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REGULAR ARTICLE

Time-dependent density functional theory benchmarking for the calculations of atomic spectra: efficiency of exc-ETDZ basis set

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Abstract We present a time-dependent density functional theory (TD-DFT) benchmarking of recently constructed basis set, namely exc-ETDZ (Guevara et al. in J Chem Phys 131: 064104, 2009) for predicting the atomic spectra of the first-row atoms. A systematic testing with 31 density functional methods has been performed to see whether convincing performance of this basis set carries over the TD-DFT formalism. The efficiency of exc-ETDZ basis set for reproducing atomic spectra has been compared with Pople- and Dunning-style basis sets. We focused on the atomic low-lying valence excited states with single excitation character for our benchmarking, and the calculated excitation energies were compared to experimental data. On average, the functionals providing the best match with exc-ETDZ basis are BMK, BH&HLYP and ωB97. Moreover, on the basis of comparison between the results of these superior functionals with CIS(D) estimates, it turned out that TD-DFT and CIS(D) errors are of the same order of magnitude, once the exc-ETDZ basis set is used. Finally, the results of present study indicate that different functionals show results that are highly dependent on the atomic configuration as well as the basis set.

Keywords TD-DFT · Atomic spectra · Electronic excitation energy · First-row atoms · exc-ETDZ basis set

1 Introduction

Electronic excitation energy is a significant physical property, which implies inherent structural information and electronic properties. Thus, the accurate calculation for the electronic excitation energy is one of the important topics in computational chemistry. Quantum chemical methods have been developed beyond the level of just reproducing experimental data and can now accurately predict the electronic excitation energies that are unknown or uncertain experimentally. Among all methods, density functional theory (DFT) [1, 2] has been proven quite reliable for many chemically interesting systems. During the history of DFT, which has established its status as a standard tool for studying ground state properties of matter, a continuous effort has been taken to extend DFT to treat excited states. Over the past decades, time-dependent density functional theory (TD-DFT) [3–5] provides a promising and rigorous framework in the study of excited state properties [6] as well as response to external time-dependent perturbation. A major advantage of TD-DFT is its low computational cost [7], roughly comparable with single-excitation theories based on the Hartree–Fock (HF) ground state such as configuration interaction with singles or the random phase approximation. Moreover, TD-DFT calculations can be standardized and are thus user friendly: no need to define an active space or to select reference configurations.

Despite its successes and versatility, however, TD-DFT is limited and suffers an important drawback: the quality of the obtained results is profoundly functional-dependent. Indeed, the appropriate selection of the exchange–correlation form is often crucial to grasp chemically sound conclusions. Therefore, many approximate functionals have been proposed, and new ones are introduced every year. This constitutes a problem for the investigations, especially for non-specialists who want to take advantage of the computational efficiency of TD-DFT.

Several studies have appeared in recent years that compare performance of various functionals for different

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systems, from single atoms to large molecules [8–15]. However, despite the progress in theoretical measurements, calculation of excitation energy of the main elements has received much less attention than the calculation on transition metals [16, 17]. To the best of our knowledge, no systematic TD-DFT investigation on the excitation energies of main elements has been conducted thus far. Accordingly, the motivation of the present study is to report systematic tests on the performance of a number of DFT functionals within the TD-DFT formalism for description of the low-lying excited states of the first-row atoms.

Apart from the method, the selection of suitable basis set is another task that should be carried out with care in order to advance safely to prediction of reliable properties. Large variety of atomic Gaussian basis sets available for the first-row elements give a flexible opportunity for a basis set selection, leading to correct description of properties at the required precision. Nevertheless, there exist several attempts in the literature to generate universal Gaussian basis sets (i.e., a basis set with appropriate parameters that might be suitable for several atoms) using the generator coordinate HF method [18, 19] and even-tempered exponent sequences [20–23] to describe the ground state energy of several systems for static processes. However, most of the common basis sets constructed for use in electronic structure are inadequate for the representation of electrons participating in nonadiabatic time-dependent dynamic calculations. In this respect, Canal Neto et al. [24] used the generator coordinate HF method to generate Gaussian basis sets for low-lying excited states of neutral atoms. Recently, Guevara et al. [25] provided an approach to construct minimal-accuracy basis sets for the first-row atoms suited for dynamical processes. The constructed basis set, which was labeled by exc-ETDZ, has been claimed to be useful for methods that involve calculation of excited states, such as TD-DFT and configuration interaction with single substitution (CIS) [26] and CIS with perturbative doubles corrections (CIS(D)) [27, 28]. Accordingly, in the present work, the quality of this basis set in comparison with Pople- and Dunning-style [29] basis sets has been assessed in a basis set benchmarking. In fact, we intend to shed light on both methods' performance and basis sets efficiency for the treatment of atomic excitation energies.

