Regarding the use and misuse of retinal protonated Schiff base photochemistry as a test case for time-dependent density-functional theory

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The excited-state relaxation of retinal protonated Schiff bases (PSBs) is an important test case for biological applications of time-dependent (TD) density-functional theory (DFT). While well-known shortcomings of approximate TD-DFT might seem discouraging for application to PSB relaxation, progress continues to be made in the development of new functionals and of criteria allowing problematic excitations to be identified within the framework of TD-DFT itself. Furthermore, experimental and theoretical ab initio advances have recently lead to a revised understanding of retinal PSB photochemistry, calling for a reappraisal of the performance of TD-DFT in describing this prototypical photoactive system. Here, we re-investigate the performance of functionals in (TD-)DFT calculations in light of these new benchmark results, which we extend to larger PSB models. We focus on the ability of the functionals to describe primarily the early skeletal relaxation of the chromophore and investigate how far along the out-of-plane pathways these functionals are able to describe the subsequent rotation around formal single and double bonds. Conventional global hybrid and range-separated hybrid functionals are investigated as the presence of Hartree-Fock exchange reduces problems with charge-transfer excitations as determined by the Peach-Benfield-Helgaker-Tozer Λ criterion and by comparison with multi-reference perturbation theory results. While we confirm that most functionals cannot render the complex photobehavior of the retinal PSB, do we also observe that LC-BLYP gives the best description of the initial part of the photoreaction. © 2015 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4916354]

I. INTRODUCTION

Just as density-functional theory (DFT)¹–⁵ has become the standard workhorse for electronic structure calculations on the ground states of large systems or when large numbers of electronic structure calculations are required for medium-size systems, so time-dependent (TD) DFT⁶–¹⁰ has become the standard workhorse for electronic structure calculations of excited states when applicable, particularly when other methods prove to be too expensive. It is natural then that TD-DFT should be used for photochemical modeling and indeed it seems fair to say that TD-DFT has become one of many standard tools in the photochemical modeller's toolbox. However, photochemical processes are complicated and also very sophisticated methods can fail to give even a qualitatively correct description of some aspect of a photochemical problem.¹¹ It is known that the domain of applicability of standard TD-DFT is severely restricted when it comes to photochemical reactions. However, the border defining what is a conservative “safe use” of TD-DFT continues to expand with the development of new functionals and techniques. (The supplementary material¹² provides a brief review of the current state of TD-DFT for photochemical applications.) Sufﬁce it to say for the moment that the present recommendation is to use functionals with some contribution of exact exchange⁶,¹⁰ and to restrict the use of conventional TD-DFT to the Franck-Condon (FC) region of photochemical reactions.⁸,¹⁰ Even here, as with standard ground-state Kohn-Sham DFT, one can and should be properly skeptical¹³ and validate methodology on similar systems and properties before using it to model these properties in interesting new systems.

One intensely interesting system is, of course, the photochemistry of vision. In visual opsin pigments like rhodopsin, the chemical reaction that ultimately leads to vision is initiated by an ultrafast photosomerization of the retinal chromophore from the 11-cis to the all-trans isomer.¹⁴–¹⁶ Numerous experimental¹⁶–²⁹ and theoretical²⁹–⁵⁶ studies have therefore been devoted to understand the excited-state relaxation of the retinal chromophore as well as the role of the protein environment in modulating the speed of photoisomerization. Much effort has also been put into trying to make DFT-based methods work for describing the photochemistry of vision⁴²,⁵⁵,⁵⁷–⁶⁶ with varying degrees of success. One of the problems has however been the confusion regarding the quality of ab initio wave function calculations against which to compare these DFT-based
methods. In the past, TD-DFT has been assessed against calculations with the complete active space self-consistent field (CASSCF) method for the description of the photochemistry of retinal protonated Schiff base (PSB) models and been found wanting.\textsuperscript{50,51,69}

