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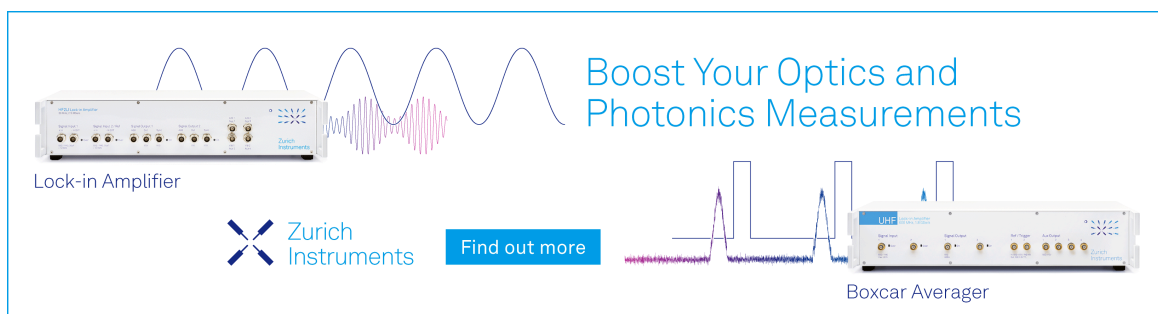
## Accurate non-adiabatic couplings from optimally tuned range-separated hybrid functionals

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# Accurate non-adiabatic couplings from optimally tuned range-separated hybrid functionals

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## AFFILIATIONS

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## ABSTRACT

Precise theoretical calculations of non-adiabatic couplings, which describe the interaction between two Born–Oppenheimer surfaces, are important for the modeling of radiationless decay mechanisms in photochemical processes. Here, we demonstrate that accurate non-adiabatic couplings can be calculated in the framework of linear-response time-dependent density functional theory by using non-empirical, optimally tuned range-separated hybrid (OT-RSH) functionals. We focus on molecular radicals, in which ultrafast non-radiative decay plays a crucial role, to find that the OT-RSH functional compares well to wave-function-based reference data and competes with the accuracy of semi-empirical CAM-B3LYP calculations. Our findings show that the OT-RSH approach yields very accurate non-adiabatic couplings and, therefore, provides a computationally efficient alternative to wave-function-based techniques.

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Radiationless decay mechanisms play an important role in photochemistry,<sup>1–3</sup> particularly in the photostability of organic molecules.<sup>4–6</sup> For example, under irradiation with ultraviolet (UV) light, organic molecules tend to fragment or decompose. However, when a molecule in the excited state encounters a conical intersection (CI) that is a crossing point of two potential energy surfaces,<sup>7,8</sup> energy can dissipate through this crossing without a photon being emitted.<sup>2,9</sup> When this decay mechanism of excitation through a CI occurs fast enough, the molecule can return to the ground state before fragmentation can take place. This occurs, for example, in nucleic acids<sup>5,6</sup> that are building blocks for life on earth.

First-principles calculations can provide deep insights into such non-radiative decay of molecular excited states.<sup>4,5,10,11</sup> When approaching a CI, the motion of electrons and nuclei becomes coupled, and the Born–Oppenheimer (BO) approximation, in which electronic and ionic degrees of freedom are assumed to be decoupled and treated separately, becomes invalid,<sup>12,13</sup> also because two (or more) electronic states can strongly interact at a CI. The terms to augment the BO approximation in order to describe these non-adiabatic interactions among different states are called non-adiabatic couplings (NACs),<sup>14</sup> which play key roles in locating CIs by static calculations<sup>15</sup> as well as in non-adiabatic molecular

dynamics (NAMMD).<sup>16,17</sup> For example, in the surface-hopping variant of NAMMD, the NACs determine the probability of switching from state  $I$  to state  $J$ .<sup>18</sup> Therefore, accurate and efficient techniques for NAC calculations are important for describing radiationless transitions among excited states.