2 Method

To assess the accuracy of existing DFT methods for describing atomic excitation energies, 31 functionals have been chosen. The selected methods can be classified in three major categories: hybrid generalized gradient approximation (H-GGA), hybrid meta GGA (HM-GGA) and range-separated hybrid GGA (RH-GGA). In the first category, we have picked up fourteen methods, namely, MPW1PW91 [30, 31], B3LYP [32–34], B3P86 [32–35], B97-1 [36], B97-2 [37], B98 [37], BH&HLYP [33, 34], PBE0 [38], X3LYP [39], MPW3LYP [30, 31, 34], O3LYP [40, 41], mPW1PBE [30, 42, 43], mPW3PBE [30, 42, 43] and HSEh1PBE [43, 44]. From the HM-GGA class, twelve methods have been chosen: BMK [45], M05 [46], M05-2X [47], MPW1B95 [30, 31, 48], MPWB1K [48], PBE1KCIS [42, 49, 50], TPSS1KCIS [49, 51, 52], TPSSh [52, 53], M06 [54], M06-2X [54], M06-HF [55, 56] and THCTH-hyb [57]. The RH-GGA constitutes the last category and uses a growing fraction of HF exchange when the interelectronic distance increases. Such a procedure was originally proposed by Savin [58], Leininger et al. [59] and Toulouse et al. [60]. This is formally performed by partitioning the two-electron operator into two terms using the standard error function

$$\frac{1}{r_{12}} = \frac{1 - \mathrm{erf}(\omega r_{12})}{r_{12}} + \frac{\mathrm{erf}\,(\omega r_{12})}{r_{12}} \tag{1}$$

where the parameter ω determines the partition ratio. The first term of this equation describes the short-range (SR) effect and is modeled through DFT exchange, whereas the second term accounts for the long-range (LR) contribution. The key in the long-range-corrected (LC) exchange functional scheme for DFT is that the DFT exchange interaction is included using the first term (short range), and the long-range orbital–orbital exchange interaction is described with the HF exchange integral via the complementary term.

Yanai et al. [61] generalized the form of Eq. 1 using two extra parameters α and β as,

$$\frac{1}{r_{12}} = \frac{1 - [\alpha + \beta\ \mathrm{erf}\ (\omega r_{12})]}{r_{12}} + \frac{\alpha + \beta\ \mathrm{erf}\ (\omega r_{12})}{r_{12}} \tag{2}$$

while α and $\alpha + \beta$ define the HF exchange percentage at $r_{12} = 0$ and $r_{12} = \infty$, respectively, and the relations $0 \le \alpha + \beta \le 1$, $0 \le \alpha \le 1$ and $0 \le \beta \le 1$ should be satisfied. The LC models use $\alpha = 0$ and $\beta = 1$ in Eq. 2, that is, short-range semilocal DFT exchange is combined with long-range HF exchange integrals. Since $\alpha + \beta = 1$, the exchange potential in LC functionals has the HF asymptotic behavior.

The RH-GGA functionals that we have used in this work include CAM-B3LYP [61] ($\alpha = 0.19$, $\beta = 0.46$ and $\omega = 0.33$ bohr^{-1}), LC-ωPBE [62–64] ($\alpha = 0$ and $\omega = 0.4$ bohr^{-1}), ωB97 [65] ($\alpha = 0$ and $\omega = 0.4$ bohr^{-1}), ωB97X [65] ($\alpha = 0.16$ and $\omega = 0.3$ bohr^{-1}) and ωB97X-D [66] ($\alpha = 0.2$ and $\omega = 0.2$ bohr^{-1}), which uses empirical dispersion corrections.

In this article, we are only concerned with calculating linear response by TD-DFT; linear-response TD-DFT may be considered as a correlation-corrected version of linear-response time-dependent HF theory [6, 67]. Practical applications of linear-response TD-DFT usually employ the adiabatic approximation, by which the exchange–correlation functional is independent of frequency, and it is usually taken to be the same as one of the exchange–correlation approximations originally developed for the static ground state [7, 68].

For the actual benchmarking study, all calculations were performed with four basis sets, which are: the standard 6-31G basis set, the 6-31+G(d) augmented by diffuse and polarization functions, the Dunning's correlation-consistent valence double-zeta basis set augmented by diffuse polarization functions, aug-cc-pVDZ, [29, 69, 70] and the recently published exc-ETDZ basis set constructed by augmentation 6-31G basis with extra uncontracted *s*- and *p*-functions for all first-row atoms. The new orbital exponents of *s*- and *p*-orbitals added to 6-31G basis set for constructing exc-ETDZ basis for Li through Ne are, respectively, 0.0163594, 0.0379981, 0.0447004, 0.0523006, 0.0582180, 0.0719134, 0.0265100 and 0.1170 [25]. Only fluorine required an additional *d*-function with exponent of 0.1170, and neon required the second *sp* function with exponent of 0.03080 [25].

