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Assessment of the Van Voorhis–Scuseria exchange–correlation functional for predicting excitation energies using time-dependent density functional theory

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Abstract. We assess the performance of the Van Voorhis–Scuseria exchange–correlation functional (VSXC), a kinetic-energy-density-dependent exchange–correlation functional recently developed in our group, for calculating vertical excitation energies using time-dependent density functional theory in a benchmark set of molecules. Overall, *VSXC* performs very well, with accuracy similar to that of hybrid functionals such as the hybrid Perdew–Burke–Ernzerhof functional and Becke's three parameter hybrid method with the Lee, Yang, and Parr correlation functional, which contain a portion of Hartree–Fock exchange.

Key words: Density functional theory – Kinetic-energy-density-dependent functional – Time-dependent density functional theory – Excitation energy

1 Introduction

Electronically excited states are of great interest for research areas such as electronic spectroscopy, photochemistry, and molecular optics. Calculated excited states are of significant help when predicting molecular spectra and are particularly relevant when working with spectroscopic assignments and ordering of states. In this article, we assess the performance of an exchange–correlation functional developed in our group, the Van Voorhis–Scuseria exchange–correlation functional (VSXC) [1], for calculating vertical excitation energies.

Density functional theory (DFT) [2] is a successful method for modeling ground states of chemical systems. DFT satisfactorily models electron exchange and correlation, predicting numerous properties in similar or better agreement with experimental data than conventional correlated ab initio methods such as second-order Møller–Plesset perturbation theory. Since reliable treatment of electronic excitations in atoms and molecules requires, in general, a proper inclusion of the static and dynamic effects of electron correlation, there has been great interest in studying excited states using DFT. The computational cost effectiveness of DFT over conventional methods is an additional attractive feature [3].

The extension of DFT to modeling excited states has led to several different approaches [4]. Among these, time-dependent DFT (TD-DFT) [5] offers a rigorous route for calculating vertical excitation energies, which are the result of evaluating the linear response of the charge density to a TD electromagnetic field in the adiabatic approximation. TD-DFT has been shown to be a useful tool in modeling low-lying excited states for a variety of functionals and chemical systems [3, 6, 7, 8]. Nevertheless, the deterioration in the quality of the results for higher excitation energies is a problem that has not been completely solved. Tozer and Handy [9] proposed a modification to correct the asymptotic behavior of functionals, thus improving the representation of the virtual Kohn–Sham orbitals. Casida [5] has proposed criteria for recognizing high states for which TD-DFT gives unreliable results.

The quest for new exchange and correlation functionals that may improve the performance of TD-DFT is a relevant area of research. Kinetic-energy-density-(τ) dependent functionals have recently attracted much attention [10, 11]. Our research group has developed an exchange–correlation functional of this kind, known as VSXC [1]. The quality of VSXC has been assessed for calculations of different ground-state properties, such as atomization energies [1], proton-transfer barriers [12], vibrational frequencies [13], thermodynamic properties [14], and hydrogen-bonding structures [15]. The quality of the results obtained with VSXC is quite remarkable even though VSXC does not include Hartree–Fock exchange. Hartree–Fock exchange mixing has been used to improve the accuracy of exchange–correlation functionals [16, 17]. However, hybrid functionals are computationally more elaborate than traditional exchange–correlation functionals because of the necessity of

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evaluating exact exchange. The accuracy of VSXC for most of the properties mentioned previously is comparable to gradient-corrected hybrid functionals, such as Becke's three parameter hybrid method with the Lee, Yang, and Parr correlation functional (B3LYP) [16] and the hybrid Perdew–Burke–Ernzerhof functional (PBE0) [18] – also denoted as PBE1PBE in our previous publications [19] – usually considered among the more accurate functionals currently available.

It has been shown [9] that an important issue for the success of a functional in reproducing excited states is to have correct Coulomb asymptotic behavior of the exchange–correlation functional. As with most of the functionals, VSXC does not have this behavior. In fact, this condition is incompatible with the nonuniform scaling conditions that VSXC satisfies [1]; however, since no kinetic-energy-density-dependent functional, such as VSXC, has been tested for non-ground-state properties, in this article we assess the performance of VSXC for calculating vertical excitation energies.

