Non-empirical (Double-hybrid) Density Functionals Applied to Atomic Excitation Energies: A Systematic Basis Set Investigation

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1

Abstract

We investigate here the lowest-energy (spin-conserving) excitation energies for the set of He-Ne atoms, with the family of non-empirical PBE, PBE0, PBE0-1/3, PBE0-DH, PBE-CIDH, PBE-QIDH, and PBE0-2 functionals, after employing a wide variety of basis sets systematically approaching the basis set limit: def2-nVP(D), cc-pVnZ, aug-cc-pVnZ, and d-aug-cc-pVnZ. We find that an accuracy (i.e. Mean Unsigned Error) of 0.3-0.4 eV for TD-DFT atomic excitation energies can be robustly achieved with modern double-hybrid methods, which are also stable with respect to the addition of a double set of diffuse functions, contrarily to hybrid versions, in agreement with recent findings employing sophisticated multi-configurational DFT methods.

Key words: double-hybrid density functionals, atomic excitation energies, diffuse basis functions.

1 Introduction

Excited-state studies continue to be a topic of the most interest,[1–3] not only because the underlying theory intrinsically presents challenges for its implementation in common codes, but also due to the interplay and large number of factors affecting the final results in molecular and real systems. Whereas ground-state properties still receive much more attention in the ongoing development of Density-Functional Theory (DFT) (e.g. for built-in datasets and the associated benchmarking of density functional approximations[4,5]) the applications to atoms are recently emerging as an alternative for the benchmarking of DFT for excited-states too.[6–8] This is facilitated by the reasonable computational cost of atomic calculations compared to more complex systems, together with the lack of geometry-induced and environmental issues often difficulting the adequate comparison between various theoretical methods.

We thus apply here a set of recently developed minimally empirical models, with the Time-Dependent Density-Functional Theory (TD-DFT) formalism, to the lowest-energy and spin-conserving ($\Delta S = 0$) excited-state of atoms from He to Ne. This study aims also at complementing historical studies employing more sophisticated methods,[9–13] as well as shedding light about the performance of some last-generation DFT methods (i.e. double-hybrid functionals) from the fifth rung of the Jacob's ladder. However, dealing with atomic excitation energies unfortunately brings non-negligible (and severe) basis set issues, due to the presence of valence and Rydberg states, and the challenge they present for an accurate excited-state description in all cases. For instance, it has been recently shown[8] how adding diffuse basis functions to state-of-the-art hybrid functionals dramatically deteriorates the

results for standard TD-DFT calculations, with unreasonable errors reaching up to 1.5-2.5 eV with respect to experimental values[14] for first- and second-row atoms. Note that the recently developed Multiconfigurational Pair-Density Functional Theory[15] (MC-PDFT) was instead not affected of such basis set dependence, which clearly shows some shortcoming of standard excited-state applications for atoms with basis sets of moderate or even large size, contrarily to what is often observed in molecular applications.[16]

These results prompted us to perform here a more systematic TD-DFT investigation, taking into account that both parameterized and non-empirical functionals exist in the literature for each step of the Jacob's ladder, and that the performance and/or basis set dependence for atoms of the latter has not been yet investigated in much detail. Note also that we would like to primarily emphasize the role played by a set of modern double-hybrid density functionals, since their pioneering applications to excited-states of representative sets of medium-size organic chromophores already showed a more accurate qualitative (but even quantitative) behavior[17–21] with respect to hybrid (and universally applied) functionals. These findings were later generalized for a much larger set of systems in a recent publication,[22] and exploited for the development of low-cost datasets for excited-state benchmarking, showing that further studies are still needed to establish their accuracy and robustness. Therefore, the applications of these models to excited-state of atoms, with large basis sets including one and two sets of additional diffuse functions in some cases, would help to bracket their accuracy and further promote their use and applicability among the excited-state community.