For each method and basis set, the atomic spectra are calculated and compared to the experimental spectra as collected by National Institute of Standards and Technology (NIST) found in Ref. [71]. For each functional, we will gauge the quality of the results by mean unsigned errors (MUE) and mean signed errors (MSE) of the computed excitation energies for eighteen configurations of eight atomic species with respect to NIST data (cf. Table 1). The signed error measures a systematic deviation while the unsigned error is used to assess the absolute error from the reference value. All spectrum calculations were carried out using the Gaussian 03 [72] and Gaussian 09 [73] programs.

Table 1 Atomic spectra of the first-row elements computed at CIS(D)/exc-ETDZ level as well as corresponding experimental data (eV)

Atom	Configuration	Term	CIS(D)[a]	Exp.[b]
Li	$1s^22s$	^2S		
	$1s^22p$	^2P	1.888	1.85
	$1s^23s$	^2S	3.460	3.37
	$1s^23p$	^2P	4.053	3.83
Be	$1s^22s^2$	^1S		
	$1s^22s2p$	^3P	2.844	2.725
	$1s^22s2p$	^1P	6.114	5.278
	$1s^22s3s$	^3S	6.965	6.457
B	$1s^22s^22p$	^2P		
	$1s^22s2p^2$	^4P	3.159	3.579
	$1s^22s^23s$	^2S	4.419	4.964
C	$1s^22s^22p^2$	^3P		
	$1s^22s^22p^2$	^1D	1.733	1.264
	$1s^22s2p^3$	^5S	3.191	4.183
N	$1s^22s^22p^3$	^4S		
	$1s^22s^22p^3$	^2D	2.471	2.384
	$1s^22s^22p^23s$	^4P	10.820	10.326
O	$1s^22s^22p^4$	^3P		
	$1s^22s^22p^4$	^1D	2.560	1.967
	$1s^22s^22p^33s$	^3S	9.843	9.521
F	$1s^22s^22p^5$	^2P		
	$1s^22s^22p^43s$	^4P	12.25	12.7
	$1s^22s^22p^43s$	^2P	13.7	12.98
Ne	$1s^22s^22p^6$	^1S		
	$1s^22s^22p^5\ (^2P_{3/2})3s$	$^2[3/2]$	15.38	16.62
	$1s^22s^22p^5(^2P_{3/2})3p$	$^2[1/2]$	17.04	18.38

[a] Ref. [25]

[b] Ref. [71]

3 Results and discussion

Table 1 specifies eighteen electronic configurations arising from ground and excited states of first-row atoms as well as previous computational [25] and the experimental [71] excitation energies. Table 2 collects the MSE and MUE values for all the tested functionals and basis sets, which are sorted alphabetically for each category of functionals. For each basis set and each of the individual functional lineages, the two smallest MUE are shown in bold. Before we discuss the performance of different functionals, a brief comment on the basis set effect seems appropriate. Commencing with Pople-style basis sets, we first found a very poor performance of 6-31G basis. Augmentation of 6-31G basis by *d*-type polarization and single set of diffuse *s*- and *p*-functions in 6-31+G(d) basis set leads to significant improvement in excited state calculations and diminishes the computed errors by more than five times compared with 6-31G basis set. In fact, basis sets including diffuse functions would certainly modify the TD-DFT estimates of the excitation energy, but we have conserved 6-31G basis set for the sake of comparison between our estimates of excitation energies based on TD-DFT calculations with those reported by Guevara et al. [25] at CIS(D) level of theory. Anyway, we will not explain the results of 6-31G basis set throughout the discussion. Turning our attention to Table 2, better performance of tested DFT functionals can be observed by application of Dunning aug-cc-pVDZ and the recently published exc-ETDZ basis sets. Indeed, the exc-ETDZ provides a comparable quality of aug-cc-pVDZ at much lower computational cost.

It should be pointed out that all the basis sets used for our benchmarking were based on double-zeta 6-31G basis, except for aug-cc-pVDZ, but they differ in the extra

Table 2 Computed MSE, MUE and AMUE for the complete benchmark set and the HF exchange percentage (X) for each functional