While wave-function-based methods, such as complete active space second-order perturbation theory (CASPT2) and coupled cluster (CC), are very accurate for excited-state calculations,<sup>19</sup> they are computationally very expensive<sup>20</sup> and restricted to small- and medium-sized molecules. In contrast, linear-response time-dependent density functional theory (TD-DFT) is computationally very efficient and can be used even for large molecules.<sup>21</sup> However, at least two important issues need to be considered concerning NAC calculations: first, standard TD-DFT does not give direct access to excited-state wave-functions.<sup>22,23</sup> Nevertheless, since the first calculations of NACs with TD-DFT,<sup>24</sup> various further approaches were developed, including density matrix formalisms,<sup>25</sup> linear<sup>26</sup> and quadratic<sup>27</sup> response theory, and a pseudo-wave-function approach (PWA).<sup>28,29</sup> Second, the accuracy of TD-DFT-based NAC calculations strongly depends on the exchange–correlation (XC) functional.<sup>30,31</sup> In particular, these calculations can show large errors especially when the excited-state character is not captured well by the underlying XC functional.<sup>26,27</sup>

A promising TD-DFT approach is the use of so-called optimally tuned range-separated hybrid (OT-RSH) functionals,<sup>32–34</sup> which can be realized through a range separation of the Coulomb operator in the following way:<sup>35,36</sup>

$$\frac{1}{r} = \frac{\alpha + \beta \operatorname{erf}(\gamma r)}{r} + \frac{1 - [\alpha + \beta \operatorname{erf}(\gamma r)]}{r}, \quad (1)$$

where the choice of the parameters  $\alpha$  and  $\beta$  determines the short- and long-range fractions of Hartree–Fock exchange<sup>35,36</sup> and  $\gamma$  is the range-separation parameter. OT-RSH was shown to provide accurate excited-state properties, including vertical<sup>34,37,38</sup> and 0–0<sup>39</sup> excitation energies, vibronic band shapes,<sup>40</sup> charge transfer (CT) excitations,<sup>32,41–43</sup> and excited-state geometries.<sup>44</sup> Hence, several quantities related to NAC calculations are described accurately by OT-RSH-TD-DFT, which motivates us to consider it as an efficient non-empirical method to accurately describe nonadiabatic effects in molecules.

In this Communication, we investigate the capability of OT-RSH-TD-DFT to accurately model non-adiabatic quantities including NACs. To this end, we consider molecular systems that are known to exhibit interesting excited-state potential energy landscapes, including CIs<sup>45</sup> that can facilitate fast non-radiative decay and could, at least in principle, still be described in the realm of TD-DFT. Specifically, we focus on three molecular radical cations and compare our results to literature data from wave-function-based methods. We find that NACs computed with OT-RSH functionals are in good agreement with CC calculations for molecular radicals, and that from the here considered TD-DFT methods only the semi-empirical CAM-B3LYP functional<sup>35</sup> can compete with this accuracy. We rationalize these findings by highlighting the roles of the energies and orbital character of the states involved in the transitions to demonstrate that OT-RSH can serve as an efficient computational method to properly describe excited-state effects relevant to non-radiative decay mechanisms.

In our OT-RSH calculations, the range-separation parameter was tuned self-consistently by minimizing the difference between the highest occupied molecular orbital (HOMO) and ionization potential (IP) as well as between the lowest unoccupied molecular orbital (LUMO) and electron affinity (EA).<sup>33,36</sup> In this way, piecewise linearity<sup>46,47</sup> of the total energy with respect to fractional occupation numbers is obeyed as closely as possible,<sup>34,48,49</sup> which shares certain similarities with “Koopmans compliant” functionals.<sup>50–52</sup> The fraction of short-range exact exchange,  $\alpha$ , was set to 0.2 since this choice was found to give accurate molecular eigenvalue spectra<sup>36,53</sup> and excited-state geometries<sup>44</sup> that are both important in NAC calculations. Consequently, to ensure the correct asymptotic decay of the XC potential by having full Fock exchange in the long range,  $\beta$  was set to 0.8.

