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ROYAL SOCIETY OF CHEMISTRY

COMMENT

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Cite this: *Phys. Chem. Chem. Phys.*, 2025, **27**, 4973

Reply to the 'Comment on "Designing potentially singlet fission materials with an anti-Kasha behaviour"' by K. Jindal, A. Majumdar and R. Ramakrishnan, *Phys. Chem. Chem. Phys.*, 2025, 27, DOI: 10.1039/D4CP02863E†

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Received 12th December 2024,
Accepted 6th February 2025

DOI: 10.1039/d4cp04691a

rsc.li/pccp

In this reply to the preceding paper by K. Jindal, A. Majumdar, and R. Ramakrishnan, we argue that the results obtained in our original manuscript with the time-dependent density functional theory (TD-DFT) are reasonable and that they are not only in agreement with experimental results but also with reliable *ab initio* calculations.

We have carefully reviewed the article by Jindal, Majumdar, and Ramakrishnan (hereafter referred to as JMR) commenting on our original manuscript (OM) in which we propose a series of compounds that could potentially be applied as singlet fission materials and also exhibit anti-Kasha behavior using time-dependent density functional theory (TD-DFT) calculations.[1] Before addressing the comment made by JMR, we would like to highlight that the singlet fission (SF) process has been experimentally confirmed in azulene by Nickel and Klemp.[2] Based on their results, the value of $S_2 - 2T_1$ (Δ), the criterion we use to evaluate the SF capability, is greater than zero (700 cm^{-1}). Additionally, more recent experimental results obtained by Vosskötter *et al.*[3] show a Δ = 1000 cm^{-1} (see Table 1).

On the other hand, selecting the appropriate functional to study excited states in chemical compounds using TD-DFT does not have a defined recipe, however the most reasonable choice is to compare the results obtained with existing experimental data. In our recent work,[1] we evaluated 16 density functionals widely used for excited states using standard TD-DFT calculations and the Tamm–Dancoff approximation (TDA). We compared them with results published in the literature for azulene.

JMR criticised the selection of our level of theory, which was chosen not only based on the available experimental data but also computational results using high-level *ab initio* calculations. JMR point out that our results are the product of a fortunate coincidence due to error cancellation and that calculations of azulene-based systems should be carried out using the Tamm–Dancoff approximation. However, the results using TDA are the furthest from the experimentally and computationally reported value of the T_1 excited state, and the fact that this approximation corrects certain "instabilities" in the triplet states does not guarantee that the computed value is more accurate. Additionally, JMR used the ADC(2)[5–8] method to evaluate the excited states, where the results align with their own TDA–DFT level. However, it is important to note that this method has been recently questioned by Szalay and coworkers after evaluating the potential energy surface in excited states of a series of organic compounds taking as reference results at the coupled cluster level.[9–11]

One aspect that needs to be mentioned is that the use of density functionals with long-range corrections can lead to the appearance of unphysical (ghost) states,[12–14] typically above

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† Electronic supplementary information (ESI) available: Excitation energies for the ghost states. See DOI: https://doi.org/10.1039/d4cp04691a

Table 1 Experimental and computational published results (in cm^{-1}) for excited states of azulene. $\Delta = S_2 - 2T_1$

Azulene results	T_1	S_2	Δ
Nickel & Klemp[2]	13 800	28 300	700
Vosskötter *et al.*[3]	13 900	28 800	1000
Dunlop *et al.*[4] (NEVPT2)	15 383	31 446	680
Pino Rios *et al.*[1]	14 982	31 208	1245
ADC(2) (JMR)	15 420	30 574	−266

1000 nm. For this reason, it is crucial to select results based on the orbitals contributing to the electronic transition. In our OM, we observed the appearance of certain electronic states with orbital contributions that did not correspond to those known for azulene: T_1 = H → L, S_1 = H → L and S_2 = H−1 → L/H → L+1. For example, consider the case of azulene, at the level of theory reported in our OM, the transition energy of the T_1 state corresponds to 1693 cm^{-1} (or 0.21 eV/5906 nm). In addition to this, the contributions of the orbitals do not correspond to the transition mentioned above (among the different contributions, HOMO−9 → LUMO+9 transitions are observed, which are far from the known data). It is also necessary to mention that in some cases, ghost states present negative excitation energies (Table S1 in the ESI†).