Functional	X	6–31G		6-31+G(d)		aug-cc-pVDZ		exc-ETDZ	
		MSE	MUE	MSE	MUE	MSE	MUE	MSE	MUE
		HM-GGA							
BMK	42	0.679	0.687	0.111	**0.135**	0.109	0.131	−0.061	**0.101**
M05	28	0.712	0.714	0.065	0.151	0.069	0.152	0.049	0.139
M05-2X	56	0.646	0.672	0.102	0.157	0.092	0.156	0.082	0.123
M06	27	0.556	**0.568**	0.126	0.269	−0.005	0.137	−0.026	0.147
M06-2X	56	0.586	0.600	0.076	0.138	0.056	**0.129**	0.058	**0.107**
M06-HF	100	0.588	**0.599**	0.029	0.160	0.011	0.149	0.071	0.154
MPW1B95	31	0.661	0.668	0.075	0.141	0.029	0.149	−0.027	0.166
MPWB1 K	44	0.661	0.668	0.094	0.148	0.090	0.137	−0.016	0.173
PBE1KCIS	22	0.611	0.634	0.048	0.140	0.042	0.132	−0.031	0.139
THCTH-hyb	15	0.616	0.631	0.072	0.141	0.067	0.133	0.045	0.128
TPSS1KCIS	13	0.598	0.689	0.044	**0.130**	0.039	**0.123**	−0.026	0.160
TPSSh	10	0.608	0.714	0.055	0.145	0.049	0.138	−0.021	0.176
AMUE			*0.713*		*0.169*		*0.151*		*0.156*
		H-GGA							
B3LYP	20	0.665	0.692	0.058	0.133	0.047	**0.121**	0.027	0.122
B3P86	20	0.633	0.668	0.077	**0.127**	0.071	0.122	0.045	0.128
B97-1	21	0.673	0.685	0.065	**0.130**	0.060	**0.121**	0.040	**0.117**
B97-2	21	0.664	0.675	0.071	0.141	0.064	0.132	0.044	0.124
B98	21.98	0.664	0.679	0.067	0.133	0.061	0.124	0.042	0.119
BH&HLYP	50	0.648	0.681	0.087	0.147	0.081	0.139	0.065	**0.115**
HSEh1PBE	25	0.596	0.641	0.069	0.153	0.064	0.143	0.037	0.133
mPW1PBE	25	0.593	0.644	0.063	0.159	0.059	0.148	0.032	0.140
MPW1PW91	25	0.639	0.689	0.058	0.152	0.055	0.141	0.030	0.140
MPW3LYP	21	0.602	**0.627**	0.119	0.197	0.114	0.192	−0.042	0.124
mPW3PBE	25	0.593	**0.634**	0.059	0.148	0.055	0.137	0.027	0.135
O3LYP	16	0.661	0.684	0.051	0.147	0.045	0.143	0.037	0.173
PBE0	25	0.646	0.691	0.063	0.148	0.058	0.139	0.037	0.134
X3LYP	21	0.647	0.674	0.052	0.131	0.041	**0.118**	0.026	0.124
AMUE			*0.669*		*0.146*		*0.137*		*0.131*
		RH-GGA							
CAM-B3LYP	19–65	0.605	0.634	0.071	0.128	0.064	0.118	0.039	0.129
LC-ωPBE	0–100	0.592	0.647	0.079	0.145	0.072	0.138	0.041	0.153
ωB97	0–100	0.628	0.633	0.096	**0.112**	0.087	**0.106**	0.055	**0.113**
ωB97X	15.7–100	0.596	**0.621**	0.079	**0.118**	0.071	**0.109**	0.042	**0.114**
ωB97X-D	22.5–100	0.590	**0.622**	0.066	0.133	0.061	0.124	0.031	0.116
AMUE			*0.631*		*0.127*		*0.119*		*0.125*

Relative error = $(E_{\text{excitation}}(\text{DFT}) - E_{\text{excitation}}(\text{Exp.}))/E_{\text{excitation}}(\text{Exp.})$

functions added. Basis set comparisons were carried out with the aim of determining relatively compact basis, for the first-row atoms, that can yield quantitatively accurate excitation energies. In previous investigations, similar approach has been used for reproducing extended basis sets for estimation of first and second hyperpolarizabilities of hydrocarbons [74, 75]. It was concluded that a small augmented version of the 6-31G basis made by effective combinations of diffuse *s*- and *p*-shells on carbon and diffuse *s*-shells on hydrogen could provide a promising (in terms of quality vs size) description of hydrocarbons hyperpolarizability. Interestingly for constructing exc-ETDZ basis set, the orbital exponents of *s*- and *p*-orbitals added to 6-31G basis set on carbon (0.0523006) are almost the same value as previous reports, that is, 0.0523 in Ref. [74] and 0.05 in Ref. [75]. This indicates the reliability of exc-ETDZ in obtaining electronic properties, such as excitation energies as well as hyperpolarizability. Moreover, in another study, Liu and Dykstra have performed a basis set augmentation for the first-row elements that is moderately well suited for obtaining multipole polarizabilities and hyperpolarizabilities [76]. Although their basis sets were built based on Dunning-contracted triple-zeta core-valence, the reported orbital exponents for different elements are comparable with those we have used in the present study.

