and hence the ΔG_{Red}^0 . In the present work the ΔG_{Red}^0 was directly calculated from the optimized geometries in solvent by employing the IEF-PCM continuum solvation model,⁴⁶ including the thermal corrections and the changes in enthalpy and entropy.

Finally, the ΔG_{Red}^0 is related to the redox potential, E_{Red}^0 , by the Faraday's equation (9)

$$E_{Red}^0 = \frac{-\Delta G_{Red}^0}{nF} \quad (9)$$

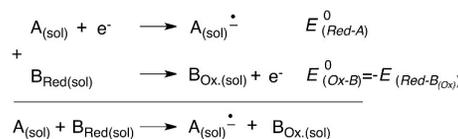
where n is the number of electrons transferred (in this case is equal to 1) and F is the Faraday constant (96485 C mol⁻¹ or 23.061 kcal mol⁻¹ V⁻¹).

It should be noted that the E_{Red}^0 represents the absolute value of half of the redox reaction, a hemi-couple, whereas the experimental values (E_{exp}^0) are relative to a reference hemi-couple where the oxidation takes place ($E_{Reference}^0$) i.e. H^+/H_2 , ferricenium/ferrrocene (II/III), Ag/Ag^+ , Hg/Hg^{+2} (Saturated Calomel Electrode, SCE); according to equation 10:

$$E_{exp}^0 = E_{Red}^0 - E_{Reference}^0 \quad (10)$$

Because of that, the difference between the computed and the experimental values corresponds to the absolute value of the oxidation potential of the reference electrode ($E_{Reference}^0$). If all the experimental values are compared to the H^+/H_2 reference the $E_{Reference}^0$ recommended is 4.44 V in water⁴⁷ and 4.60 V in acetonitrile.⁴⁸ The usual procedure is to subtract this experimental value to the computed E_{Red}^0 in order to get a computed value comparable with the E_{exp}^0 .

One alternative for the calculation of relative experimental E_{exp}^0 is to compute also the oxidation reaction in the complementary half-cell, and calculate all the redox potentials using the reactions of scheme 2. Roy *et al.* recently employed this procedure using the couple ferricenium/ferrrocene (II/III) as reference reaction.⁴⁹ Latter on, Konezny *et al.* extended this methodology to the computation of redox potentials with complexes of Ru and Ir as references.⁵⁰ This approach could be compared with the one used for the computation of $pKas$ where a reference acid is selected for the calculation *via* the proton exchange scheme.¹¹



scheme 2

The potential difference of the reaction could be expressed by eq. 11

$$\Delta E_{Total}^0 = E_{(Red-A)}^0 - E_{(Red-B_{Ox})}^0 \quad (11)$$

Finally, the experimental potential of the reaction, compared to the H^+/H_2 reference, was obtained by including the experimental potential of the reference reaction with the former electrode ($E_{exp}^0(Ox.B)$), as shown in eq. 12

$$E_{exp}^0(Red.A) = E_{(Red-A)}^0 + E_{(Ox.B)}^0 - E_{exp}^0(Ox.B) \quad (12)$$

Computational Setup

The general setup is similar to the one already described.^{27, 28} The usual procedure was, an optimization of the molecules with the corresponding DFT functional and the 6-31+G* basis set, followed by frequency calculations. Finally, the energy of the molecules was computed with the corresponding

functional and the 6-311+G(2df,p)^{51, 52} basis set as implemented in the Gaussian 09 package.⁵³ For the calculation of the anions, the HF wave function was used as initial guess in order to increase the chances of getting V states. Zero point energy corrections (ZPE) were included in the calculations of adiabatic *EAs* as indicated in eq. 4b.