The OT-RSH calculations are compared to literature data from wave-function-based methods and other TD-DFT results obtained by using various other XC functionals (see the [supplementary material](#)), particularly the semi-empirical B3LYP<sup>54</sup> and CAM-B3LYP approaches.<sup>35</sup> To allow for a numerically consistent comparison with the literature, our calculations of the radical cations employed the cc-pVDZ<sup>55</sup> basis set since this is the case for the reference values in Ref. 56 and used the geometries<sup>45</sup> for which the EOM-IP-CCSD values for NACs and energy gaps were

reported.<sup>56</sup> Furthermore, because NACs and NAC forces were studied little in comparison to energy gaps and an absolute error may not appear intuitive, mean relative deviations (MRDs) are shown in the discussion of these two quantities below. The OT-RSH tuning procedure was performed for the neutral ground state and we report data obtained from tuning of the radical cation ground state in the [supplementary material](#). The NAC calculations are performed in the PWA framework<sup>28,29,57</sup> as implemented in Q-Chem 5.3,<sup>58</sup> which uses pseudo-wave-functions constructed from the excitation and deexcitation amplitudes obtained in TD-DFT to compute NACs.<sup>28,29,57</sup>

We investigated three radical cations, namely, uracil, 1,3-cyclohexadiene (CHD), and *cis*-1,3,5-hexatriene (HT) [see Fig. 1(a)]. From previous studies on related molecular systems,<sup>59,60</sup> we expect these compounds to represent challenging cases for TD-DFT, but not due to fundamental constraints of the method as is the case, e.g., in the description of double excitations occurring in H<sub>2</sub>.<sup>61</sup> Figure 1(b) shows our results for the MRD of NACs calculated with different XC functionals for the three radical cations referenced to EOM-CCSD literature values. For an easy comparison, we average across deviations of NACs for individual transitions and report the data for all transitions in the [supplementary material](#) (Tables SII–SIV). Figure 1(b) shows that OT-RSH provides accurate NACs for these systems since MRDs are found to be between 5% and 20%. The accuracy of the OT-RSH results can be put in perspective by comparison to the popular

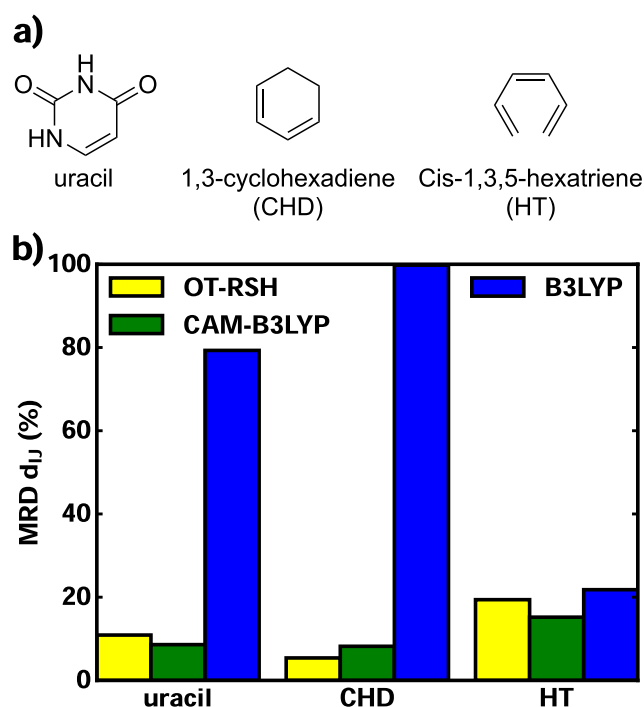


FIG. 1. (a) Chemical structures of the three closed-shell molecules from which the radical cations were derived. (b) MRDs of the NACs calculated with different XC functionals for the three radical cations. The values are compared to EOM-CCSD reference values from the literature (Ref. 56).

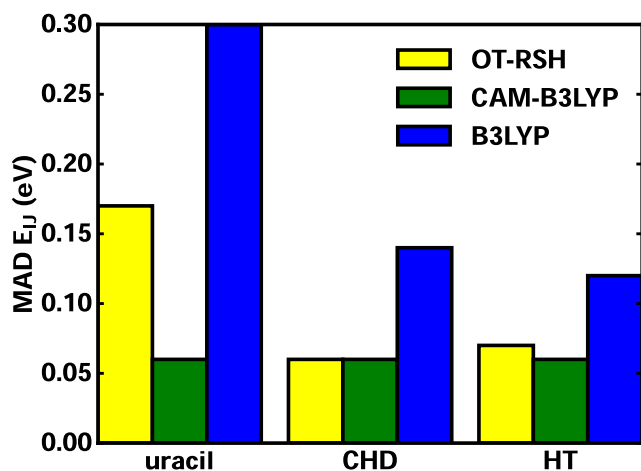
B3LYP functional, which performs significantly worse with the MRDs found to be between 20% and 100%. From the considered TD-DFT methods (see the [supplementary material](#)), we find that only the CAM-B3LYP functional performs similarly well for NACs in these systems with MRDs between 8% and 20%. It is important to note that, while CAM-B3LYP was parameterized empirically for small molecules,<sup>35,54</sup> OT-RSH is tuned by enforcing physical constraints.