4

2 Theoretical details

We present in more detail next the set of non-empirical density functionals[23,24] employed in this study. The hierarchical approximation to the construction of modern density functional starts with the typical exchange, $E_x[\rho]$, and correlation, $E_c[\rho]$, expressions, and can add tailored portions of orbital-dependent EXact-like eXchange (EXX), $E_x^{\mathrm{EXX}}[\phi]$, and second-order Perturbation Theory (PT2), $E_c^{\mathrm{PT2}}[\phi, \phi']$, to cover semi-local, global-hybrid (GH) or double-hybrid (DH) forms in a systematic fashion.[25] The final expression thus depends on the corresponding weights given to those explicit orbital-dependent terms, λ_x and λ_c, respectively, and can be casted as:

$$E_{xc} = \lambda_x E_x^{\mathrm{EXX}}[\phi] + (1 - \lambda_x)E_x[\rho] + \lambda_c E_c^{\mathrm{PT2}}[\phi, \phi'] + (1 - \lambda_c)E_c[\rho]. \quad (1)$$

Table 1 summarizes the functionals selected, from the semi-local PBE model[26] through a pair of highly representative hybrid (PBE0[27] and PBE0-1/3[28]) models widely employed for TD-DFT applications, while assessing the performance of the few existing non-empirical DH functionals such as PBE0-DH,[29] PBE-CIDH,[30] PBE-QIDH,[31] and PBE0-2.[32] Note also that: (i) the values of λ_x and λ_c of Table 1 were obtained by the developers after imposing theoretical constraints, without any further parameterization against training datasets, and are thus dubbed "non-empirical" models consequently; (ii) the functionals are presented according to their increasing λ_x and λ_c values; and (iii) each ladder (i.e. semi-local, hybrid, and double-hybrid) of methods will be also compared (*vide infra*) with representative and accurate parameterized expressions based on the BLYP functional[33,34] for the sake of completeness.

As regards the basis sets used, we choose the def2-nVP[35] (n = S, TZ, QZ) and cc-pVnZ[36] (n = D, T, Q, 5, 6) families, which will be further

augmented by a standard set of diffuse functions, i.e. the def2-nVPD[37] and the aug-cc-pVnZ[38] families respectively, or by an additional one in the case of the d-aug-cc-pVnZ casei.[39] These basis sets are widely employed for TD-DFT applications and will also allow us to compare with previous results in the literature for PBE and PBE0. More specific basis sets, e.g. (aug-)pc-n[40,41] or (aug-)cc-pwCVnZ,[42] were not considered since previous atomic applications with hybrid or range-separated functionals did not show great differences with respect to Dunning- or Ahlrichs-type basis sets.[43] Note that in the case of DH models[44] the atomic excitation energies (Ω) presented are obtained in a two-step fashion,

$$\Omega^{\mathrm{DH}} = \Omega^{\mathrm{GH}} + \lambda_c \Delta^{(\mathrm{D})}, \tag{2}$$

where the perturbative-like correction[45,46] $\Delta^{(\mathrm{D})}$ is weighted by the λ_c value, and then added to the initial excitation energies (Ω^{GH}) obtained for the underlying global-hybrid; i.e. if one sets $\lambda_c = 0$ in Eq. (1).

The atomic states and orbital transitions studied are the following:

- He (^{1}S $-$ ^{1}S): 1s^2–1s2s
- Li (^{2}S $-$ ^{2}P): 2s–2p
- Be (^{1}S $-$ ^{1}P): 2s^2–2s2p

- B (^{2}P $-$ ^{2}S): 2p–3s
- C (^{3}P $-$ ^{3}P): 2p^2–2p3s
- N (^{4}S $-$ ^{4}P): 2p^3–2p^{2}3s

- O (^{3}P $-$ ^{3}S): 2p^4–2p^{3}3s
- F (^{2}P $-$ ^{2}P): 2p^5–2p^{4}3s
- Ne (^{1}S $-$ ^{1}P): 2p^6–2p^{5}3s

Some technical details are: (i) All the calculations were done using the ORCA 4.0.1.2 quantum-chemical package[47] with experimental atomic energies taken as reference;[14] (ii) for atoms with a degenerate ground-state (e.g. B) the excitation considered does not belong to that sublevel (e.g. 2p–2p); (iii) we always used an unrestricted solution for open-shell atoms and choose the lowest energy solution keeping the orbital nature of the desired excited-state; and (iv) we discard those excitations with a pronounced deviation

of the expected $\langle \hat{S}^2 \rangle$ value for the excited-state, as determined with hybrid methods using the Gaussian 09 package[48] as a sanity check.