The continuum solvation model⁴⁶ used was the IEF-PCM⁵⁴ as implemented in Gaussian 09, using the Pauling atomic radii, as previously employed.^{27, 28} The solvents used for scanning ϵ were: water (78.4), dimethylsulfoxide (46.7), acetone (20.7), 1,2-dichloroethane (10.4), tetrahydrofuran (7.6), acetic acid (6.25), chloroform (4.9), ether (4.24), diethylamine (3.58) and benzene (2.25). Acetonitrile was used for the calculation of E_0 . A total of 23 DFT functionals were tested. In the tables they are organized or grouped into "pure" GGA functionals (BLYP, PW91, BPW91, B97D), hybrid GGA functionals (B3LYP, B3LYP-D, CAM-B3LYP, LC-BLYP, BHandHLYP, ω -B97, ω -B97X, ω -B97XD, PBE0 and LC- ω PBE), meta-GGA (pure: M06-L, TPSS and hybrid: M06, M06-HF, M06-2X, TPSSh), the double hybrid methods (B2PLYP and mPW2PLYP) and the *ab initio* methods (HF, MP2 and CCSD(T)).^{55,56}

Results and discussion

For simplifying the analysis and the discussion of the results this section is divided in two parts, one corresponding to the computation of *EAs* and the other to the computation of Redox potentials.

Calculation of *EAs*

The set of molecules employed in the evaluation of *EAs* was the one built and used by the group in previous publications. In this case 60 molecules were chosen, all of them with negative *EAs*, from -0.06 to -3.4 eV, generally determined by ETS.²⁰ This trial set of 60 molecules was built up by including different heteroatoms in the π system, third row elements, open and closed shells species, as well as a few adiabatic *EAs* (chemical structures of all compounds, the experimental *EAs* and the corresponding references are available in Charts S1-2 and Tables S1-2 in the supplementary material, SI). Besides, this set was subdivided in two sets: one set with 37 molecules (chart S1) with theoretically determined valence states anions (V) with most of the functionals. The other set contains 23 compounds (chart S2) that afforded non valence state anions (N) with almost all the functionals. The first set was employed for calculating the *EAs* applying equations 4a and 4b. The last set, which afforded N states with all the evaluated functionals, was employed for testing if the *EAs* could be calculated by the extrapolation method, employing equation 8.²⁸ From the latter set, five limiting cases were included, compounds 56-60, whose V states could not be found by extrapolation. Since the standard ETS derived data point to V anions and, as previously demonstrated,^{23,27} only these anions can be correlated with the experimental *EAs*, Figure S-0 included in the SI. The species of both groups which afforded N anions after the corresponding procedure were not considered for the correlations and further statistical analysis for benchmarking the functionals.

The absence of systematic deviations of the calculated *EAs* was determined by plotting the difference between the experimental and the computed *EA* for each compound with all the evaluated functionals; an example of this plot is presented in figure 1, the remaining plots being included in the SI, figures S1.1 to S1.36.⁵⁷

To classify the anions, two criteria were employed. First, natural bond orbital (NBO) analysis^{58, 59} was used by checking the contribution of the natural Rydberg basis. A threshold value of 0.5 was found for the limiting cases, compounds with a contribution lower than 0.5 were considered as V anions whereas with higher values were treated as N type. Finally, the spin density was visually inspected. In the graphics of the difference between the calculated and the experimental *EA* vs. the functionals the nature of the anion is also discriminated (a round mark and a triangle were used for V and N anions, respectively). Thus, the ability of finding the right anionic state was used as first criteria to assess the quality of the functionals. It should be emphasized that the rate of V anions is dependent of the quality of the initial guess. If an N-state is employed as initial guess a N-state anion would probable be obtained. On the other hand, if a V-state anion is employed as initial guess, the chances of getting a V anion increase. This V-state guess could be obtained applying a solvent model to stabilize the anion, an smaller basis set, even with another DFT functional, *i.e.* B3LYP. In the present work the HF wave function was employed as starting guess for the DFT calculations, looking for a general and unbiased procedure (same guess for all functional under evaluation). Even though, just in only 7 cases a V state was obtained with all the functionals. The mean absolute deviation (MAD) of the calculated versus experimental *EAs* and the range of the deviations are included in graphics b and c of figure 2. Also, the correlation of the calculated versus experimental *EAs* was computed and the slope and the y-intercept are included in graphics d and e of figure 2. These data, with the correlation coefficient (R^2) and the V ratio are also included in Table S6. Among the evaluated methods, BPW91, B3LYP-D, B3PW91 and B3LYP gave MADs equals or lower than 0.1 eV (the usual value for the