In recent years, progress in femtosecond spectroscopy and theoretical calculations has led to an appreciation that CASSCF provides only a first approximation to the emerging details of retinal PSB photophenomena. In particular, Valsson and Filippi recently investigated the excited-state relaxation of a reduced retinal model (consisting of four double bonds) in the gas phase\textsuperscript{56} with methods that offer a more balanced description of both static and dynamic correlation, namely, CASPT2 (i.e., CASSCF with second-order perturbation theory corrections) and quantum Monte Carlo (QMC). The minimum energy pathway (MEP) on the $S_1$ surface was found not to lead to bond inversion but rather to a more delocalized simultaneous weakening of several formal double bonds. The resultant rather flexible retinal chromophore can then follow distinct pathways characterized by rotation around either a formal single or a formal double bond. While a small barrier is found towards double-bond rotation, the MEP at the CASPT2 level corresponds to single-bond rotation and does not lead to a conical intersection, that is, nonreactive as regards the photoisomerization (see Fig. 1). Olivucci and co-workers reported recently a similar behavior for a smaller retinal model consisting of three double bonds,\textsuperscript{41} where also the MEP between the first minimum encountered in the single-bond rotation and the conical intersection region was mapped out at the CASPT2 level. It should be emphasized that these results are completely consistent with recent experimental work\textsuperscript{25} providing evidence that following the MEP leads to an $S_0$ minimum which subsequently returns to the original $S_0$ minimum by fluorescence. In contrast, photochemical isomerization seems to require surmounting a transition state on the $S_1$ surface before the conical intersection expected from qualitative reasoning and CASSCF calculations is attained.

It is thus time to return to the problem of assessing TD-DFT for modeling the initial steps of the photochemical pathway of singlet excited retinal PSB models in light of the continual evolution of functionals for (TD-)DFT and more reliable \textit{ab initio} reference data, which we expand here with new benchmark CASPT2 calculations on larger retinal models. In particular, several functionals have been criticized in the past for leading to an excited chromophore unstable towards single-bond rotations\textsuperscript{50,51} a behavior which is at least qualitatively consistent with what CASPT2 is telling us. Furthermore, recent years have seen the development of criteria allowing problematic excitations to be identified within the framework of TD-DFT itself, the best known and currently most used being the $\Lambda$ criterion by Peach et al.\textsuperscript{70–76} Given the present state-of-the-art of TD-DFT (see the supplementary material\textsuperscript{12}), it is reasonable to hope that TD-DFT with a properly chosen functional should be able to describe the MEP/fluorescence mechanism and that newer developments in TD-DFT methodology may eventually help describe photochemical processes near the conical intersection. In this paper, we place particular emphasis on the ability of global hybrid (GH) and range-separated hybrid (RSH) functionals to describe the initial out-of-plane motion of the singlet photochemistry of retinal PSB models. While we wish to emphasize that our ambitions in testing functionals for the TD-DFT description of retinal are relatively conservative (the conical intersection region being beyond the scope of the present paper), we find the results from this new assessment are more optimistic than those of previous assessments.

The paper is organized as follows. In Sec. II, we present the computational details and, in Sec. III A and Secs. III B–III D, the in-plane and out-of-plane relaxation studies, respectively. The discussion and conclusions are given in Sec. IV. The performance of TD-DFT in describing the vertical excitation energy at FC point, mainly focusing on the geometrical dependence of the excitations and on the electronic structure, is discussed in the supplementary material.\textsuperscript{12}

II. COMPUTATIONAL DETAILS

The retinal models studied in this work are shown in Fig. 2 and range from the minimal protonated Schiff base model (Fig. 2(a)) to the PSB5(1) model (Fig. 2(d)) which is only missing the $\beta$-ionone of the full 11-cis retinal chromophore (see Fig. S3 in the supplementary material\textsuperscript{12}). We employ the ground-state geometries obtained in our previous study\textsuperscript{56} and optimized within DFT with the B3LYP functional and the cc-pVDZ basis set. We use the naming convention PSBx(y) where x and y indicate the number of double bonds and methyl groups, respectively.

Most reference CASPT2, NEVPT2, QMC, CC2, coupled cluster singles and doubles (CCSD), and approximate coupled cluster singles, doubles, and triples (CC3) results are taken from our calculations in Refs. 56 and 77. The reference out-of-plane CASPT2 geometries for PSB5(1) (Fig. 2(d)) are obtained in the present work. For the CASPT2 calculations, all

FIG. 1. The excited-state out-of-plane minima obtained with CASSCF and CASPT2. The solid arrows indicate MEPs while the dashed (red) arrow indicates the presence of a transition state on the $S_1$ surface.
single-point excitations are computed with the single-state variant, while all geometrical optimizations are performed with the multi-state variant. For further details on the highly-correlated calculations, we refer the reader to Refs. 56 and 77.