In order to further analyze these findings and investigate why OT-RSH produces accurate results, we first recall the definition of NACs  $\vec{d}_{IJ}$ ,<sup>27</sup>

$$\vec{d}_{IJ} = \langle \psi_I | \nabla_{\vec{R}} | \psi_J \rangle = \frac{\langle \psi_I | \nabla_{\vec{R}} \hat{H} | \psi_J \rangle}{E_J - E_I}, \quad (2)$$

where  $\psi_{IJ}$  are wave-functions of two electronic states,  $\nabla_{\vec{R}}$  denotes taking the derivative with respect to nuclear coordinates,  $\hat{H}$  is the Hamiltonian of the system, and  $E_{IJ}$  are the energies of the states. Equation (2) shows that the energy gap between two states is a key factor determining  $\vec{d}_{IJ}$ , especially when close to a CI, the gap,  $E_J - E_I$ , approaches zero and becomes the dominant contribution to  $\vec{d}_{IJ}$ . Conversely, in regions far away from any CI, there can be further factors, such as the character of the orbitals involved in the transition, which may play a significant role in determining NACs. Note that the term “energy gap” in this work denotes an energy difference between two states and not between two orbitals.

To investigate the role of the energy gap in the accuracy of the NAC calculations, we first show in [Fig. 2](#) their mean absolute deviations (MADs). For each system, they were calculated for the energy gaps averaged over all transitions that are reported in the [supplementary material](#) as deviations by OT-RSH, CAM-B3LYP, and B3LYP from EOM-CCSD. The deviations of OT-RSH and CAM-B3LYP from EOM-CCSD are very similar and generally very low. Notably, the somewhat larger but still relatively small deviations ( $\approx 0.15$  eV) of OT-RSH for uracil do not drastically influence the deviations of NACs (cf. [Fig. 1](#)) since these larger deviations



**FIG. 2.** MADs of the energy gaps calculated with different XC functionals for the three radical cations. The values are compared to EOM-CCSD reference values from the literature (Ref. 56).

mostly stem from larger energy gaps that do not strongly contribute to the error of the NACs [see Eq. (2) and [Table I](#)]. It is noted that when the radical cationic ground state is used in the tuning procedure of this molecule, the OT-RSH results become significantly worse (see the [supplementary material](#)). We also find the deviations in the NACs produced by B3LYP to be partially rooted in deviations of the calculated gaps, which are severely underestimated (see [Table I](#)). On the other hand, the trend for deviations of B3LYP NACs and energy gaps differ, as B3LYP by far shows the largest error in NACs for the case of CHD, for which it, however, still produces relatively accurate gaps (cf. [Figs. 1](#) and [2](#) and [Table I](#)). This suggests that the above-mentioned orbital character is the main source of error in the B3LYP calculations of NACs in the case of CHD.

While the errors in the gaps are straightforward to evaluate, quantifying how the character of orbitals influences NAC calculations by a given method is less obvious. To this end, we follow a previous strategy<sup>56</sup> to analyze the NAC force,

$$\vec{h}_{IJ} = (E_J - E_I) \vec{d}_{IJ}. \quad (3)$$

Inserting Eq. (3) into Eq. (2) gives

$$\frac{\vec{h}_{IJ}}{E_J - E_I} = \frac{\langle \psi_I | \nabla_{\vec{R}} \hat{H} | \psi_J \rangle}{E_J - E_I}, \quad (4)$$

and, consequently, leads to an expression for  $\vec{h}_{IJ}$ , which does not depend on the energy gap,

$$\vec{h}_{IJ} = \langle \psi_I | \nabla_{\vec{R}} \hat{H} | \psi_J \rangle. \quad (5)$$

Hence, analyzing the NAC force is particularly insightful when comparing NACs calculated from TD-DFT with different XC functionals that generally under- or overestimate the gaps by varying amounts.