After a brief discussion on the influence of the basis set quality, at this point, we start functional benchmarking. To facilitate our analysis, first let us check the performance of the functionals of each category and specify which functionals display the best performance in each case. Table 2 shows that among the tested HM-GGA methods, BMK gives the best results for exc-ETDZ (MUE = 0.101) followed by M06-2X, M05-2X and THCTH-hyb with MUE of 0.107, 0.123 and 0.128, respectively. Behind these four are M05, PBE1KCIS and M06, with the other five functionals being significantly less accurate. The results reveal that BMK has a mean unsigned error of 0.131 for aug-cc-pVDZ basis set, a level of accuracy that is significantly exceeded by TPSS1KCIS functional (MUE = 0.123). Through the application of aug-cc-pVDZ and 6-31+G(d) basis sets, TPSS1KCIS is found to be the top functional of HM-GGA class. The functionals that appear in the second rank are M06-2X and BMK for aug-cc-pVDZ and 6-31+G(d) basis sets, respectively. Moreover, Table 2 includes an average MUE (AMUE) over all functionals of the same class for individual basis set. In HM-GGA class, the AMUE values show that the performance of aug-cc-pVDZ and exc-ETDZ basis sets exhibit almost similar behaviors, although some functionals provide larger error in one compared with another. This is the case for TPSSh and MPWB1K by which aug-cc-pVDZ remarkably outperforms in comparison with exc-ETDZ.

In H-GGA group of functionals, the combination of BH&HLYP with exc-ETDZ gives the best estimation of atomic spectra with less deviations from experimental ones (MUE = 0.115). The next two functionals are B97-1 and B98 with MUE = 0.117 and 0.119, respectively. With the aug-cc-pVDZ basis set, the most prominent functional is X3LYP (MUE = 0.118), and both B3LYP and B97-1 functionals with MUE = 0.121 are placed in the second rank. When using 6-31+G(d) basis set, B3P86 (MUE = 0.127) outperforms all other functionals in H-GGA class. Interestingly, we see that B97-1 appears within the top two functionals of H-GGA category for the three discussed basis sets. Finally, in the RH-GGA lineage, ωB97 and ωB97X perform better than other methods for the three discussed basis sets. However, comparing the AMUE values of different basis sets demonstrates that the Dunning basis set has improved estimation of atomic spectra when combined with range-separated functionals.

Up to this point, we have assessed the performance of various functionals within their corresponding categories. Now, let us proceed with an analysis of the global performance of all functionals. In general, 6-31+G(d) and aug-cc-pVDZ basis sets are more suited to use with range-separated hybrid functionals such as ωB97 and ωB97X. The new published exc-ETDZ basis set can be recommended as a good compromise between performance and accuracy if used in combination with BMK and M06-2X.

In order to study the relationship between the performance of different functionals and the percent of HF exchange, we could not reach a general conclusion upon systematic variation of the HF exchange, and rather contrary conclusions evolved with respect to the optimum amount of HF exchange admixture. First, consider the combination of exc-ETDZ basis set and a series of density functionals with the same exchange functional but various percent of HF exchange, that is, the B3LYP ($X = 20$) and BH&HLYP ($X = 50$) methods. As can be seen from the results of Table 2, BH&HLYP that incorporates a larger fraction of HF exchange provides more reliable estimates of excitation energies. However, this is not an extendable conclusion, and a closer look at the results indicates that, for instance, in a series of functionals with common MPW exchange functional, the MUE = 0.173 for MPWB1K with $X = 44$, which is much larger than MUE = 0.124 of MPW3LYP method with $X = 21$. The performance of RH-GGA functionals in which the fraction of HF exchange increases with increasing interelectronic distances, eventually reaching 100% at the asymptote, is much better than methods with small HF exchange. In general, among all tested functionals, the best results are observed for intermediate values of HF exchange, between 42 and 56%, which is in agreement with previous observation that about 50% HF exchange was optimal for excitation energy calculations [77, 78]. Moreover, there is not a direct relationship between the short-range parameter and the functional performance. Table 2 shows that using exc-ETDZ basis set, the MUE for ωB97 (0.113) with $\alpha = 0$ is almost similar to ωB97X (MUE = 0.114), which includes small fraction of short-range HF exchange ($\alpha = 0.16$).

In addition to the above analysis, also of interest here is investigating the performance of some selective functionals