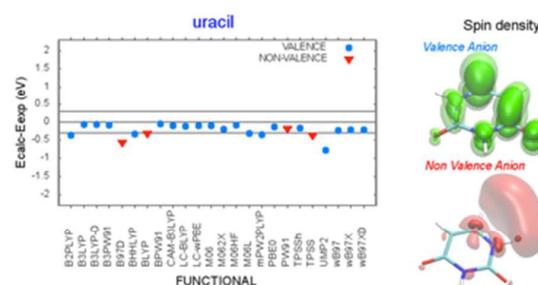


Figure 1: Example of the analysis of valence character of the calculated radical anion, and the residuals obtained in the prediction of the *EA* of uracil. V anions are represented with a round mark, while N anions with a triangle. To show the differences in the nature of the V (green) and N (red) anions the spin density are presented. For this plot isovalues of 0.0015 and 0.003 were employed. In figures S1.1 to S1.36 of the SI, are the plots for all the studied compounds.

experimental error). The following functionals: BLYP, M06, TPSS, PW91, CAM-B3LYP, PBE0, B97-D and TPSSh should be included in a second group with MADs between 0.1 and 0.15 eV. The range of the deviations could be used to evaluate the dispersion of the calculated *EAs*. Low dispersion values (0.32 to ~0.40 eV) were obtained with hybrid GGA (CAM-B3LYP, ω -

B97XD, BHandHLYP, B3PW91 and PBE0) and meta-GGA functionals (M06, M06-2X, M06L and TPSSh). Whereas higher dispersions were obtained for the double hybrid functionals (~0.45 eV) and GGA functionals (~0.49 to 0.60 eV).

On the other side, at the end of the table are listed the *ab initio* methods, with a regular performance, which could