These states (T_1, S_1, and S_2) must be correctly assigned for accurate interpretations. We ensured that the values obtained for azulene were not only close to those reported in the literature, but also that the electronic transitions had the expected molecular orbital (MO) contributions. In our OM, the triplet ghost state has been disregarded because neither the numerical value nor the MO contributions align with the references used. The following one has been selected considering the nature of the electronic transition and the value of the T_1 energy using DFT. This point was not adequately explained in our OM, so we take this opportunity to clarify it.

To confirm the results obtained at our level of theory, we reoptimized some of the systems studied in our OM (and shown by JMR in Fig. 3 of their manuscript) to the ωB97xD[15]/def2-TZVP[16] level using Gaussian 16 program[17] and calculated the excited states using the domain-based local pair natural orbital similarity transformed equation of motion coupled cluster singles and doubles (DLPNO-EOM-CCSD) method[18] incorporating spin–orbit corrections, employing the same basis set, and including auxiliary functions for higher computational cost efficiency using ORCA 5.0 software.[19] Table 2 shows the results for azulene and the CN-substituted systems reported by JMR.

The trend $\Delta > 0$ is conserved for azulene (537 cm^{-1}), close to the experimental values reported by Weinkauf *et al.*[3] and Nickel & Klemp.[2] Additionally, the monosubstituted systems CN2 and CN4 present positive values, while for CN1 Δ is negative. The case of CN5 is peculiar since, in our OM, we obtained a value of −447 cm^{-1}, while at the DLPNO-EOM-CCSD level, the value is 1427 cm^{-1}. For the case of the disubstituted systems, the trend remains consistent, except for the case of CN57, which yields a value of 2111 cm^{-1}.

On the other hand, we performed calculations using the TDA. For the case of azulene, the value is negative (−282 cm^{-1}), which deviates significantly from both the experimental and computational values taken as reference, so at this level of theory, it would not meet the criteria used to carry out the SF process. However, the values obtained with TDA for the CN-substituted systems show the same trend (with lower Δ values) and excellent correlation (r^2 = 0.99) compared to those obtained using traditional TD-DFT. It is necessary to mention that our calculations at TD-DFT level correspond with all the mentioned references and are reliable as long as a revision of the numerical values and the nature of the electronic transition is conducted. Without this process, our work could not have been carried out.

In summary, we consider that the results obtained in our OM are adequate and reproducible since they are not only in agreement with experimental results but also with reliable *ab initio* calculations.

However, caution is needed when selecting the electronic states since it is not only essential to match numerically with some reference (either experimental or computational) but also to take into account the contributions of the orbitals to the electronic transition.

We agree with JMR's point indicating that, for the selection of the density functional for the study of excited states using TD-DFT methods, the results should be compared with accurate wavefunction methods. However, we also believe that the use of experimental results (if available) is also very useful and should be considered as long as the experimental conditions can be correctly simulated. An ideal exercise would be using both data to select the most appropriate functional properly. Finally, we concur with JMR that the results of the anti-Kasha behavior of azulene derivatives should be confirmed; that said, it is known that certain azulene-based compounds conserve this anomalous behavior.[20]

Table 2 Energy values for T_1, S_2, and Δ (in cm^{-1}) at the DLPNO-EOM-CCSD/def2-TZVP//ωB97xD/def2-TZVP level. Δ(OM) show the results from our original manuscript and Δ(TDA) show the results at the LC-ωHPBE/6-311G** level using the Tamm–Dancoff approximation

System	T_1[a]	S_2	Δ	Δ(OM)	Δ(TDA)
Azulene[b]	15 715	31 967	537	1244	−282
CN1	15 691	31 312	−71	−1279	−2430
CN2	15 425	31 690	840	2528	949
CN4[c]	13 955	30 073	2163	3741	2284
CN5[c]	14 525	30 476	1427	-447	−1878
CN6	14 499	30 961	1962	4682	2735
CN13	15 839	30 785	−893	−3104	−4107
CN26	14 001	30 579	2578	4624	2975
CN48	13 246	29 115	2623	5581	3537
CN57	13 583	29 278	2111	−1832	−2400

[a] Excitation energies of ghost states can be found in Table S1 of the ESI. [b] Experimental Δ values in Table 1. [c] CN8 = CN4, CN5 = CN7.