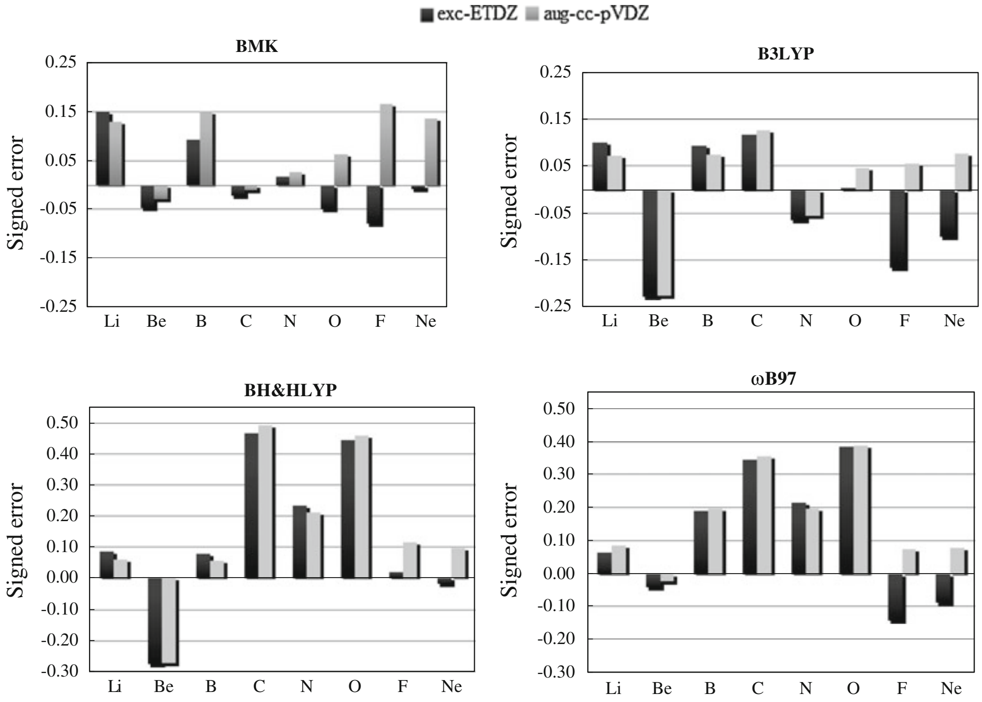

Fig. 1 Signed errors for the first excitation energies of the first-row atoms calculated at BMK, B3LYP, BH&HLYP and ωB97 levels with exc-ETDZ and aug-cc-pVDZ basis sets

atom-per-atom. Figure 1 gives further comparison of the aug-cc-pVDZ and exc-ETDZ basis sets for individual atoms. In particular, it shows the computed signed errors (SE) of the first excitation energies for BMK, BH&HLYP and ωB97 functionals as representatives of each lineage, and also B3LYP as one of the most widely used DFT methods. It can be seen that for both basis sets, the selected methods behave in a similar fashion resulting in overestimation of the first excitation energy for lithium and boron and underestimation for beryllium. For lithium, BH&HLYP and ωB97 outperform BMK and B3LYP. The underestimating of beryllium first excitation energy is more pronounced in BH&HLYP and B3LYP methods, while the overestimation in boron excitation energy is greater in ωB97 functional. In the case of carbon and nitrogen, the best performance has been observed for BMK, while for oxygen, B3LYP outperforms. For the last two atoms, exc-ETDZ basis set delivers fairly smaller error than the aug-cc-pVDZ when combined with BH&HLYP and BMK, whereas together with B3LYP and ωB97, aug-cc-pVDZ basis outperforms. However, we see that the optimal functional within TD-DFT framework differs atom-per-atom.

Besides DFT benchmarking, we carried out a comparative study between the performance of TD-DFT and CIS(D) methods for the prediction of atomic spectra. In fact, we want to compare the efficiency of exc-ETDZ basis set when it is applied with CIS(D) as an illustrative of wave function theory (WFT) methods, and BMK, BH&HLYP and ωB97 as three representatives of density functional methods. The atomic spectra at CIS(D)/exc-ETDZ level [25] are collected in Table 1. The overall trends in the calculated first excitation energies in this work together with CIS(D) results are depicted in Fig. 2. To have a meaningful comparison, this figure includes experimental data too. The first observation is that the exc-ETDZ basis set can reproduce the correct trend for the variation of atomic first excitation energy in both WFT and TD-DFT formalisms. Moreover, the calculated excitation energies are quantitatively in agreement with the experimental ones. However, there exist some discrepancies when the results of different functionals are compared to CIS(D) and experimental values. For instance, the excitation energy of beryllium computed by BH&HLYP functional falls far below the experimental data by more than 0.74 eV while it is overestimated by CIS(D) about 0.12 eV. For boron, CIS(D) underestimates the excitation energy while DFT methods overestimate. For carbon, nitrogen and oxygen CIS(D) and DFT methods behave in a similar manner with an overestimation of excitation energy. However, for nitrogen and oxygen, the overestimations of DFT methods are more pronounced compared with CIS(D) results. With an overestimation of first excitation energy of fluorine by 0.24 eV, BH&HLYP outperforms CIS(D) and other two DFT methods. For neon, CIS(D) and ωB97 underestimate the excitation energy by more than 1.2 eV while the

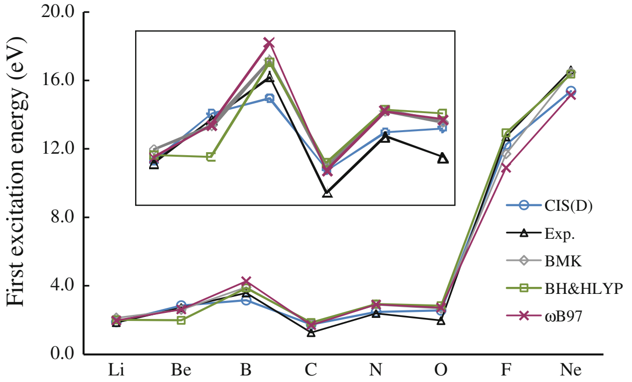

Fig. 2 Comparison of experimental first excitation energies for the first-row atoms with the results obtained at BMK, BH&HLYP, ωB97 and CIS(D) levels using exc-ETDZ basis. *Inset* shows expanded region for lithium through oxygen

underestimation is less than 0.3 eV in BMK and BH&HLYP functionals. In general, for beryllium and neon, BMK emerges as the promising approach whereas the performance of BMK is modest for other atoms.

