

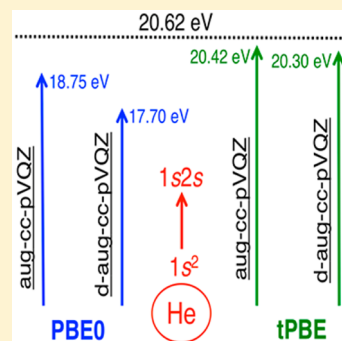
Multiconfiguration Pair-Density Functional Theory Spectral Calculations Are Stable to Adding Diffuse Basis Functions

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S Supporting Information

ABSTRACT: Time-dependent Kohn–Sham density functional theory (TD-KS-DFT) is useful for calculating electronic excitation spectra of large systems, but the low-energy spectra are often complicated by artificially lowered higher-energy states. This affects even the lowest energy excited states. Here, by calculating the lowest energy spin-conserving excited state for atoms from H to K and for formaldehyde, we show that this problem does not occur in multiconfiguration pair-density functional theory (MC-PDFT). We use the tPBE on-top density functional, which is a translation of the PBE exchange-correlation functional. We compare to a robust multireference method, namely, complete active space second-order perturbation theory (CASPT2), and to TD-KS-DFT with two popular exchange-correlation functionals, PBE and PBE0. We find for atoms that the mean unsigned error (MUE) of MC-PDFT with the tPBE functional improves from 0.42 to 0.40 eV with a double set of diffuse functions, whereas the MUEs for PBE and PBE0 drastically increase from 0.74 to 2.49 eV and from 0.45 to 1.47 eV, respectively.



Excited-state chemistry poses difficult challenges for electronic structure theory. For complex systems, the method of choice, because of its affordable cost, is usually time-dependent Kohn–Sham density functional theory (TD-KS-DFT) with the linear-response and adiabatic approximations and using approximate exchange-correlation functionals developed mainly for ground-state chemistry.^{1–14} A problem with TD-KS-DFT calculations is that, “Although TD-DFT excitation energies are typically reasonably accurate for the lowest few valence excited states, those for higher-lying excited states are typically underestimated by standard functionals.... The errors in high-energy excited states have been ascribed to the incorrect asymptotic behavior of the exchange correlation potential”² and “they introduce many spurious excited states at too low energy which may mix with valence excited states, resulting in wrong excited state compositions.”¹⁵

Therefore,¹⁶ “When basis sets are extended, in particular with diffuse basis functions, the many Rydberg states that exist (just) below the zero of energy will become increasingly represented among the virtual orbitals of the calculation, while their shape is not very accurate.... But since the LUMO and other valence virtual orbitals have been shifted up, they actually will appear in between the (spurious) Rydberg orbitals. As consequence one will find in large basis set calculations increasing contamination of the excited state spectrum with many spurious Rydberg states.”

The consequences of this bad situation have been summarized as follows,⁷ “In many cases the assignment of the calculated TDDFT transitions is not unambiguous because some high-energy states are overstabilized..., and they incorrectly appear at energies comparable to those of the low-energy transitions of interest. This is a general problem

with TDDFT when one considers a range of excitation energies for a given molecule rather than just the lowest one or two states.... The problem is exacerbated when large and diffuse basis sets are used, but one needs to use such well-augmented basis sets in order to treat the Rydberg states correctly. Using a less diffuse basis set usually reduces...the contamination and improves the SCF convergence; for this reason, a calculation with a smaller basis set might help with the assignments (and one can possibly even obtain more accurate results for the pure valence states), but it can deteriorate the quality of the results for the entire spectrum including the Rydberg states.”

This problem can be ameliorated by using higher percentages of Hartree–Fock exchange, but this can lead to worsening of ground-state properties. It has recently been shown that the problem can be mitigated without significantly affecting ground-state properties by increasing the local exchange at large values of the reduced (i.e., dimensionless) gradient of the density,¹³ but the problem remains for standard functionals. The ability of density functional theory to predict accurate excited states even with diffuse basis sets is one test of how well the method overcomes the incorrect asymptotic behavior problem that plagues most aspects of density functional predictions of excited state spectra. It has recently been proposed that studying the excited states of atoms is a good way to test density functional methods because the intrinsic problems of excited-state energy prediction are not entangled with other problems such as incorrect treatment of charge