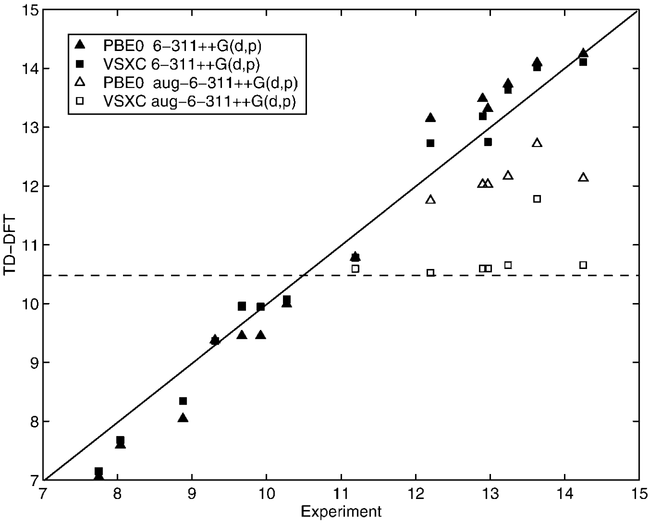

Fig. 1. Effect of different basis sets on the vertical excitation energies of the nitrogen molecule for two functionals: the Van Voorhis–Scuseria exchange correlation functional (*VSXC*) and the hybrid Perdew–Burke–Ernzerhof functional (*PBE0*). The basis sets are 6-311+ +G(d,p) and aug-6-311+ +G(d,p), which is 6-311+ +G(d,p) augmented with a second set of diffuse functions. The *horizontal line* marks the location of $-\varepsilon^{VSXC}{}_{HOMO}$, which is the same for both basis sets. This correlation plot compares computed time-dependent density functional theory (*TD-DFT*) results with experimental data

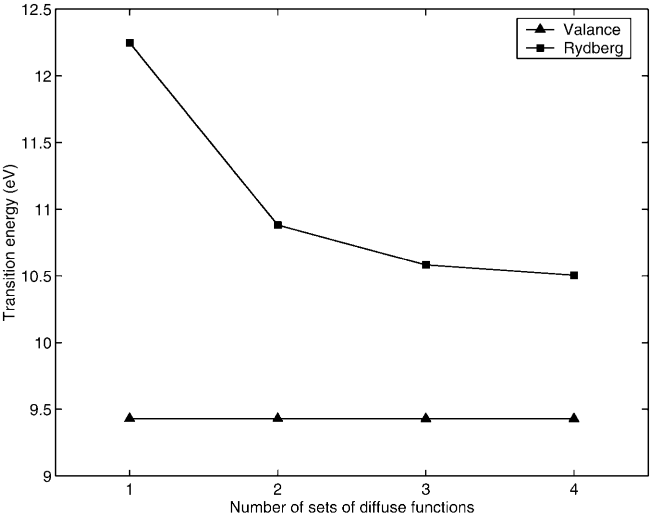

Fig. 2. Effect of the addition of diffuse sets on a few vertical excitation energies of the nitrogen molecule for VSXC. The basis set is correlation-consistent polarized valence triple zeta with different numbers of diffuse sets indicated in the abscissa

2 Computational procedures

All calculations in this work were carried out using a developmental version of the Gaussian suite of programs [20], which includes an implementation of TD-DFT developed in our group [3].

We selected a standard set of 11 molecules as a benchmark for the calculation of vertical excitation energies. Our set of molecules begins with the small systems N_2, CO, H_2CO, and C_2H_2, which have previously been used in several studies of the performance of TD methods [9, 21, 22, 23]. We also included seven medium-sized molecules, acetone, benzene, pyridine, naphthalene, butadiene, azulene, and 1,4-dimethylaminobenzonitrile, to better understand the behavior of VSXC and to confirm that the trends obtained with the first set of molecules were also valid for larger molecules. Singlet–singlet and singlet–triplet excitations were considered for most of the molecules whenever experimental or high-accuracy calculations were available. Equilibrium structures of the molecules in their ground states were optimized for each functional with the 6-311G(d,p) basis set following Adamo et al. [24].

Wiberg et al. [6] and Adamo et al. [24] suggested the 6-311+ +G(d,p) basis set for calculating excitation energies with TD-DFT. We followed this suggestion, and we also considered an augmented version of this basis with additional diffuse and polarized functions as done by Casida et al. [23]. N_2 was utilized to calibrate the different basis sets. To rule out numerical instabilities, various integration tests were performed for different integration grids.