The MRDs for the NAC forces (see [Fig. 3](#)) find OT-RSH and CAM-B3LYP to generally provide very good results. Visual inspection of the orbitals involved in the transitions (shown in [Figs. SI–SIII](#) in the [supplementary material](#)) confirms that these two functionals result in wave-functions that appear to be very similar to the ones obtained with EOM-CCSD for the three radical cations (see Ref. 45). Furthermore, the order of molecular orbitals that contribute most to the transitions is the same for OT-RSH and CAM-B3LYP for the radical cations.

B3LYP, on the other hand, produces a large deviation for the NAC force in the case of CHD. As we show in the [supplementary material](#), the large MRD, in this case, has its origin in the wrong ordering of the  $D_1$  and  $D_2$  states, which also strongly increases the MRD for the NAC in this case (see [Fig. 1](#)) that we have discussed above. Further inspection of the molecular orbitals calculated by B3LYP (see the [supplementary material](#)) shows that it also results in a different orbital ordering compared to OT-RSH and CAM-B3LYP for uracil but agrees with them for the case of HT. Together with the low errors in the gaps for HT, this explains the accurate description of the NACs in this system by B3LYP. These results for the case of B3LYP, together with data obtained by further TD-DFT calculations using different XC functionals, showcase the commonly observed issues of standard TD-DFT calculations for

**TABLE I.** Norms of NACs ( $\|\vec{d}_{IJ}\|$ , 1/bohr) and energy gaps ( $E_{IJ}$ , eV) for EOM-IP-CCSD calculations, as reported in Ref. 56, as well as the absolute deviations produced by the different XC functionals for the three radical cations.

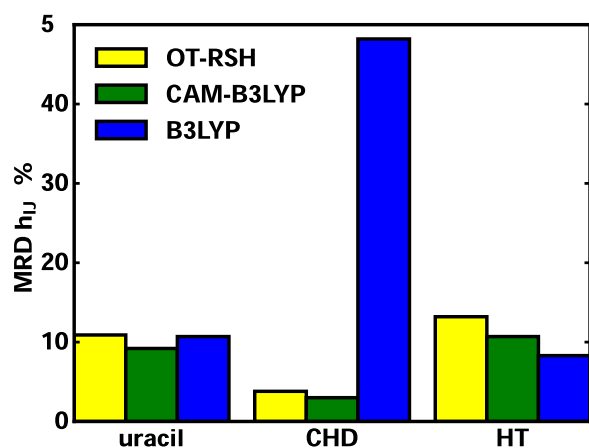
Method	0 → 1		0 → 2		0 → 3		1 → 2		1 → 3		2 → 3	
	$\ \vec{d}_{IJ}\ $	$E_{IJ}$	$\ \vec{d}_{IJ}\ $	$E_{IJ}$	$\ \vec{d}_{IJ}\ $	$E_{IJ}$	$\ \vec{d}_{IJ}\ $	$E_{IJ}$	$\ \vec{d}_{IJ}\ $	$E_{IJ}$	$\ \vec{d}_{IJ}\ $	$E_{IJ}$
Uracil												
EOM-IP-CCSD <sup>56</sup>	0.79	0.60	2.28	1.01	0.38	1.57	1.24	0.41	3.97	0.98	1.00	0.57
Difference between TD-DFT and EOM-IP-CCSD												
OT-RSH	-0.17	0.26	-0.15	0.17	-0.03	0.31	-0.06	-0.09	-0.11	0.04	-0.23	0.13
CAM-B3LYP	-0.08	0.09	0.18	0.02	-0.01	0.08	-0.15	-0.07	0.18	-0.02	-0.16	0.05
B3LYP	2.34	-0.45	1.00	-0.28	0.12	-0.55	-0.32	0.17	-0.68	-0.11	0.59	-0.27
CHD												
EOM-IP-CCSD <sup>56</sup>	0.88	2.73	0.57	2.94	0.40	3.41	5.82	0.21	2.23	0.68	8.71	0.47
Difference between TD-DFT and EOM-IP-CCSD												
OT-RSH	0.06	0.11	-0.01	0.09	0.00	0.07	0.72	-0.02	0.23	-0.04	0.10	-0.02
CAM-B3LYP	0.04	0.11	-0.01	0.06	0.00	0.05	1.66	-0.05	0.31	-0.06	0.07	-0.02
B3LYP	-0.28	0.03	0.26	-0.10	0.02	-0.21	10.48	-0.13	6.52	-0.24	-3.82	-0.11
HT												
EOM-IP-CCSD <sup>56</sup>	1.13	1.97	0.68	3.01	0.41	3.61	1.62	1.04	1.12	1.65	3.34	0.60
Difference between TD-DFT and EOM-IP-CCSD												
OT-RSH	0.23	-0.01	0.06	0.10	0.07	-0.02	-0.37	0.11	0.01	-0.02	1.55	-0.13
CAM-B3LYP	0.15	0.01	0.05	0.10	0.05	-0.01	-0.35	0.09	0.01	-0.03	1.17	-0.11
B3LYP	-0.04	0.02	0.04	-0.01	0.04	-0.22	-0.37	-0.03	0.18	-0.25	2.48	-0.21