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Table 1. Excitation Energies (in eV) of Atoms^a

	states	type	CASSCF	CASPT2	tPBE ^b	PBE ^c	PBE0 ^c	exp ²⁶
H	² S– ² S	1s–2s	10.22	10.22	9.88	8.05	8.67	10.20
He	¹ S– ¹ S	1s ² –1s2s	20.15	20.72	20.42	17.61	18.75	20.62
Li	² S– ² P	2s–2p	1.84	1.84	1.60	2.00	1.97	1.85
Be	¹ S– ¹ P	2s ² –2s2p	5.59	5.42	3.82	4.99	4.99	5.28
B	² P– ² S	2p–3s	4.51	4.93	5.01	4.14	4.56	4.96
C	³ P– ³ P	2p ² –2p3s	6.88	7.52	7.50	6.29	6.90	7.48
N	⁴ S– ⁴ P	2p ³ –2p ² 3s	9.31	10.49	9.84	8.76	9.57	10.33
O	³ P– ³ S	2p ⁴ –2p ³ 3s	10.07	9.79	10.93	8.97	9.62	9.51
F	² P– ² P	2p ⁵ –2p ⁴ 3s	12.74	13.66	13.67	12.66	13.68	12.98
Ne	¹ S– ¹ P	2p ⁶ –2p ⁵ 3s	15.38	18.05	16.28	15.85	17.02	16.71
Na	² S– ² P	3s–3p	1.97	2.05	1.94	2.13	2.09	2.10
Mg	¹ S– ¹ P	3s ² –3s3p	4.04	4.41	3.64	4.24	4.25	4.35
Al	² P– ² S	3p–4s	2.71	3.08	3.03	2.73	2.96	3.14
Si	³ P– ³ P	3p ² –3p4s	4.48	4.93	4.82	4.29	4.62	4.92
P	⁴ S– ⁴ P	3p ³ –3p ² 4s	6.40	7.04	6.74	6.07	6.52	6.96
S	³ P– ³ S	3p ⁴ –3p ³ 4s	6.75	7.00	7.50	6.85	7.30	6.82
Cl	² P– ² P	3p ⁵ –3p ⁴ 4s	8.95	9.52	9.65	8.86	9.41	9.19
Ar	¹ S– ¹ P	3p ⁶ –3p ⁵ 4s	11.25	12.29	11.77	11.04	11.70	11.68
K	² S– ² P	4s–4p	1.40	1.57	1.43	1.57	1.53	1.61
MSE ^d			–0.32	0.20	–0.06	–0.71	–0.24	
MUE ^e			0.41	0.22	0.42	0.74	0.45	
SD ^f			0.42	0.35	0.60	0.80	0.63	

^adef2-QZVP²⁷ basis set was used for the valence excitations (Li, Be, Na, Mg, K) and aug-cc-pVQZ^{28–31} was used for Rydberg excitations (the other atoms). ^bMC-PDFT. ^cTD-KS-DFT. ^dMean signed error with respect to experiment. ^eMean unsigned error with respect to experiment. ^fStandard deviation of the signed errors from their mean.

localization or charge transfer in the ground state.¹² Furthermore, it was found that the prediction of excited-state spectra in atoms is very challenging,¹² in many respects more challenging than even the prediction of excited states in molecules.

Multiconfiguration pair-density functional theory (MC-PDFT)¹⁷ is a recently developed alternative to KS-DFT. The full details of the theory can be found in ref 17, but here we provide a brief summary. In MC-PDFT a multiconfiguration self-consistent field (MCSCF)¹⁸ wave function is used to compute the contributions to the MC-PDFT energy in a post-MCSCF procedure. The MC-PDFT energy consists of the MCSCF electronic kinetic energy, the classical Coulombic interactions of electrons and nuclei, and the on-top energy. The on-top energy plays an analogous role to the exchange-correlation energy from KS-DFT but is a functional of the MCSCF density and on-top pair density as opposed to being a functional of the alpha and beta densities. The on-top functional used in this work is tPBE,¹⁷ which is related to the PBE exchange-correlation functional¹⁹ by a simple translation. We have tested MC-PDFT^{17,20} and developed better on-top functionals for ground-state properties.²¹ We recently began testing tPBE for excited states too and found that many of the problems KS-DFT has for charge transfer are no longer present in MC-PDFT.²² In this work we investigate the performance of tPBE for atomic excitations and determine if it has the same problems as KS-DFT when diffuse functions are added, as is necessary for the treatment of Rydberg states. We show below that MC-PDFT does not have this problem, even with such a simple local functional as tPBE.