The results showed that the 6-311+ +G(d,p) basis set is appropriate for low-lying states but that it is inadequate when Rydberg states are considered. For high-lying states, our tests suggested that additional diffuse functions considerably changed the results, while the low-lying states were not affected. This behavior is illustrated in Fig. 1. In this figure, the results for low-lying states with the augmented basis set completely overlap those obtained with the 6-311+ +G(d,p) basis set. On the other hand, addition of one set of diffuse functions dramatically changes the results for excitation energies above the ionization potential, as shown in the top part of Fig. 1. Thus, it appears that the relative good Rydberg energies obtained with 6-311+ +G(d,p) using VSXC are merely fortuitous and are not converged with respect to the basis set. In contrast, the valence excitation energies are well converged at the 6-311+ +G(d,p)/VSXC level. In order to study in more detail the effect of additional diffuse basis functions, we chose a few representative excited states for N_2. The $^1\Pi_g(\sigma_g \rightarrow \pi_g)$ valence state and the $^1\Sigma_g^+(\sigma_g \rightarrow 3s\ \sigma_g)$ Rydberg state were compared as shown in Fig. 2. The correlation-consistent polarized valence triple zeta basis set was utilized, and up to four sets of diffused functions were added for this comparison. The valence state is not affected by the addition of diffuse functions. On the other hand, the Rydberg state changes dramatically with the addition of diffuse functions. This effect persists at least up to the addition of a fourth diffuse set, where the excitation energy seems to converge. A comparison of the experimental result for the $^1\Sigma_g^+$ state, which is 12.2 eV, with the calculated values shows a deterioration in the results with the size of the basis set. The error with respect to the experimental value goes from 0.4% for one set of diffuse functions to 13.4% for four sets, making the result totally unreliable. Similar results were obtained for many other Rydberg states. Most importantly, all the functionals considered in this work (including PBE0 and B3LYP) showed the same behavior with respect to the basis set for both valence and Rydberg states, i.e., the latter suffer from substantial errors even when large basis are used, whereas the former is fairly converged with 6-311 + + G(d,p).

3 Results and discussion

In order to assess VSXC, we compare its performance at reproducing vertical excitation energies with PBE0. The effectiveness of each functional is determined by calculating the error with respect to experimental excitation energies when these are available or otherwise with respect to high-accuracy quantum chemical computations.

In order to give a more general idea of the performance of VSXC with respect to PBE0, we have compared the overall mean absolute error (MAE) of vertical excitation energies in Table 1. This summary includes 172 different excitation energies from 11 molecules. For the 73 valence states calculated, PBE0 and VSXC yield very similar results, with the former having a slightly smaller MAE. A set of tables with the complete data for each molecule can be found in the Appendix.

As mentioned before, the change of basis sets significantly affects the excitation energies of Rydberg states for both functionals. Although 6-311 + + G(d,p) is not

Table 1. Vertical excitation energy errors

	Excitation energy errors (eV)	
	PBE0	VSXC
All states (172 states considered)		
$\overline{\lvert x \rvert}$	0.26	0.36
σ_x	0.36	0.44
Max (+) dev	0.95	1.30
Max (–) dev	–1.61	–1.23
Rydberg states (87 states considered)		
$\overline{\lvert x \rvert}$	0.27	0.41
σ_x	0.39	0.49
Max (+) dev	0.95	1.30
Max (–) dev	–1.61	–1.23
Valence states (73 states considered)		
$\overline{\lvert x \rvert}$	0.26	0.30
σ_x	0.34	0.37
Max (+) dev	0.93	1.25
Max (–) dev	–0.79	–0.64

Table A1. Calculated vertical excitation energies for N_2 with a 6-311 + + G(d,p) basis set and comparison to experiment