As metrics to quantify the performance of all methods, Mean Signed Error (MSE), Mean Unsigned Error (MUE), and Mean Absolute Percentage Error (MAPE) are used hereafter to quantify the deviations between computational (a_i) and reference or forecast (f_i) results:

$$\text{MSE} \;=\; \frac{1}{N} \sum_i^N (a_i - f_i) \,,$$

$$\text{MUE} \;=\; \frac{1}{N} \sum_i^N |a_i - f_i| \,,$$

$$\text{MAPE} \;=\; \frac{100}{N} \sum_i^N \left| \frac{a_i - f_i}{a_i} \right| \,.$$

3   Results and discussion

3.1   The def2-nVP(D) family of basis sets

We first analyze the performance of the def2-nVP family of basis sets, widely used for TD-DFT applications in molecular systems, for all the considered functionals. As can be seen from Table 2, very large and inconvenient MUE values are obtained for all the functionals, although the errors are roughly reduced an order of magnitude upon increasing the basis set size going from the cost-effective def2-SVP to the def2-QZVP one. This situation drastically changes when adding a set of diffuse functions (D) to any of the def2-SVP, def2-TZVP, and def2-QZVP basis sets (see also Table 2) to become def2-SVPD, def2-TZVPD, and def2-QZVPD, respectively. Looking more specifically at the results obtained at the highest def2-QZVPD level,

relatively low MUE values between 0.5-1.0 eV are obtained with the set of PBE-based functionals, with the hybrid functionals PBE0 and PBE0-1/3 slightly outperforming the rest of double-hybrid methods, which prompts for the use of still larger basis sets, also including more diffuse functions, to investigate if this trend will remain upon increasing the basis set size.

3.2 The (aug-)cc-pVnZ family of basis sets

The use now of the cc-pVnZ family (Table 3) does not change too much the situation with respect to the def2-nVP former results, with all the functionals selected still affected by large errors. Once more, these errors are roughly reduced an order of magnitude upon increasing the basis set size going from the modest cc-pVDZ to the cc-pV5Z one. Note also that the cc-pV6Z basis set is not available for Li and Be, and thus we prefer in the following to exclude it from any quantitative discussion. Remarkably, augmenting the cc-pVnZ basis sets with one set of diffuse functions, i.e. the aug-cc-pVnZ family, brings the results again much closer to the experimental ones (Table 4). Looking carefully to the results obtained with the very large aug-cc-pV5Z basis set (the aug-cc-pV6Z is neither available for Li and Be) the MUE values are comprised between 0.4-1.1 eV for the PBE-based family of expressions. Interestingly, there is now a qualitative improvement upon going through the hierarchy of density functionals: the best DH methods (PBE0-DH and PBE-CIDH give very close values) behave better than the hybrid methods (PBE0 and PBE0-1/3) and these better than the semi-local PBE expression. For comparison purposes with previous works on molecules,[49] we also run calculations with the modest but cost-effective 6-31+G(d,p) basis set, leading to an almost constant (and large) MUE of 4.0-4.2 eV for all the functionals considered in this work, thus pointing out

8

the role of core functions in atoms.