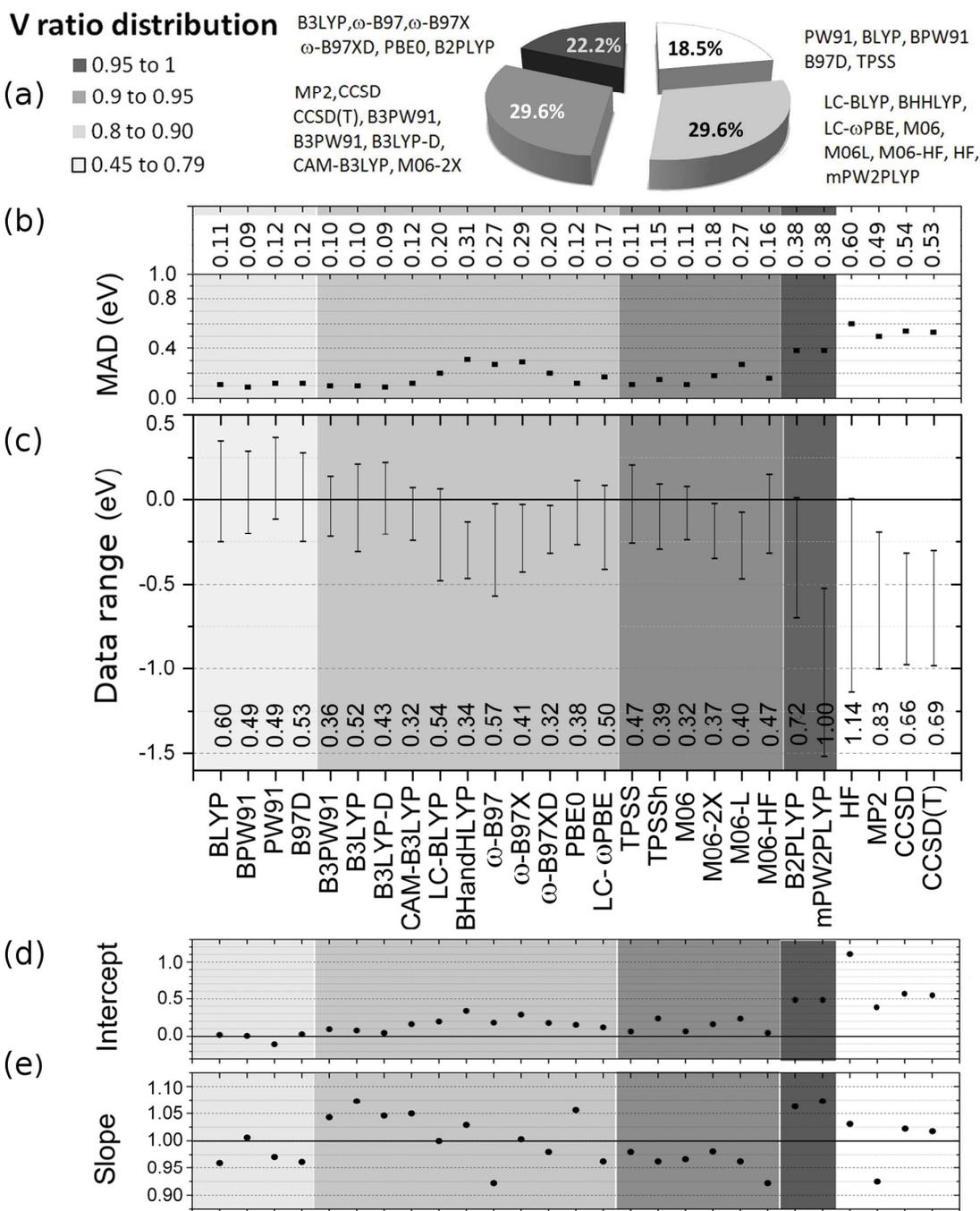


Figure 2. Results of the calculations of the *EAs* of compounds from chart S1 with different DFT functionals. a) ratio of V state anions over total number of compounds. b) MAD of the calculated vs. experimental *EA* values for V anions. c) Difference between the biggest and smallest deviation to measure the dispersion of the calculated values. d-e) Results of the plots of calculated vs. experimental *EAs*. All the extrapolations are included in the supporting information, figures S2.1 to S2.24. Graphics b-e are colored grouping the functionals, from left to right: pure GGA (light grey), hybrid GGA (grey), meta-GGA (dark grey), double hybrids (very dark grey) and *ab initio* (white).

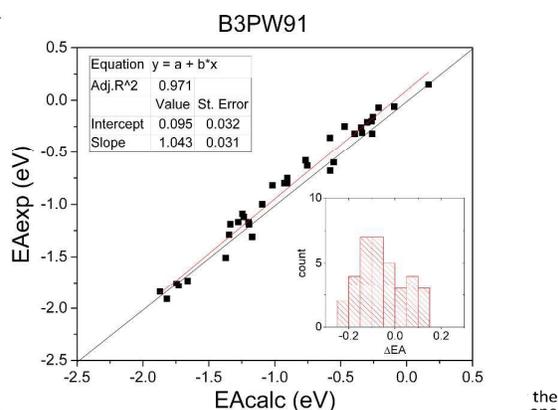


Fig. 3
B3PW91 represents the linear fit of the data. The residuals are presented in the inset.

improve increasing the size of the basis set, as presented in table S6.27. For proven approaches as CCSD(T), further improvements would be expected by enlarging the bases beyond 6-311+G(2d,p); at expenses of much higher computational costs. A similar result was obtained in previous work by Vera *et al.*²³ Double hybrid functionals (mPW2PLYP and B2PLYP) gave MADs higher than 0.35 eV and could be included in the same group of regular methods for dealing with these systems.

As seen, the MAD and deviation range do not strictly reflect the behavior of all the functionals. When considering the slope and the y-intercept, the ideal method should give a slope equal to 1 and an intercept equal to 0. In some cases with acceptable MADs between 0.1 and 0.2 eV, a deviation range below 0.4 eV and slopes between 0.95 and 1.05, high values of intercept were obtained showing a systematic deviation of the calculated values (*i.e.* CAM-B3LYP, LC-BLYP, TPSSH). In order to check this kind of errors a set of graphics with the fit of experimental vs. calculated EA, including the ideal fit and a histogram of the residuals was employed. The results for the B3PW91 functional are presented in figure 3, while a compilation with all the graphics is included in the SI, figures S2.1 to S2.24.