In our final analysis, we examine the performance of all tested functionals to estimate the energy levels for the three and two low-lying configurations of lithium and neon, respectively (cf. Table 1). We rely on exc-ETDZ basis set, and the behaviors of all 31 functionals have been checked for calculating the atomic spectra of the first and the last members of our atomic set as representative examples. In Fig. 3 (top), we have plotted the computed signed errors for the three low-lying configurations of lithium atom using all the applied DFT methods. Apparently, most of maximum errors are related to the first excitation with general overestimation for all functionals (except M06). Across the computed errors for the first excitation, we see LC-ωPBE outperforms other 30 functionals with SE = 0.017 and ωB97X, ωB97X-D and M05-2X are functionals with relative errors less than 0.04. For the second configuration of lithium, the computed errors are not systematic. The functional with minimum error (SE = 0.004) is B97-1, whereas maximum error (SE = −0.298) belongs to M06 functional. It is also observed that for the third configuration, 9 of 31 tested functionals (B3LYP, B3P86, BH&HLYP, BMK, LC-ωPBE, M05-2X, MPW1PW91, PBE0 and ωB97) tend to overestimate the excitation energy. In general, B3LYP yields the best estimation for the third configuration ($SE < 0.001$) followed by ωB97 (SE = 0.004).

For neon, Fig. 3 (bottom), a systematic underestimation has been observed for all 31 studied functionals. M06-HF appears to be the superior functional with signed error by about −0.013 for both the first and the second excitations of neon. This method is followed by BH&HLYP and BMK functionals.

It should be noted that the performance of various functionals for a specific atom may not correlate with their overall performance in Table 2. For instance, BMK with the best overall performance with exc-ETDZ basis set and the minimum value of MUE does not perform very well for the three configurations of lithium. On the contrary, among H-GGA class functionals, O3LYP with much weaker overall performance than the top ranked BH&HLYP functional reproduces reasonable estimates for the second and third configurations of lithium. Also, we realized that new functionals do not necessarily outperform older ones, at least for the atomic excitations studied here. In fact, a relatively old functional as B98 performed as well as recent ones such as CAM-B3LYP and LC-ωPBE; although the latter two were designed for the description of excited states, the former was not.

4 Conclusions

Using the recently constructed exc-ETDZ basis set provided by Guevara et al. [25], we have benchmarked a large panel of functionals in the TD-DFT framework for estimation of the first-row atomic spectra. For the sake of comparison, three other double-zeta basis sets, 6-31G, 6-31+G(d) and aug-cc-pVDZ, have also been employed to assess the efficiency of exc-ETDZ basis. Our analysis was based on the comparison between DFT results for the excitation energies of eighteen low-lying configurations in eight atoms with experimental data. The results show that these computationally economical methods exhibit very diverse predictive capability, which is highly dependent on the systems as well as the basis sets, with acceptable results in many cases but quite poor results in others.

From these assessments, we draw the following general conclusions:

1. For exc-ETDZ basis set, the best estimation was obtained with BMK, BH&HLYP and ωB97 methods of HM-GGA, H-GGA and RH-GGA classes, respectively. Among other functionals, B98, ωB97X, B97-1 and M06-2X provided satisfying overall performance. However, BMK exhibits a superior performance among all 31 tested functionals.
2. The optimum functionals for aug-cc-pVDZ basis are TPSS1KCIS, B3LYP and ωB97 among HM-GGA, H-GGA and RH-GGA categories, respectively. However, better performance of aug-cc-pVDZ basis set has been observed when it is combined with RH-GGA group functionals.
3. Among newly implemented range-separated hybrid functionals, ωB97 and ωB97X project reasonable global results, but the same does not hold for