3.3 The d-aug-cc-pVnZ extension

We finally explore the effect of adding an additional set of diffuse functions to the aug-cc-pVnZ basis sets, except for the Li and Be atoms due to its unavailability, which helps to better reconcile theory and experiment (see Table 5) allowing to interpret the results according to the hierarchy of functionals, i.e. the Jacob's ladder is now more consistently preserved. Note first that semi-local and hybrid methods have a not stable behavior upon adding this second set of diffuse functions, which was also observed before in Ref. 8, since the MUE values are now considerably higher than those obtained with the simpler aug-cc-pVnZ family. However, the results for double-hybrid methods do not deteriorate upon the addition of this second set of diffuse functions, and show a more robust accuracy: we found MUE values between 0.3-0.6 eV for all the functionals considered together with any member of the d-aug-cc-pVnZ (n =D–5) basis sets. Particularly remarkable is the performance of the PBE-QIDH model with these d-aug-cc-pVnZ basis sets, with MUE values as low as 0.3-0.4 eV in all cases. Figure 1 shows how the MUE evolves along the sequence of employed functionals, ordered according to the increasing value of λ_x, for both aug-cc-pV5Z and d-aug-cc-pV5Z basis sets. Note that for the proper comparison of values, the Li and Be atoms are excluded from the former since the d-aug-cc-pV5Z is not available for these atoms.

3.4 Dependence of the results on the λ_x and λ_c values

Upon inspecting closely the individual values for the atomic excitation energies, we observed an increase of values upon increasing the λ_x weight, see Eq. (1). This can be clearly seen in Figure 2, which presents the MSE along the sequence of employed functionals, and with high quality basis sets without excluding (cc-pV5Z and def2-QZVP) and including (def2-QZVPD, aug-cc-pV5Z, and d-aug-cc-pV5Z) diffuse basis functions. The key role played by diffuse functions is easily seen. Improving the basis set always yields to lower excitation energies on average, irrespectively of the funcional used. This leads to their severe underestimation by the semi-local PBE functional, which is partly remedied using hybrid expressions (i.e. PBE0 and PBE0-1/3). Double-hybrid methods also follow that trend, with a delicate compromise between the basis sets size and the composition (i.e. λ_x and λ_c values) of the functional. Concerning the dependence of the results only with respect to λ_c values for double-hybrid methods, although its specific impact is state- and basis-dependent, some trends also emerge. Therefore, looking at the variation of the $\lambda_c \Delta^{(\mathrm{D})}$ energy correction, we can state that: (i) we always observe a larger impact on atomic excitation energies following the order PBE0-2 > PBE-QIDH > PBE-CIDH > PBE0-DH, that is, upon increase of λ_c values (see Table 1); and (ii) for the (d-)aug-cc-pV5Z basis set taken as example, that impact oscillates between the lowest for the B atom (–0.02 to –0.06 eV for the sequence PBE0-2, PBE-QIDH, PBE-CIDH, and PBE0-DH) to the highest for the Ne atom (–0.49 to –1.43 eV for the sequence PBE0-2, PBE-QIDH, PBE-CIDH, and PBE0-DH) as it was also expected according to the own magnitude of the atomic excitation energies inspected.

10

3.5 Comparison with BLYP-based models

We compare next (see Table 6) the results between the PBE- and BLYP-based families of density functionals for each comparable category (i.e. semi-local, hybrid, and double-hybrid methods) to disclose if there are any tangible difference between parameterized (i.e. BLYP-based) and non-empirical (i.e. PBE-based) models. We choose for this purpose the highly representative BLYP ($\lambda_x = \lambda_c = 0$), B3LYP ($\lambda_x = 0.2, \lambda_c = 0$), B2-PLYP ($\lambda_x = 0.53, \lambda_c = 0.27$), and B2GP-PLYP ($\lambda_x = 0.55, \lambda_c = 0.36$) functionals, and fixed the aug-cc-pV5Z for the proper comparison between both families of methods. Note that B2GP-PLYP has emerged in previous studies[20] as one of the most accurate DH model for TD-DFT, reaching an accuracy close to 0.2 eV for singlet-singlet excitation energies of large organic molecular systems. Interestingly, the MUE (eV) for these parameterized functionals is 1.20, 0.67, 0.34, and 0.37, respectively, with the corresponding MAPE (%) being 13.5, 7.4, 3.5, and 2.9, clearly showing the gain in accuracy with the increasing level of complexity of the functional form (i.e. from semi-local to hybrid to double-hybrid methods). Compared with the corresponding non-empirical expression, we note that: (i) slightly lower MUE and MAPE values for PBE (1.11 eV / 12.3%) and PBE0 (0.52 eV / 5.5%) are obtained with respect to BLYP and B3LYP, respectively; (ii) similar MUE and MAPE values for PBE0-DH (0.39 eV / 3.1%) and PBE-CIDH (0.37 eV / 2.8%) are obtained with respect to B2-PLYP and B2GP-PLYP; and (iii) slightly higher but still competitive MUE and MAPE values are obtained in the case of PBE-QIDH (0.61 eV / 4.8%) and PBE0-2 (0.82 eV / 8.0%) double-hybrid models.