Transition		Excitation energies (eV)		
		PBE0	VSXC	Exp.[a]
$^1\Sigma_u^+$	…	14.49	14.40	14.48
$^1\Sigma_u^+$	…	14.24	14.11	14.25
$^1\Pi_u$	$\sigma_u \rightarrow \pi_g$	14.10	14.02	13.63
$^1\Pi_u$	$\pi_u \rightarrow 3s\ \sigma_g$	13.73	13.64	13.24
$^1\Sigma_u^+$	$\sigma_g \rightarrow 3p\ \sigma_u$	13.48	12.75	12.97
$^1\Pi_u$	$\sigma_g \rightarrow 3p\ \pi_u$	13.31	13.18	12.90
$^1\Sigma_g^+$	$\sigma_g \rightarrow 3s\ \sigma_g$	13.14	12.73	12.2
$^1\Delta_u$	$\pi_u \rightarrow \pi_g$	9.99	10.07	10.27
$^1\Sigma_u^-$	$\pi_u \rightarrow \pi_g$	9.45	9.94	9.92
$^1\Pi_g$	$\sigma_g \rightarrow \pi_g$	9.38	9.37	9.31
$^3\Sigma_g^+$	$\sigma_g \rightarrow 3s\ \sigma_g$	12.28	11.89	12.0
$^3\Pi_u$	$\sigma_u \rightarrow \pi_g$	10.79	10.78	11.19
$^3\Sigma_u^-$	$\pi_u \rightarrow \pi_g$	9.45	9.95	9.67
$^3\Delta_u$	$\sigma_g \rightarrow \pi_g$	8.04	8.35	8.88
$^3\Pi_g$	$\pi_u \rightarrow \pi_g$	7.59	7.68	8.04
$^3\Sigma_u^+$	$\pi_u \rightarrow \pi_g$	7.06	7.15	7.75
Statistics				
$\overline{\lvert x \rvert}$		0.41	0.29	–
σ_x		0.50	0.35	–
Max (+) dev		0.84	0.60	–
Max (–) dev		0.94	0.53	–

[a] Ref. [25]

Table A2. Calculated vertical excitation energies for CO with a 6-311 + + G(d,p) basis set and comparison to experiment

Transition		Excitation energies (eV)		
		PBE0	VSXC	Exp.[a]
$^1\Sigma^+$	$\sigma \rightarrow 3d\ \sigma$	12.01	13.40	12.4
$^1\Pi$	$\sigma \rightarrow 3p\ \pi$	11.49	11.25	11.53
$^1\Sigma^+$	$\sigma \rightarrow 3p\ \sigma$	11.39	10.98	11.40
$^1\Sigma^+$	$\sigma \rightarrow 3s$	10.75	10.48	10.78
$^1\Delta$	$\pi \rightarrow \pi^*$	10.23	10.19	10.23
$^1\Sigma^-$	$\pi \rightarrow \pi^*$	9.81	10.13	9.88
$^1\Pi$	$\sigma \rightarrow \pi^*$	8.45	8.52	8.51
$^3\Pi$	$\sigma \rightarrow 3p\ \pi$	11.24	10.85	11.55
$^3\Sigma^+$	$\sigma \rightarrow 3p\ \sigma$	10.96	10.60	11.3
$^3\Sigma^+$	$\sigma \rightarrow 3s$	10.10	10.08	10.4
$^3\Sigma^-$	$\pi \rightarrow \pi^*$	9.81	9.78	9.88
$^3\Delta$	$\pi \rightarrow \pi^*$	8.66	8.77	9.36
$^3\Sigma^+$	$\pi \rightarrow \pi^*$	7.87	7.81	8.51
$^3\Pi$	$\sigma \rightarrow \pi^*$	5.74	5.99	6.32
Statistics				
$\overline{\lvert x \rvert}$		0.25	0.41	–
σ_x		0.26	0.46	–
Max (+) dev		0.70	0.70	–
Max (–) dev		0.00	1.00	–

[a] Ref. [26]

Table A3. Calculated vertical excitation energies for formaldehyde with a 6-311 + + G(d,p) basis set and comparison to experiment

Transition		Excitation energies (eV)		
		PBE0	VSXC	Exp.[a]
$^1A_2$	$n \rightarrow 3d\ b_1$	9.45	9.43	9.22
$^1A_2$	$n \rightarrow 3p\ b_1$	8.15	9.20	8.38
$^1B_1$	$\sigma \rightarrow \pi^*$	8.55	8.34	8.68
$^1B_2$	$n \rightarrow 3p\ a_1$	7.85	7.60	8.12
$^1A_1$	$n \rightarrow 3p\ b_2$	7.76	7.17	7.97
$^1B_2$	$n \rightarrow 3s\ a_1$	6.78	6.22	7.09
$^1A_2$	$n \rightarrow \pi^*$	3.98	4.10	3.94
$^3B_2$	$n \rightarrow 3p\ a_1$	7.65	7.41	7.96
$^3A_1$	$n \rightarrow 3p\ b_2$	7.53	6.88	7.79
$^3B_2$	$n \rightarrow 3s\ a_1$	6.53	5.97	6.83
$^3A_1$	$\pi \rightarrow \pi^*$	5.36	5.65	5.53
$^3A_2$	$n \rightarrow \pi^*$	3.20	3.40	3.50
Statistics				
$\overline{\lvert x \rvert}$		0.23	0.52	–
σ_x		0.16	0.55	–
max (+) dev		0.31	0.91	–
max (–) dev		0.23	0.82	–