As can be seen in figure 1, there are some deviations in the EA predicted by the different functionals. The plots of the residuals for every compound (figures S1.1 to S1.36) and the histogram distribution of the residuals (figures S2.1 to S2.24) show that not systematic deviations were observed for most of the functionals, except for the ω -B97 variants, M06-L and M06-2X, LC-BLYP and BHandHLYP as well as the double hybrid functionals and the *ab initio* methods. For these methods a tendency to give EAs more negative than the experimental ones was observed.

Analysing the results presented in figure 2 and table S.5, it is in principle possible to conclude which functionals are better for this problem. The exact functional is the one close to give the ideal slope and y-intercept (1.00 and 0.00 respectively). Whereas the functionals with lower range of dispersion and MADs are the more precise ones. According to these two ideas, pure GGA functionals are good in terms of exactitude

but not so good in their precision as reflected in the dispersion of the residuals (besides, the V ratio is low). Among the hybrid GGA, ω -B97XD, CAM-B3LYP, B3PW91, BHandHLYP, and PBE0 are good in terms of precision, but B3PW91 is the one that combines precision and exactitude (plus a good rate of V anions). Finally, we could select M06 as the better meta-GGA functional for dealing with these anions.⁶⁰

From the collected amount of data more analysis could be carried out, such as, the effect of long range and van der Waals "D" corrections⁶¹ and of changes in the nature of the exchange functional. (*i.e.* M06, M06-L, M06-2X and M06-HF). When adding long range corrections to the pure GGA functionals (*i.e.* BLYP vs. LC-BLYP) the V ratio increased, however higher MAD were obtained with a sub-estimation of the EAs as reflected in the increase of the y-intercept. Nevertheless, when adding the dispersion corrections (*i.e.* B3LYP vs. B3LYP-D, or ω -B97 vs. ω -B97XD) there was an improve in the performance of the functionals. Finally, as previously stated by Jensen,²⁶ an increase in the HF contribution to the exchange functional (*i.e.* BLYP, B3LYP and BHandHLYP, or PW91, BPW91 and B3PW91) help to give V anions.

For the compounds included in Chart S2 and Table S2, it was not possible to find the V anion following the straightforward methodology. These are the most difficult cases, frequently found when the EAs are lower than -1.5 eV. In order to obtain the EAs, the extrapolation method was employed by stabilizing the anions with the field of a polarizable continuum solvent model.^{28, 62} The ability of stabilizing the V anions with solvent models for obtaining EAs of the valence states was also evaluated for each functional, the results are summarized in figure 4 (and included in Table S7). It should be noted that for some limiting cases, 2-butyne (-3.43 eV), tetrafluoroethylene (-3.00 eV), acetonitrile (-2.82 eV), ethylisocyanate (-2.63 eV) and dimethylformamide (-2.40 eV), it was not possible to obtain V anions upon solvent stabilization with most of the functionals, lowering the V ratio to a range of 0.5 to 0.72. Since the EA of these compounds are more difficult to calculate, bigger MADs are expected and the correlation with the experimental values are not as good as with the previous group of compounds.

The EAs of compounds of chart S2 were obtained as the intercept ($\epsilon=1$) of the plot of equation 8. The intercept could be calculated after a linear, or a quadratic fit as detailed in Table 2. In general, better values were found after a quadratic fit. A plot with an example of the fitting curves and tables for each DFT functional are included in the SI, Figure S3 and Tables S8.1 to S8.21.⁶³

The lowest EA, which afforded a V state, was included in figure 4 as a limiting value of the method, graphic b. For most of the functionals a limit of -2.4 eV was found, but some of them reached more negative values (B3PW91, BPW91, PBE0, LC- ω PBE and M06-HF), at expense of higher deviations (\sim 0.2 to 0.3 eV) in the calculated EA. For these limiting cases (compounds with EAs lower than -1.5 eV, or that afforded N anions) BPW91 could be recommended as the best pure GGA functional together with PBE0 (the best hybrid GGA functional)