3.6 Comparison with ab initio and MC-PDFT results

It is also interesting to compare these TD-DFT results with the available CASSCF and CASPT2 calculations using the aug-cc-pVQZ basis set (values taken directly from the literature[8]). These costly multiconfigurational methods gave MUE (MAPE) values of 0.55 and 0.31 eV (6.0 and 2.4%) respectively. Whereas the CASSCF errors compare favourably with the best hybrid method from the BLYP- or the PBE-based family (see Table 4 again), reaching the accuracy of CASPT2 would possibly need the use of double-hybrid methods. Actually, expanding the set of systems tested including first- and second-row atoms, literature results showed a MUE between 0.4-0.6 eV (0.2-0.4 eV) for CASSCF (CASPT2) with the sequence of aug-cc-pVTZ, aug-cc-pVQZ, and aug-cc-pV5Z basis sets.[8] The double-hybrid functionals seem also competitive with the MC-PDFT method (with the translated tPBE functional incorporating a dependence on the density and the on-top pair density[50]) also tested for challenging optical excitations in molecules with great success.[51] For the set of He-Ne atoms, discarding Li and Be, MC-PDFT gives a MUE of 0.35 eV (0.41 eV) with the aug-cc-pVQZ (d-aug-cc-pVQZ) basis set, close to the values found here (see Tables 4 and 5).

4 Conclusions

We have assessed in this work a set of non-empirical hybrid and double-hybrid functionals, the latter increasingly applied within the TD-DFT framework, to spin-conserving atomic excitation energies. Generally speaking, reasonable good results are obtained with those models with large basis sets including diffuse functions, with the same or slightly higher quality than

other parameterized functionals also tested. Interestingly, the double-hybrid functionals behave consistenly better and sufficiently accurate when the basis set is further expanded with additional diffuse functions, contrarily to the hybrid versions, which could be of interest to calculate Rydberg states on molecular systems too.

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Supplementary Material

The Supplementary Material contains in this order: (i) Standard deviations of the unsigned errors from their mean; (ii) Individual results for atoms with the def2-nVP(D) family of basis sets; (iii) Individual results for atoms with the cc-pVnZ family of basis sets; (iv) Individual results for atoms with the aug-cc-pVnZ family of basis sets; (v) Individual results for atoms with the d-aug-cc-pVnZ family of basis sets; (vi) Individual results for atoms with the BLYP-based functionals.

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Table 1: Summary of the λ_x and λ_c values entering into the PBE-based family of non-empirical functionals considered.

Functional	λ_x	λ_c
PBE	0	0
PBE0	$\frac{1}{4}$	0
PBE0-1/3	$\frac{1}{3}$	0
PBE0-DH	$\frac{1}{2}$	$\frac{1}{8}$
PBE-CIDH	$6^{-\frac{1}{3}}$	$\frac{1}{3}$
PBE-QIDH	$3^{-\frac{1}{3}}$	$\frac{1}{3}$
PBE0-2	$\left(\frac{1}{2}\right)^{\frac{1}{3}}$	$\frac{1}{2}$

Table 2: MUE (in eV) for atomic excitation energies with the family of def2-nVP(D) basis sets.

	def2-SVP	def2-SVPD	def2-TZVP	def2-TZVPD	def2-QZVP	def2-QZVPD
PBE	14.33	1.08	6.25	1.15	3.26	0.96
PBE0	14.08	1.12	6.11	0.72	3.33	0.46
PBE0-1/3	14.14	1.29	6.21	0.78	3.50	0.55
PBE0-DH	13.97	1.46	6.15	0.91	3.61	0.61
PBE-CIDH	14.00	1.51	6.18	0.87	3.67	0.76
PBE-QIDH	14.08	1.64	6.24	1.15	3.78	0.98
PBE0-2	14.14	1.65	6.26	1.20	3.88	1.05