non-adiabatic properties.<sup>26,27</sup> For example, it has been shown before that other conventional hybrid functionals can be similarly inaccurate for NACs as B3LYP.<sup>26,27</sup> The OT-RSH results for NACs, gaps, and wave-function characters show that, on the other hand, this

functional allows for reliable descriptions of non-adiabatic properties in TD-DFT with an accuracy that is close to EOM-CCSD reference values and on par with the performance of the empirical CAM-B3LYP functional.

Finally, we note that, in this work, we used pre-calculated molecular geometries for an easy and transparent comparison with literature data when one could also optimize the geometry by each method. It is interesting that we find NAC calculations with B3LYP, performed on B3LYP-optimized geometries instead, to strongly reduce (close to 50%) the MRD for the NACs in the case of uracil and CHD. However, the same procedure yields deviations from EOM-CC values for NACs that are essentially doubled for HT and, for all three molecules, become larger for either the energy gaps (CHD), NAC forces (uracil), or both (HT). This indicates an intricate interplay of effects in the level of theory used to optimize the geometry and the NAC calculations, which remains as an interesting open question for future studies.

In summary, we investigated the capability of OT-RSH functionals to predict accurately and reliably NACs of molecular radicals, which is a significant challenge for TD-DFT. Focusing on three model systems for which reference values from the literature were available, we showed that OT-RSH compares well to EOM-CCSD calculations, can compete with the accuracy of the semi-empirically parameterized CAM-B3LYP method, and greatly outperforms the B3LYP functional when calculating NACs. Our analysis demonstrated that this is because OT-RSH delivers several

**FIG. 3.** MRDs of the NAC forces calculated with different XC functionals for the three radical cations. The values are compared to EOM-CCSD reference values from the literature (Ref. 56).

excited-state properties that are required for NAC calculations with high precision, particularly a correct description of excited-state characters and energy gaps. Conversely, we also showed that larger deviations produced by other functionals can often be traced back to underestimations of energy gaps, erroneous descriptions of excited-state characters, and spurious mixing and wrong ordering of orbitals. We conclude that TD-DFT calculations with the OT-RSH functional are an efficient and accurate first-principles method to compute non-adiabatic properties of molecular systems. In view of the non-empirical tuning procedure in OT-RSH, we expect it to provide reliable NAC calculations for a great variety of molecular systems.

See the [supplementary material](#) for additional data regarding tuned range-separation parameters for the radical cations, norms of NACs, energy gaps, norms of NAC forces, and wave-functions of orbitals involved in the transitions.

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## AUTHOR DECLARATIONS

### Conflict of Interest

The authors have no conflicts to disclose.

### Author Contributions

**Bernhard Kretz:** Data curation (equal); Investigation (equal); Validation (equal); Visualization (equal); Writing – original draft (equal); Writing – review & editing (equal). **David A. Egger:** Conceptualization (equal); Investigation (equal); Supervision (equal); Writing – original draft (equal); Writing – review & editing (equal).

### DATA AVAILABILITY

The data that support the findings of this study are available within the article and its [supplementary material](#).

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