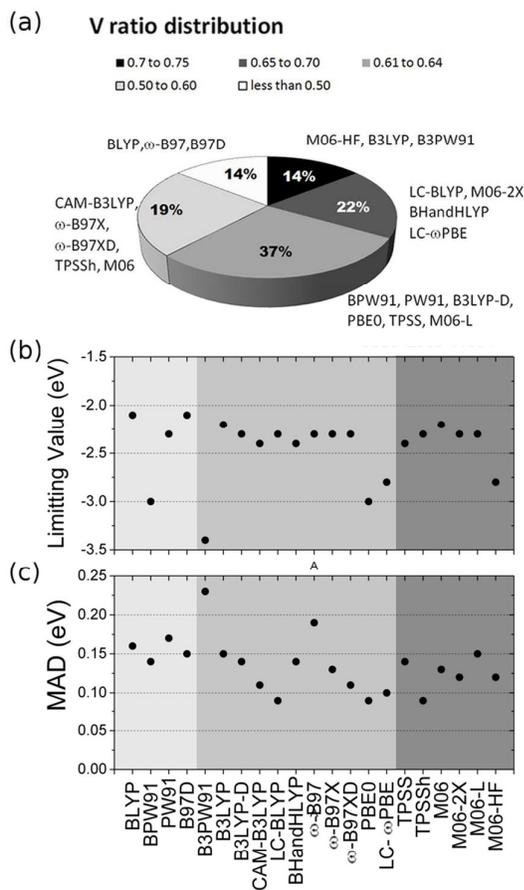


Figure 4. Results of the calculations of the EAs of compounds from chart S2 with different DFT functionals.

and M06-HF as the best meta-GGA. Once again, the application of long range corrections (LC)⁶⁴ could help to improve the V ratio, as well as the inclusion of a HF contribution in the exchange functional (i.e. BLYP, B3LYP and BHandHLYP).

Calculation of reduction potentials

In the calculation of the redox potential, care should be taken in the election of the experimental data for the benchmark, because there are different experimental variables that should be controlled such as the solvent, the reference electrode (i.e. H^+/H_2 , ferricenium/ferrocene (II/III), Hg/Hg²⁺, Ag/Ag⁺), the ionic strength, supporting electrolyte, among others.³¹

The selected redox potentials were determined in acetonitrile, one of the most employed organic solvents for these measurements, with either SCE, or NHE as reference electrodes. The data set includes 62 molecules with different functional groups covering a wide range of values (from 0.06 V to -2.71 V). The set includes neutral molecules and radicals, which afforded radical anions and anions after receiving the extra electron, respectively. All the molecules are included in charts S.3ab and Table S.3 with the experimental values and

the respective references.⁶⁵ The performance of all the DFT functionals is presented in figure 5.

The correlation between the computed absolute E_{Red}^0 (Eq. 9) vs. the experimental E_{exp}^0 was employed for an evaluation of the methods. The parameters used for the analysis were the slope, the y-intercept and the correlation coefficient (R^2). The ideal method should give a linear plot with a slope of 1.00 and an y-intercept equal to the oxidation potential of the reference electrode (-4.48 V).⁴⁸

In general, good correlations between experimental and computed values were achieved with most of the functionals, to allow useful linear or statistical relationships. As shown in Table 3, for almost all the methods the slope is over 0.93 indicating a good correlation with the experimental results. In the case of the functionals M06HF, BHandHLYP, LC-BLYP and LC-ωPBE important deviations were found as reflected in the values of the slope, the R^2 coefficient and dispersion. The y-intercept ranges from -3.82 to -4.44 V, being PW91, BPW91 and M06-L the functionals that gave the better results with a slope closed to the ideal one (1.017, 1.019 and 1.012), R^2 close to 1 (0.966, 0.967 and 0.968) and a low dispersion range (0.56, 0.55 and 0.62). A similar deviation in the y-intercept was found in a recent work employing B3LYP and M06-2X for the calculation of oxidation and reduction potentials.⁶⁶