[a] Ref. [21]

Table A4. Calculated vertical excitation energies for acetone with a 6-311++G(d,p) basis set and comparison to experiment

Transition	Excitation energies (eV)			
	B3LYP[a]	PBE0	VSXC	Exp.[b]
$^1A_2$	7.47	7.92	7.94	8.09
$^1B_2$	7.21	7.45	7.29	7.49
$^1A_1$	6.83	7.06	6.36	7.41
$^1A_2$	6.96	7.21	6.94	7.36
$^1B_2$	6.11	6.11	5.51	6.36
$^1A_2$	4.44	4.47	4.40	4.43
$^3A_2$	6.95	8.15	7.53	7.90
$^3A_2$	5.80	6.03	6.89	6.26
$^3A_1$	5.84	5.59	5.52	5.88
$^3A_2$	3.86	3.79	3.86	4.18
Statistics				
$\overline{\lvert x\rvert}$	0.39	0.22	0.44	–
σ_x	0.28	0.19	0.45	–
Max (+) dev	0.95	0.39	1.05	–
Max (–) dev	0.01	0.25	0.63	–

[a] Ref. [24]
[b] Ref. [27]

Table A5. Calculated vertical excitation energies for ethene with a 6-311++G(d,p) basis set and comparison to experiment

Transition		Excitation energies (eV)		
		PBE0	VSXC	Exp.[a]
$^1B_{1u}$	$\pi \rightarrow 3d\ \pi$	9.30	9.41	9.33
$^1B_{2u}$	$\pi \rightarrow 3d\ \delta$	9.09	9.32	9.05
$^1B_{3u}$	$\pi \rightarrow 3d\ \delta$	8.82	9.98	8.90
$^1B_{3u}$	$\pi \rightarrow 3d\ \sigma$	8.69	9.12	8.62
^1A_g	$\pi \rightarrow 3p\ \pi$	8.08	8.69	8.28
$^1B_{1u}$	$\pi \rightarrow \pi^*$	7.60	7.58	8.0
$^1B_{2g}$	$\pi \rightarrow 3p\ \sigma$	7.62	7.42	7.90
$^1B_{1g}$	$\pi \rightarrow 3p\ \sigma$	7.59	7.58	7.80
$^1B_{3u}$	$\pi \rightarrow 3s$	6.99	6.84	7.11
$^3B_{3u}$	$\pi \rightarrow 3d\ \sigma$	8.66	8.57	8.57
^3A_g	$\pi \rightarrow 3p\ \pi$	8.34	8.14	8.15
$^3B_{1g}$	$\pi \rightarrow 3p\ \sigma$	7.42	7.26	7.79
$^3B_{3u}$	$\pi \rightarrow 3s$	6.85	6.68	6.98
$^3B_{1u}$	$\pi \rightarrow \pi^*$	3.94	4.15	4.36
Statistics				
$\overline{\lvert x\rvert}$		0.19	0.34	–
σ_x		0.19	0.45	–
Max (+) dev		0.42	0.53	–
Max (–) dev		0.19	1.08	–

[a] Ref. [28]

Table A6. Calculated vertical excitation energies for butadiene with a 6-311++G(d,p) basis set and comparison to CASPT2 results

Transition		Excitation energies (eV)		
		PBE0	VSXC	CASPT2[a]
^1B_g	$1b_g \rightarrow 3s$	6.04	5.87	6.21
^1B_u	$\pi \rightarrow \pi^*$	5.76	5.59	6.24
^1A_g	$\pi \rightarrow \pi^*$	6.84	6.36	6.24
^1A_u	$1b_g \rightarrow 3p\ \sigma$	6.30	6.08	6.52
^1B_u	$1b_g \rightarrow 3p\ \pi$	7.80	7.79	6.57
^1A_u	$1b_g \rightarrow 3p\ \sigma$	6.42	6.21	6.66
^1A_g	$\pi \rightarrow \pi^*$	7.86	7.70	6.97
^1B_g	$1b_g \rightarrow 3d\ \delta$	7.24	7.07	7.39
^1B_g	$1b_g \rightarrow 3d\ \delta$	7.26	7.15	7.42
^1B_g	$1b_g \rightarrow 3d\ \sigma$	8.25	7.90	7.51
^3B_u	$\pi \rightarrow \pi^*$	2.67	2.81	3.15
^3A_g	$\pi \rightarrow \pi^*$	4.81	4.93	4.80
^3B_g	$1b_g \rightarrow 3s$	5.97	5.79	6.17
^3A_u	$1b_g \rightarrow 3p\ \sigma$	6.25	5.98	6.50
Statistics				
$\overline{\lvert x\rvert}$		0.45	0.42	–
σ_x		0.54	0.55	–
Max (+) dev		0.65	0.48	–
Max (–) dev		1.22	1.23	–