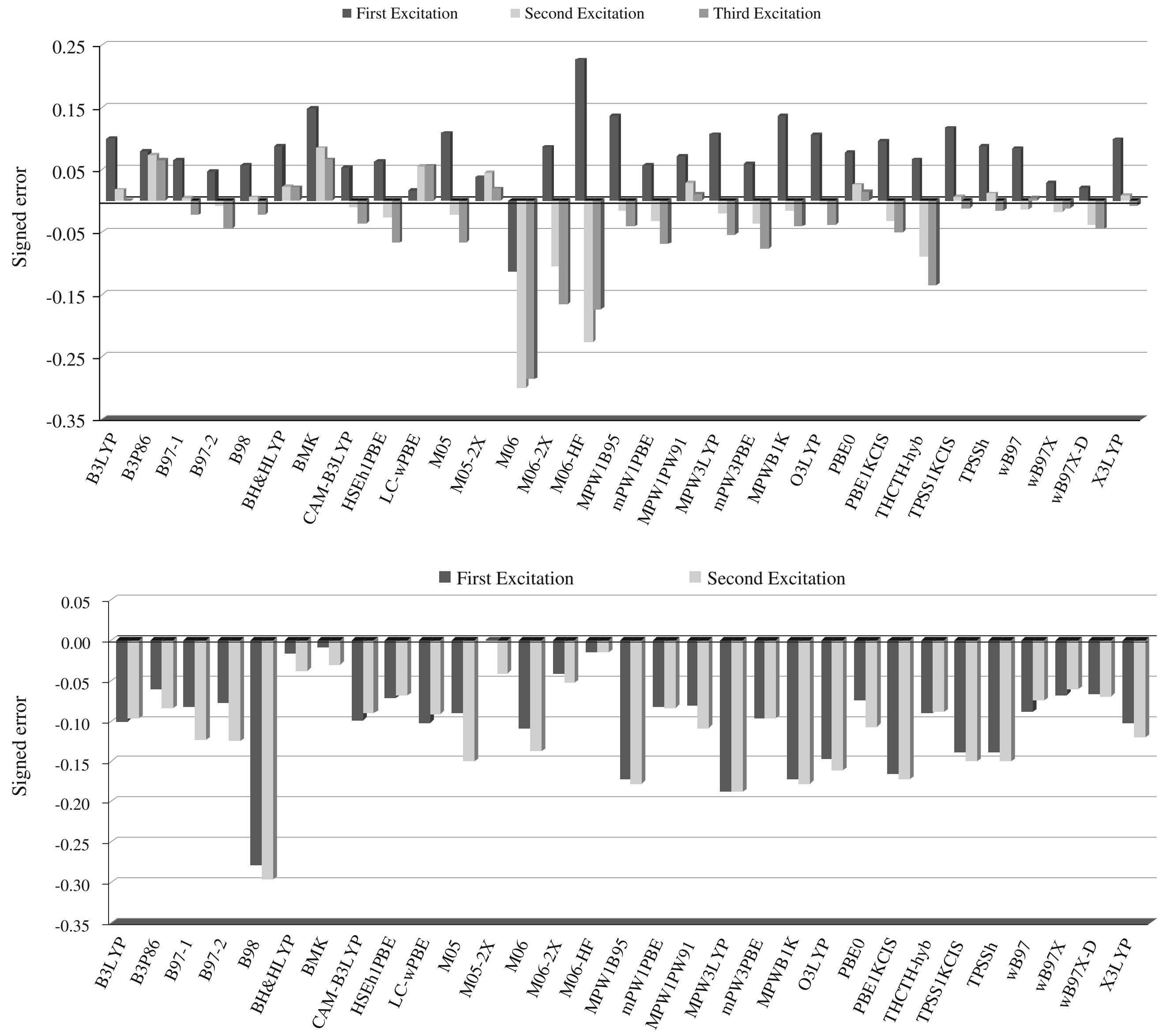

Fig. 3 Signed errors of the three low-lying configurations of lithium (*top*) and two low-lying configurations of neon (*bottom*) computed with all the studied DFT methods in combination with exc-ETDZ basis set

LC-ωPBE, which performs poorer for both aug-cc-pVDZ and exc-ETDZ basis sets.

4. The numerical results confirm that the efficiency of exc-ETDZ in TD-DFT calculations is comparable with CIS(D) method.
5. Considering the performance versus cost trade-off, exc-ETDZ basis with only one or two additional *sp* functions achieves most of the accuracy of the larger aug-cc-pVDZ basis set.

Our DFT assessments have revealed that even when statistically good results were obtained for a specific functional, a more detailed study deserves to be done with respect to the atomic configuration under study. To summarize, since there are differences in the accuracy of density functionals when used with different basis sets, careful consideration should be given as to which basis set to use with any of discussed functionals before calculations on atomic spectra.

Finally, it should be pointed out that in addition to excitation energy, the electronic transitions are also characterized by oscillator strength. Since the investigation on both methods' performance and basis sets efficiency has its own complexity, we preferred to focus just on the excitation energy calculations in the current study. Moreover, recent studies on the TD-DFT assessment for the evaluation of oscillator strength indicate that the behavior of each functional might be different for estimating both the excitation energy and the oscillator strength [79–81]. However, the issue of estimating the oscillator strength using TD-DFT methods is another interesting topic that deserves an independent and comprehensive research which is far from the scope of present study, but can be considered in future works.

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