To test MC-PDFT, we applied the tPBE functional to the lowest-energy spin-conserving excitations of all 19 atoms from H to K. We chose not to go beyond potassium to avoid the

added complication of d orbitals. In addition to the calculations on atoms, we computed the lowest spin-conserving Rydberg excitation of formaldehyde. To compare density functional theory to wave function theory (WFT), we calculate the excitation energies with a robust but more expensive multi-reference method, namely, complete active space second-order perturbation theory (CASPT2).²³ We also present complete active space self-consistent field (CASSCF)²⁴ results because the CASSCF wave function is used in generating the CASPT2 and tPBE results. Finally we compare to TD-KS-DFT calculations with the PBE¹⁹ and PBE0²⁵ exchange-correlation functionals. This comparison is of interest because the PBE exchange-correlation functional is used to generate the tPBE functional.

We report our first set of findings in Table 1, where we compare our calculations to experimental²⁶ values. Table 1 shows that tPBE is less accurate than CASPT2 (mean unsigned error (MUE) of 0.22 eV), which is, however, not a candidate for applications to large systems due its unaffordable cost. In comparing more affordable methods based on density functionals, we see that tPBE with an MUE of 0.42 eV outperforms PBE, which has an MUE of 0.74 eV and performs in a comparable fashion to PBE0, which has an MUE of 0.45 eV. Curiously, the CASSCF method performs better than expected for these cases, with an MUE of 0.41 eV, which is surprising because CASSCF lacks dynamic correlation; we shall return to this finding below.

In Table 1 we also report also the standard deviation, SD, of the signed errors from their mean. This gives an indication of the width of the distribution of signed errors.

In addition to providing the above general test of MC-PDFT for excitation energies, we analyzed the basis set dependence for Rydberg excitations computed with MC-PDFT. (We also

Table 2. Rydberg Excitation Energies (in eV) of First- and Second-Row Atoms upon Doubling the Number of Diffuse Basis Functions

	states	basis set	CASSCF	CASPT2	tPBE ^a	PBE ^b	PBE0 ^b	exp ²⁶
H	² S– ² S	aug-cc-pVQZ	10.22	10.22	9.88	8.05	8.67	10.20
		d-aug-cc-pVQZ	10.21	10.21	9.89	7.64	8.44	
He	¹ S– ¹ S	aug-cc-pVQZ	20.15	20.72	20.42	17.61	18.75	20.62
		d-aug-cc-pVQZ	19.88	20.46	20.30	16.21	17.70	
B	² P– ² S	aug-cc-pVQZ	4.51	4.93	5.01	4.14	4.56	4.96
		d-aug-cc-pVQZ	4.45	4.88	5.03	3.85	4.37	
C	³ P– ³ P	aug-cc-pVQZ	6.88	7.52	7.50	6.29	6.90	7.48
		d-aug-cc-pVQZ	6.68	7.35	7.38	5.77	6.52	
N	⁴ S– ⁴ P	aug-cc-pVQZ	9.31	10.49	9.84	8.76	9.57	10.33
		d-aug-cc-pVQZ	8.85	10.23	9.50	8.00	9.00	
O	³ P– ³ S	aug-cc-pVQZ	10.07	9.79	10.93	8.97	9.62	9.51
		d-aug-cc-pVQZ	9.30	9.05	10.48	7.59	8.48	
F	² P– ² P	aug-cc-pVQZ	12.74	13.66	13.67	12.66	13.68	12.98
		d-aug-cc-pVQZ	11.59	12.64	12.84	10.31	11.48	
Ne	¹ S– ¹ P	aug-cc-pVQZ	15.38	18.05	16.28	15.85	17.02	16.71
		d-aug-cc-pVQZ	13.68	16.63	16.25	13.53	15.01	
MSE ^c		aug-cc-pVQZ	–0.32	0.20	–0.06	–0.71	–0.24	
		d-aug-cc-pVQZ	–1.02	–0.17	–0.14	–2.49	–1.47	
MUE ^d		aug-cc-pVQZ	0.42	0.21	0.45	0.79	0.50	
		d-aug-cc-pVQZ	1.02	0.17	0.40	2.49	1.47	