[a] Ref. [29]

Table A7. Calculated vertical excitation energies for benzene with a 6-311++G(d,p) basis set and comparison to CASPT2 results

Transition		Excitation energies (eV)			
		B3LYP[a]	PBE0	VSXC	CASPT2[b]
$^1B_{2u}$	$\pi \rightarrow \pi^*$	5.39	5.5	5.38	4.84
$^1B_{1u}$	$\pi \rightarrow \pi^*$	6.05	6.17	6.04	6.30
$^1E_{1u}$	$\pi \rightarrow \pi^*$	6.93	6.94	7.00	7.03
$^1E_{1g}$	$\pi \rightarrow \sigma^*$	6.06	6.37	6.16	6.38
$^1A_{2u}$	$\pi \rightarrow \sigma^*$	6.55	6.89	6.72	6.86
$^1E_{2u}$	$\pi \rightarrow \sigma^*$	6.58	6.93	6.73	6.91
$^1A_{1u}$	$\pi \rightarrow \sigma^*$	6.93	7.00	6.78	6.99
$^1E_{1g}$	$\pi \rightarrow \sigma^*$	7.44	7.59	7.39	7.57
$^1B_{2g}$	$\pi \rightarrow \sigma^*$	7.44	7.59	7.40	7.58
$^3B_{1u}$	$\pi \rightarrow \pi^*$	3.82	3.64	3.81	3.89
$^3E_{1u}$	$\pi \rightarrow \pi^*$	4.70	4.73	4.66	4.49
$^3B_{2u}$	$\pi \rightarrow \pi^*$	5.05	5.13	5.09	5.49
$^3E_{2g}$	$\pi \rightarrow \pi^*$	7.18	7.39	7.20	7.12
$^3E_{1g}$	$\pi \rightarrow \sigma^*$	6.02	6.31	6.10	6.34
$^3A_{2u}$	$\pi \rightarrow \sigma^*$	6.51	6.8	6.61	6.80
$^3E_{2u}$	$\pi \rightarrow \sigma^*$	6.58	6.91	6.69	6.90
$^3A_{1u}$	$\pi \rightarrow \sigma^*$	6.67	6.91	6.78	7.00
$^3E_{1g}$	$\pi \rightarrow \sigma^*$	7.21	7.43	7.17	7.57
$^3B_{1g}$	$\pi \rightarrow \sigma^*$	7.19	7.39	7.16	7.53
$^3B_{2g}$	$\pi \rightarrow \sigma^*$	7.33	7.44	7.18	7.53
Statistics					
$\overline{\lvert x\rvert}$		0.26	0.13	0.23	–
σ_x		0.23	0.21	0.22	–
Max (+) dev		0.44	0.36	0.40	–
Max (–) dev		0.55	0.66	0.54	–

[a] Ref. [24]
[b] Ref. [30]

the optimal basis set for this purpose, for the sake of completeness we have also compared the errors for 87 Rydberg states. PBE0 yields results that are closer to the experimental or high-level quantum mechanical calculations, while VSXC has a larger MAE than that of PBE0. Overall, for the valence and Rydberg states combined, PBE0 is more accurate than VSXC. Whereas PBE0 tends to overestimate the excitation energies, VSXC tends to underestimate them.

For the molecules studied in this work, we conclude that PBE0 more accurately reproduces excitation energies of carboxylic groups and small unsaturated hydrocarbons, while VSXC is better at modeling conjugated systems and molecules with high bond orders.