To search for an explanation of the differences obtained in the y-intercept (due to a systematic bias in the E_{Red}^0) 10 molecules were selected to evaluate the effect of the different components in the calculation of $E_{Red}^0(EA, \Delta\Delta G_{(solv. A^- - A)})$ (see scheme 1) and the rmsd between the geometries).⁶⁷ It was found that there are differences in the EAs and in the solvation energies, especially for the anions. Those differences are the origin of the variations in the obtained E_{Red}^0 . As a tendency, E_{Red}^0 deviates in the same manner as $-EA$ according to eq. 6. However, solvation energies tend to compensate this deviation and make the differences for the E_{Red}^0 obtained with the different DFT functionals smaller. Those differences are represented in Figure S5 and tables S10.1 to S10.3 of the SI.

The problem of the solvation energies of charged species for the calculation of redox potentials was previously studied and different solvent methods were evaluated.^{35, 68} Implicit solvent models have been observed to exhibit systematic errors for redox potentials that could be cancelled out by computing the redox potential of the oxidation complementary reaction employed as an internal reference.^{49, 50} This procedure was successfully employed for the calculation of the E_{Red}^0 of metal organic complexes employing complexes of Fe, Ru and Ir as internal references. In our case, we selected the oxidation of naphthyl radical anion to naphthalene ($E_{ox}^0 = 2.42$ V vs. NHE in acetonitrile)⁶⁹ used as standard.

By using the procedure outlined in scheme 2 and equation 12 the E_{expRed}^0 were computed and compared with experimental values.⁷⁰ This correlation should ideally give a slope equal to 1, and a y-intercept equal to zero. As presented in Table 3, pure GGA functionals gave good results, being BLYP the best one. The results with these functionals could be

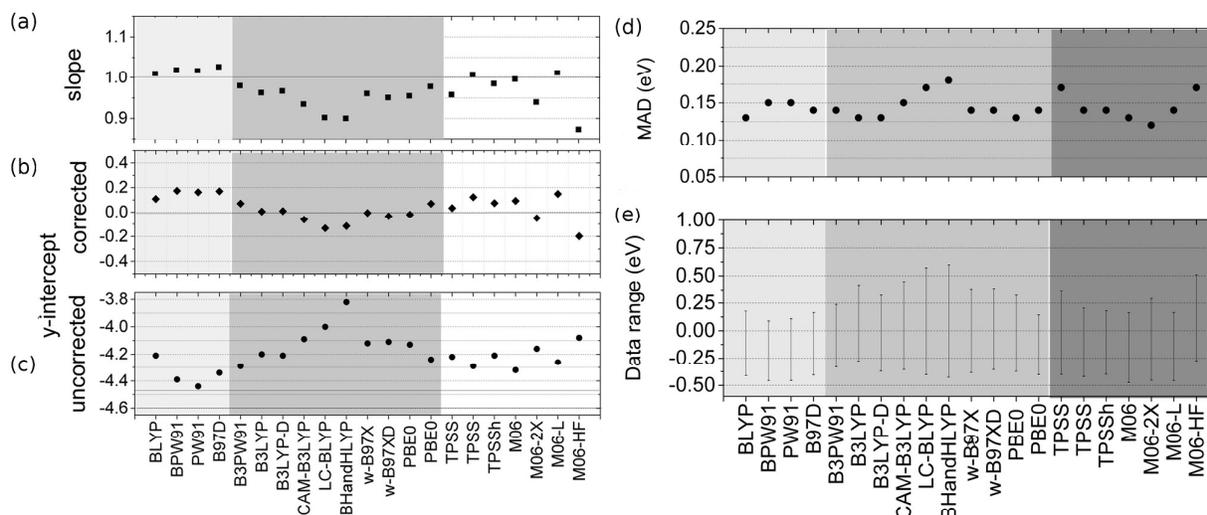


Figure 5. Results of the calculations of the E_{Red}^0 and E_{expRed}^0 potentials of compounds from chart S3ab with different DFT functionals. a-c) Results of the plot of calculated E_{Red}^0 vs. experimental E_{Red}^0 (Eqs. 9 and 12). All the extrapolations are included in the supporting information, figures S4.1 to S4.21 d) MAD of the calculated E_{Red}^0 (by using eq. 12). e) Difference between the biggest and smallest deviation of the calculated E_{expRed}^0 to measure the dispersion of the calculated values.