^aMC-PDFT. ^bTD-KS-DFT. ^cMean signed error. ^dMean unsigned error.

tested some valence excitations, but there was little to no change as shown in Table S1 of Supporting Information.) Specifically, we analyzed the question of whether results for Rydberg excitations deteriorate in accuracy upon the addition of a set of diffuse basis functions, as is often the case for TD-KS-DFT. To test this question, we selected the Rydberg excitations of first-row and second-row atoms from Table 1 and computed excitation energies with the d-aug-cc-pVQZ³¹ basis set, which has two sets of diffuse basis functions and with the aug-cc-pVQZ basis set, which is identical except for not having the second set of diffuse functions. The findings are reported in Table 2.

The results in Table 2 show a dramatic effect on the TD-KS-DFT results in going from aug-cc-pVQZ to d-aug-cc-pVQZ. The PBE and PBE0 sets of excitation energies both worsen drastically and systematically when an extra set of diffuse basis functions is added. In particular, the PBE MUE increases from 0.79 to 2.49 eV, and the PBE0 MUE increases from 0.50 to 1.47 eV. The decrease in TD-KS-DFT accuracy as more diffuse functions are added is consistent with the previous experience summarized in the introductory remarks. This is confirmed by the large magnitude of the mean signed errors, which are negative; however, tPBE does not have the same behavior as PBE and PBE0; the MUE goes from 0.45 eV with aug-cc-pVQZ to 0.40 eV with d-aug-cc-pVQZ. In fact, the behavior of tPBE with respect to adding more diffuse functions is quite similar to CASPT2 (MUE goes from 0.21 to 0.17 eV), which is very encouraging. As for the performance of CASSCF, we find that the accuracy obtained in Table 1 was a fortuitous result due to an insufficient basis set; the MUE increases from 0.42 eV with aug-cc-pVQZ to 1.02 eV with d-aug-cc-pVQZ.

We also explored the behavior of PBE, PBE0, tPBE, and CASPT2 excitation energies of Rydberg states with augmented and doubly augmented polarized valence triple- ζ (...TZ) and quintuple zeta (...SZ) basis sets. The full details are in the Supporting Information, and the MUEs are in Table 3. We see

Table 3. Mean Unsigned Errors in Rydberg Excitation Energies (in eV) of First- and Second-Row Atoms upon Doubling the Number of Diffuse Basis Functions

basis set	CASSCF	CASPT2	tPBE ^a	PBE ^b	PBE0 ^b
aug-cc-pVTZ	0.49	0.42	0.48	1.07	0.85
aug-cc-pVQZ	0.42	0.21	0.45	0.79	0.50
aug-cc-pVSZ	0.68	0.24	0.48	1.51	0.78
d-aug-cc-pVTZ	1.01	0.24	0.56	2.48	1.46
d-aug-cc-pVQZ	1.02	0.17	0.40	2.49	1.47
d-aug-cc-pVSZ	1.02	0.13	0.63	2.50	1.48

^aMC-PDFT. ^bTD-KS-DFT.

that with these two augmented basis sets tPBE is significantly more accurate (by 0.30 to 1.03 eV) than PBE and PBE0, which already show the pathology of TD-KS-DFT with just a single set of diffuse functions. Furthermore, the MUE increases less upon double augmentation. In particular, it increases by 0.08 to 0.15 eV for tPBE, by 0.61 to 0.70 for PBE0, and by 0.99 to 1.41 eV for PBE with the new basis sets of Table 3.

Finally, we show an example calculation on a molecule as evidence that the stability of MC-PDFT with respect to diffuse basis functions is present for molecules as well as atoms. In Table 4 the lowest energy spin-conserving Rydberg state of formaldehyde is reported. The errors with the jul-cc-pVTZ basis set are similar to those with the aug basis sets in Table 3,

Table 4. Lowest Energy Singlet-to-Singlet Rydberg Excitation Energy (in eV) of Formaldehyde upon Doubling the Number of Diffuse Basis Functions

basis set	CASSCF	CASPT2	tPBE ^a	PBE ^b	PBE0 ^b	ref ^c
jul-cc-pVTZ ³²	6.32	7.03	6.66	6.11	6.99	7.08
d-jul-cc-pVTZ ³²	6.12	6.88	6.57	5.78	6.71	

^aMC-PDFT. ^bTD-KS-DFT. ^cExperimental value based on the assignment of ref 3.

except that CASSCF is less accurate, which is expected for molecules, and PBE0 is more accurate. When adding an extra set of diffuse functions to formaldehyde, CASPT2 and tPBE errors change by <0.10 eV, whereas the PBE and PBE0 errors change by 0.33 and 0.28 eV, respectively. This finding indicates that MC-PDFT is stable upon adding an extra set of diffuse basis functions in the treatment of Rydberg states for molecules as well as for atoms.