Table A8. Calculated vertical excitation energies for pyridine with a 6-311+ +G(d,p) basis set and comparison to CASPT2 results

Transition		Excitation energies (eV)			
		B3LYP[a]	PBE0	VSXC	CASPT2[b]
$^1B_2$	$\pi \rightarrow \pi^*$	5.54	5.63	5.48	4.84
$^1A_1$	$\pi \rightarrow \pi^*$	6.24	6.42	6.25	6.42
$^1A_1$	$\pi \rightarrow \pi^*$	6.90	7.21	6.66	7.23
$^1B_2$	$\pi \rightarrow \pi^*$	7.25	7.37	7.17	7.48
$^1A_1$	$\pi \rightarrow \pi^*$	7.70	7.98	7.49	7.96
$^1B_1$	$n \rightarrow \pi^*$	4.80	4.88	4.63	4.61
$^1A_2$	$n \rightarrow \pi^*$	5.09	5.20	4.77	5.17
$^1A_1$	$\sigma \rightarrow \pi^*$	6.32	6.56	5.95	6.70
$^1A_2$	$\sigma \rightarrow \pi^*$	6.42	6.69	6.50	6.75
$^1B_2$	$\sigma \rightarrow \pi^*$	6.74	7.06	6.47	7.21
$^1B_1$	$\sigma \rightarrow \pi^*$	6.93	7.21	7.03	7.25
$^1B_1$	$\sigma \rightarrow \pi^*$	7.08	7.38	7.14	7.39
$^1A_1$	$\sigma \rightarrow \pi^*$	7.32	7.44	7.25	7.35
$^1A_2$	$\sigma \rightarrow \pi^*$	7.18	7.46	7.26	7.52
$^1A_2$	$\sigma \rightarrow \pi^*$	7.64	7.73	7.33	7.98
$^1B_2$	$\sigma \rightarrow \pi^*$	7.45	7.76	7.25	7.41
$^1A_2$	$\sigma \rightarrow \pi^*$	7.67	7.99	7.70	8.03
$^1B_1$	$\sigma \rightarrow \pi^*$	7.73	8.01	7.77	7.45
$^1B_1$	$\sigma \rightarrow \pi^*$	7.83	8.11	7.81	8.03
$^1B_1$	$\sigma \rightarrow \pi^*$	7.84	8.15	7.88	8.14
$^3A_1$	$\pi \rightarrow \pi^*$	3.99	3.8	3.94	4.05
$^3B_2$	$\pi \rightarrow \pi^*$	4.57	4.56	4.48	4.56
$^3A_1$	$\pi \rightarrow \pi^*$	4.91	4.92	4.83	4.73
$^3B_2$	$\pi \rightarrow \pi^*$	5.68	5.72	5.61	6.02
$^3A_1$	$\pi \rightarrow \pi^*$	6.86	7.14	6.58	7.34
$^3B_2$	$\pi \rightarrow \pi^*$	6.71	7.01	6.41	7.28
$^3B_1$	$n \rightarrow \pi^*$	4.08	4.09	3.97	4.41
$^3A_2$	$n \rightarrow \pi^*$	4.95	5.04	4.64	5.10
Statistics					
$\overline{\lvert x \rvert}$		0.28	0.17	0.37	–
σ_x		0.27	0.25	0.33	–
Max (+) dev		0.57	0.32	0.87	–
Max (–) dev		0.70	0.79	0.64	–

[a] Ref. [24]
[b] Ref. [31]

4 Conclusions

VSXC gives good results for valence excitation energies, with PBE0 yielding very similar results for the set of 11 benchmark molecules studied in this work. For the basis set considered, the accuracy of PBE0 for Rydberg states is better than that of VSXC, but these results are largely affected by the choice of basis set. We do not recommend the use of PBE0 or VSXC for high-lying excited states.

The novel form of VSXC, which includes the kinetic energy density along with electron density, does not show a large improvement over hybrid functionals. Instead, it shows similar disadvantages as the asymptotically incorrect functionals. In this context, the performance of VSXC is quite remarkable given that it does not include a portion of exact exchange.

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Appendix

This appendix includes 11 tables with the vertical excitation energies for N_2, CO, H_2CO, C_2H_2, acetone, benzene, pyridine, naphthalene, butadiene, azulene, and 1,4-dimethylaminobenzonitrile.