Table 3: MUE (in eV) for atomic excitation energies with the family of cc-pVnZ basis sets.

	cc-pVDZ	cc-pVTZ	cc-pVQZ	cc-pV5Z	cc-pV6Z[a]
PBE	14.47	8.15	5.30	2.91	1.92
PBE0	15.06	8.41	5.63	3.38	2.65
PBE0-1/3	15.19	8.50	5.74	3.55	2.46
PBE0-DH	15.31	8.62	5.84	3.74	3.20
PBE-CIDH	15.36	8.66	5.89	3.80	3.29
PBE-QIDH	15.41	8.70	5.97	3.91	3.45
PBE0-2	15.53	8.82	6.03	3.98	3.57

[a] Not available for Li and Be atoms.

Table 4: MUE (in eV) for atomic excitation energies with the family of aug-cc-pVnZ basis sets.

	aug-cc-pVDZ	aug-cc-pVTZ	aug-cc-pVQZ	aug-cc-pV5Z	aug-cc-pV6Z[a]
PBE	0.99	1.09	1.16	1.52	1.63
PBE0	0.57	0.60	0.54	0.52	0.72
PBE0-1/3	0.60	0.60	0.52	0.46	0.63
PBE0-DH	0.69	0.52	0.45	0.39	0.41
PBE-CIDH	0.75	0.55	0.44	0.37	0.51
PBE-QIDH	0.85	0.60	0.54	0.61	0.80
PBE0-2	1.03	0.77	0.65	0.82	1.22

[a] Not available for Li and Be atoms.

Table 5: MUE (in eV) for atomic excitation energies with the family of d-aug-cc-pVnZ[a] basis sets.

	d-aug-cc-pVDZ	d-aug-cc-pVTZ	d-aug-cc-pVQZ	d-aug-cc-pV5Z	d-aug-cc-pV6Z[b]
PBE	2.21	2.16	2.16	2.26	1.76
PBE0	1.32	1.31	1.31	1.42	0.97
PBE0-1/3	0.97	0.96	0.96	0.96	0.71
PBE0-DH	0.64	0.59	0.59	0.59	0.38
PBE-CIDH	0.53	0.51	0.50	0.50	0.38
PBE-QIDH	0.35	0.31	0.30	0.43	0.52
PBE0-2	0.35	0.47	0.46	0.46	0.70

[a] Not available for Li and Be atoms.
[b] Only available for B to O atoms.

Table 6: MSE (in eV), MUE (in eV), and MAPE (%) for atomic excitation energies with the family of BLYP- and PBE-based functionals and the aug-cc-pV5Z basis set.

	MSE (eV)	MUE (eV)	MAPE (%)
BLYP	−1.16	1.20	13.5
B3LYP	−0.60	0.67	7.4
B2LYP	−0.17	0.34	3.5
B2GP-PLYP	0.21	0.37	2.9
PBE	−1.07	1.11	12.3
PBE0	−0.40	0.52	5.5
PBE0-1/3	−0.18	0.46	4.5
PBE0-DH	0.07	0.39	3.1
PBE-CIDH	0.14	0.37	2.8
PBE-QIDH	0.52	0.61	4.8
PBE0-2	0.80	0.82	8.0

- **Figure 1.** Evolution of the MUE (eV) for PBE-based functionals and the (d-)aug-cc-pV5Z basis sets, as a function of the λ_x values. A threshold of 0.4 eV is also indicated (in red) as a guide to the eye.