In summary, we have tested MC-PDFT with the tPBE on-top density functional for main-group spin-conserving atomic excitations and one molecular excitation. We find that the accuracy of tPBE is already better on average than PBE and PBE0, but it is not as accurate as CASPT2. The improvement over TD-KS-DFT is encouraging because tPBE has a much lower cost than CASPT2, and furthermore its accuracy can be improved because it is an unoptimized on-top functional. In addition, we tested the sensitivity of tPBE to expanding the diffuse basis set for Rydberg excitations. We find that the PBE and PBE0 excitation energies significantly worsen upon expanding the basis set, which is a persistent and debilitating problem that plagues TD-KS-DFT. In contrast, tPBE behaves more like CASPT2, where the results either improve upon an additional set of diffuse functions or only slightly degrade, even though the CASSCF and PBE0 results become much worse, and PBE results become very much worse. This behavior is also confirmed in the case of formaldehyde. We conclude that MC-PDFT is significantly improved over TD-KS-DFT for calculations of Rydberg electronic excitations.

■ COMPUTATIONAL DETAILS

The CASSCF, CASPT2, and tPBE calculations were performed in a locally modified developer version of *Molcas* 7.9.³³ (MC-PDFT is available in *Molcas* 8.³⁴) The CASSCF calculations in this work were state-averaged (SA),³⁵ where the number of states averaged is equal to the sum of the number of degenerate components for each state for atoms (e.g., an S to P excitation averages over four states), and equal weights were assigned to each of the states averaged. The formaldehyde calculation was averaged over three states that were equally weighted. Defining n as the number of valence electrons, we used an active space of n electrons in four orbitals (the s and p orbitals) for valence states of atoms and n electrons in five orbitals (s and p subshells plus an additional diffuse s orbital) for Rydberg states of atoms. Two atoms were exceptions (H and He), where they used an n in 2 orbitals (1s plus an additional diffuse s orbital). For formaldehyde we used an active space of two electrons in three orbitals (n orbital on oxygen, π^* orbital of the carbonyl, and a carbon Rydberg orbital). The resulting state-averaged wave function was the first step, providing the reference wave function for both the CASPT2 and the tPBE calculations. The CASPT2 calculations were done with multistate CASPT2 (MS-CASPT2);³⁶ they used a standard imaginary shift³⁷ of 5.44 eV to alleviate intruder-state problems, and they incorporated the standard empirical IPEA shift³⁸ of 6.80 eV.

The PBE and PBE0 calculations were performed with standard linear-response TD-KS-DFT using *Gaussian* 09.³⁹ The reference Slater determinant used was unrestricted, and we used the lowest energy excited state with the correct orbital character that has $M_S = S$ (where S is the total spin quantum number of the ground state) and with an $\langle S^2 \rangle$ that deviates by <1.5 from the desired value (because a state excluded by this criterion does not adequately model a same-spin excitation). For atoms with a degenerate ground state, we ignored the

excitations that correspond to them. For example, consider an atom like boron with a P ground state; the TD-KS-DFT reference would be one component of the P state, and the first two excitations from that reference are the other two components of the P state. We ignored those excitations. After the ignored excited states are removed from consideration, we chose the lowest energy solution that has the orbital character of the desired excited state.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.5b01888.

Basis set dependence of selected valence excitations (Be, Na, and Mg) is studied by presenting results with the aug-cc-pVQZ basis set for comparison with those with the def2-QZVP basis in Table 1. Results for Rydberg states with aug-cc-pVTZ, aug-cc-pVSZ, d-aug-cc-pVTZ, and d-aug-cc-pVSZ basis sets are also reported. All total energies and the $\langle S^2 \rangle$ values of the TD-KS-DFT calculations are included. (PDF)

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Notes

The authors declare no competing financial interest.

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