Table A9. Calculated vertical excitation energies for naphthalene with a 6-311+ +G(d,p) basis set and comparison to CASPT2 results

Transition		Excitation energies (eV)		
		PBE0	VSXC	CASPT2[a]
$^1B_{3u}$	$\pi \rightarrow \pi^*$	4.48	4.18	4.03
$^1B_{2u}$	$\pi \rightarrow \pi^*$	4.58	4.34	4.56
^1A_u	$1a_u \rightarrow 3s$	5.50	5.32	5.54
^1A_g	$\pi \rightarrow \pi^*$	7.00	5.96	5.39
$^1B_{1g}$		5.62	5.18	5.53
$^1B_{3u}$	$\pi \rightarrow \pi^*$	6.23	5.95	5.54
$^1B_{2g}$	$1a_u \rightarrow 3p\ \sigma$	5.84	5.66	5.94
$^1B_{3g}$	$1a_u \rightarrow 3p\ \sigma$	5.84	5.67	5.98
$^1B_{2u}$		5.99	5.81	5.93
$^1B_{1u}$	$2b_{1u} \rightarrow 3s$	6.29	6.05	6.03
$^1B_{1g}$		6.35	6.16	5.87
$^1B_{2g}$	$2b_{1u} \rightarrow 3p\ \sigma$	6.68	6.41	6.45
$^1B_{1u}$	$1a_u \rightarrow 3d\ \sigma$	6.44	6.29	6.50
$^1B_{3g}$	$1a_u \rightarrow 3d\ \pi$	6.62	6.28	6.48
^1A_g		6.24	6.39	6.08
^1A_g	$2b_{1u} \rightarrow 3p\ \pi$	7.01	6.70	6.79
$^3B_{2u}$	$\pi \rightarrow \pi^*$	2.64	3.86	3.04
$^3B_{3u}$		3.99	2.71	3.84
$^3B_{1g}$		4.09	4.17	4.18
$^3B_{2u}$		4.31	4.15	4.24
$^3B_{3u}$		4.46	4.30	4.40
^3A_g		5.27	5.27	5.22
$^3B_{1g}$		5.68	5.15	5.56
$^3B_{1g}$		6.24	6.39	6.18
^3A_g		5.97	5.66	5.77
^3A_g		6.23	5.83	5.85
Statistics				
$\overline{\lvert x \rvert}$		0.24	0.26	–
σ_x		0.36	0.37	–
Max (+) dev		0.40	1.13	–
Max (–) dev		1.61	0.82	–

[a] Ref. [32]

Table A10. Calculated vertical excitation energies for azulene with a 6-311+ +G(d,p) basis set and comparison to experiment

Transition		Excitation energies (eV)		
		PBE0	VSXC	Exp.[a]
$^1B_2$	$\pi \rightarrow \pi^*$	2.42	2.37	2.10
$^1A_1$	$\pi \rightarrow \pi^*$	3.97	3.51	3.60
$^1A_1$	$\pi \rightarrow \pi^*$	5.02	4.90	4.50
$^1B_1$	$\pi \rightarrow \pi^*$	5.23	5.05	5.22
Statistics				
$\overline{\lvert x \rvert}$		0.31	0.23	–
σ_x		0.21	0.28	–
Max (+) dev		0.00	0.17	–
Max (–) dev		0.52	0.40	–

[a] Ref. [33]

Table A11. Calculated vertical excitation energies for 1,4-dimethylaminobenzonitrile with a 6-311++G(d,p) basis set and comparison to experiment

Transition		Excitation energies (eV)		
		PBE0	VSXC	Exp.[a]
$^1B_2$	$\pi \rightarrow \pi^*$	4.50	4.08	4.09
$^1A_1$	$\pi \rightarrow \pi^*$	4.75	4.44	4.55
$^1B_1$	$\pi \rightarrow 3s$	4.80	4.45	5.75
$^1A_2$	$n \rightarrow \pi^*$	5.38	5.06	6.31
$^1B_1$	$n \rightarrow 3p_z$	5.51	5.23	6.36
$^1A_2$	$n \rightarrow \pi^*$	6.08	5.47	6.45
$^1B_2$	$n \rightarrow \pi^*$	6.03	5.55	5.71
$^1B_1$	$n \rightarrow 3d_{x^2-y^2}$	5.97	5.68	6.78
$^1A_1$	$\pi \rightarrow \pi^*$	5.93	5.81	6.34
$^1B_1$	$n \rightarrow 3d_{z^2}$	6.04	5.85	6.86
$^3A_1$	$n \rightarrow \pi^*$	3.12	3.10	3.12
$^3B_2$	$n \rightarrow \pi^*$	3.73	3.45	3.51
$^3A_1$	$\pi \rightarrow \pi^*$	4.30	4.23	4.45
$^3B_2$	$\pi \rightarrow \pi^*$	4.94	4.77	4.68
Statistics				
$\overline{\lvert x \rvert}$		0.48	0.57	–
σ_x		0.52	0.54	–
Max (+) dev		0.95	1.30	–
Max (−) dev		0.41	0.09	–

[a] Ref. [34]

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