Data availability

The data supporting this article have been included in the manuscript.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by the financial support of the National Agency for Research and Development (ANID) through

FONDECYT project 1230571 (R. P.-R.). Powered@NLHPC: this research was partially supported by the supercomputing infrastructure of the NLHPC (ECM-02) of the Universidad de Chile. M. S. is grateful for the financial support from the Ministerio de Ciencia e Innovación (Project PID2023-147424NB-I00) and the Generalitat de Catalunya (Project 2021-SGR-623 and ICREA Academia Prize 2024). D. W. S. acknowledges financial support from the National Science Centre, Poland (2021/42/E/ST4/00332).

Notes and references

1 R. Pino-Rios, R. Báez-Grez, D. W. Szczepanik and M. Solà, *Phys. Chem. Chem. Phys.*, 2024, **26**, 15386–15392.
2 B. Nickel and D. Klemp, *Chem. Phys.*, 1993, **174**, 297–318.
3 S. Vosskötter, P. Konieczny, C. M. Marian and R. Weinkauf, *Phys. Chem. Chem. Phys.*, 2015, **17**, 23573–23581.
4 D. Dunlop, L. Ludvíková, A. Banerjee, H. Ottosson and T. Slanina, *J. Am. Chem. Soc.*, 2023, **145**, 21569–21575.
5 J. Schirmer, *Phys. Rev. A*, 1982, **26**, 2395–2416.
6 A. B. Trofimov and J. Schirmer, *J. Phys. B: At., Mol. Opt. Phys.*, 1995, **28**, 2299–2324.
7 J. Schirmer, *Phys. Rev. A*, 1991, **43**, 4647–4659.
8 J. Schirmer and A. B. Trofimov, *J. Chem. Phys.*, 2004, **120**, 11449–11464.
9 A. Tajti, J. F. Stanton, D. A. Matthews and P. G. Szalay, *J. Chem. Theory Comput.*, 2018, **14**, 5859–5869.
10 A. Tajti, L. Tulipán and P. G. Szalay, *J. Chem. Theory Comput.*, 2020, **16**, 468–474.
11 A. Tajti and P. G. Szalay, *J. Chem. Theory Comput.*, 2019, **15**, 5523–5531.
12 M. Campetella, F. Maschietto, M. J. Frisch, G. Scalmani, I. Ciofini and C. Adamo, *J. Comput. Chem.*, 2017, **38**, 2151–2156.
13 F. Maschietto, M. Campetella, J. Sanz García, C. Adamo and I. Ciofini, *J. Chem. Phys.*, 2021, **154**, 204102.
14 D. Mester and M. Kállay, *J. Chem. Theory Comput.*, 2022, **18**, 1646–1662.
15 J.-D. Chai and M. Head-Gordon, *Phys. Chem. Chem. Phys.*, 2008, **10**, 6615–6620.
16 F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297–3305.
17 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, *Gaussian 16, Rev. B.01*, Gaussian, Inc., Wallingford CT, 2016.
18 R. Berraud-Pache, F. Neese, G. Bistoni and R. Izsák, *J. Chem. Theory Comput.*, 2020, **16**, 564–575.
19 F. Neese, *Wiley Interdiscip. Rev.: Comput. Mol. Sci.*, 2022, **12**, e1606.
20 L. Ou, Y. Zhou, B. Wu and L. Zhu, *Chin. Chem. Lett.*, 2019, **30**, 1903–1907.