- **Figure 2.** Evolution of the MSE (eV) for PBE-based functionals and different basis sets, as a function of the λ_x values. A threshold of 0.0 eV is also indicated (in red) as a guide to the eye.
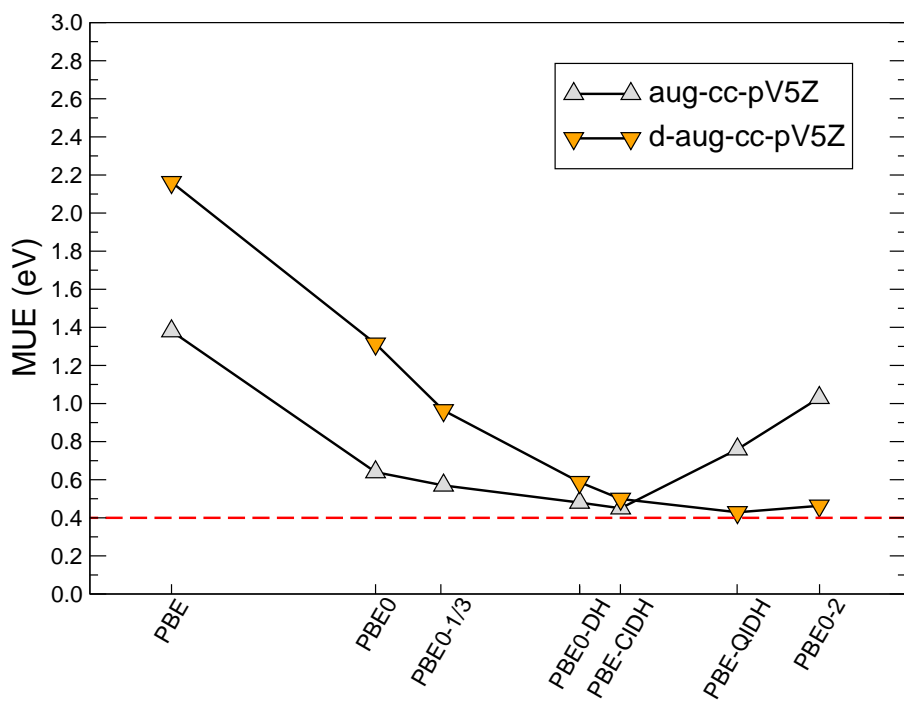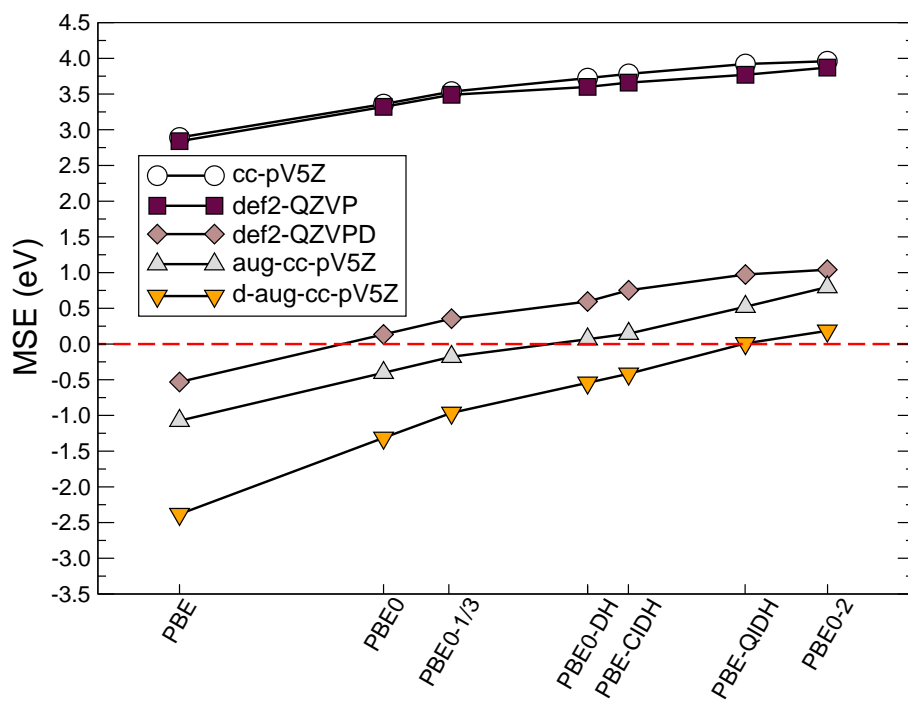
Figure 1.

Figure 2.