improved by changing the internal reference and hence the y -intercept. For the group of hybrid GGA functionals B3LYP and B3LYP-D are the most exact ones, however they show high dispersion values. Because of that, B3PW91 and PBE0 could be the most balanced functionals good in precision and exactitude. Finally, even though the y -intercept obtained with M06-2X is close to ideal, TPSSh and M06 are the better ones from the group of meta-GGA functionals. In this case the inclusion of LC corrections, and the increase in the HF contribution to exchange functional did not improve the results.

The inclusion of a reference reaction could be compared with the pK_a calculation via the proton exchange scheme by using a reference acid.¹¹ The results could improve by selecting the best solvation methods for the calculation of both $\Delta G_{(solv)}$ together with the best method for computing EA . However the idea is to evaluate a simple method that allows a direct calculation of the redox potential as proposed by Ho without a complex thermodynamic cycle, but with faster methods.¹³ Another factor that could help to improve the results is the selection of a different reference reaction, future investigations into an evaluation of different redox partners are in progress.

Conclusions

The present work provides a baseline assessment of different DFT methods for the treatment of anions by the prediction of electron affinities and reduction potentials for neutral compounds. The ideal scenario should give a podium with some functionals that outperform the others. However, as usually stated by the developers of DFT functionals, there is a suitable DFT functional for each problem instead of a universal functional that could solve almost all the situations

within different conditions, as is claimed by some people waiting the holy or magical functional.

For studying compounds with negative electron affinities higher than -1.75 eV, hybrid GGA functionals gave better results than pure GGA (BPW91 been the best pure GGA) because the higher chances of getting the right anion (V state) and the lower dispersion of the calculated values. From the hybrid GGA functionals we should emphasize the performance of B3PW91 with good exactitude and precision. B3LYP-D, and B3LYP could be mentioned as exact but not so precise as reflected in the dispersion of the results. M06 gave the best results among the meta-GGA functionals. The other functionals gave good correlations when the computed values are compared to the experimental ones with some systematic deviations that vary from 0.1 to 0.35 eV. On the other hand, double hybrid functionals (B2PLYP and mPW2PLYP) and *ab initio* methods yield a regular performance with MAD of 0.38 and 0.49-0.60 eV respectively.

For limiting cases, compounds with EAs lower than -1.75 eV there are more chances of getting a good estimated value with hybrid GGA functionals, being PBE0 the best functional of this group. BPW91 could be recommended as the best pure GGA functional and M06-HF as the best meta-GGA.

The calculations of redox potentials are dependent on the quality of the solvation energies of the charged species. This was evidenced in the biased values of the y -intercept of the correlation of calculated absolute E_{Red}^0 vs. experimental E_{Red}^0 . The obtained y -intercept varied from -3.77 to -4.41 V instead of -4.60 V, which is the experimental value (eq. 10). However, there is a significant improvement in the values of the redox potentials obtained after the use of a proper redox partner. The best results were obtained with hybrid GGA functionals, especially B3PW91 and PBE0. From the meta-GGA functionals TPSSh and M06 are the better ones. Pure GGA functionals gave

good results, with low dispersion of the calculated values, but high MAD, that could improve by choosing a proper reference.

Finally, after the thorough study of various density functionals carried out and as a concluding remark we could recommend B3PW91 and M06 as the best functionals for studying anions. The popular functionals B3LYP and PBE0 presented a correct behaviour and care should be taken when using double hybrid functionals and *ab initio* methods.

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- 60 Double hybrid functionals and ab-initio methods are neither precise nor exact.
- 61 Only the methods available within the B.01 g09 were used
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