All TD-DFT calculations are performed with the 

\[ \text{CAM-B3LYP} \]

code and default convergence criteria for the excited-state geometrical relaxations. The calculations of the Peach-Benfield-Helgaker-Tozer \(^{70,71}\) criterion for the excited-state TD-DFT geometries are performed using the \textsc{dantos}2011\(^{79-81}\) code. This code does not support the LC-BLYP functional, so we employ the CAM-B3LYP orbitals when calculating the \( \Lambda \) criterion for the LC-BLYP excited-state geometries. Thus, we are implicitly assuming that differences in optimized geometries due to choice of functional are more important than orbital differences, which seems a reasonable first approximation.

### A. Exchange-correlation functionals

All calculations carried out in this paper are spin-restricted. We list the exchange-correlation functionals used in the TD-DFT calculations, their references, and relevant parameters in Table I. For the purpose of analysis, we broadly classify them into three groups: Semi-local functionals with no Hartree-Fock exchange such as generalized gradient approximations (GGA) or meta-GGAs, global hybrids (GH) with a fixed amount of Hartree-Fock exchange (HFX), and range-separated hybrid (RSH) functionals with a variable percentage of Hartree-Fock exchange, depending on the distance between electrons.

For the GH, the relevant parameter is the fixed amount of Hartree-Fock exchange while, for the long-range corrected functionals, we have the percentage of Hartree-Fock exchange at short (HFX-SR) and long range (HFX-LR) along with a damping parameter (\( \omega \)) which controls the decay of the short-range DFT exchange. For more information on the RSH functionals and their construction, we refer the reader to the original references.

We note that the LC-GGA long-range correction of Refs. 94–96 can be applied to any semi-local DFT functional. Here, we combine this correction with the BLYP, PBE, and M06-L functionals, which yield the LC-BLYP, LC-PBE, and LC-M06-L long-range corrected functionals, respectively.

![Model retinal chromophores: A PSB3(0), B PSB3(1), C PSB4(1), and D PSB5(1). The naming PSB(x,y) denotes the number of double bonds and methyl groups, x and y, respectively. The atom numbering for the full 11-cis retinal chromophore is used for all models (see Fig. S3 in the supplementary material)\(^{72}\), so the cis bond is always between C\(_{11}\) and C\(_{12}\). The torsional angles are defined as \( \theta = \text{Dih}(C_{10′}-C_{11}-C_{12}-C_{13}) \) and \( \gamma = 180° - \text{Dih}(C_{11}-C_{12}-C_{13}-C_{14}) \).](https://jchemphys.aip.org/authors/rights-and-permissions)
preferentially single-bond rotation reaching a very flat region of the PES but can also follow a path of double-bond rotation towards a conical intersection.

The behavior of the PSB4(1) chromophore is illustrated in Fig. 3 where we compare the ground- and excited-state CASPT2 minimum energy path (MEP) with the CASPT2 energies computed along the CASSCF MEP (panel (a)). The CASPT2 MEP proceeds mainly along a rotation around the single bond C_{12}–C_{13} (torsional angle γ), while there is very little rotation around the double bond C_{11}–C_{12} (the angle θ is less than 13° along the whole path). At an angle γ of about 43.6°, the system encounters a small barrier to rotation of 0.03 eV beyond which one finds an optimal structure characterized by a much larger angle, γ = 112.7° (results not shown). The excited-state energies along the CASPT2 MEP and up to the second minimum are rather constant and the excitation gap is always very large. This behavior is very different from the CASSCF MEP, which proceeds via rotation around the double bond and reaches a conical intersection region.

If we perform a constrained geometrical optimization at the CASPT2 level along the double bond, we obtain another excited-state CASPT2 path, characterized by a very small barrier of around 0.06 eV and leading to a conical intersection (panel (b)). Therefore, in contrast to the conventional CASSCF picture, CASPT2 yields a rather flexible PSB4(1) retinal model in the excited state, which can access two pathways for the excited-state relaxation, characterized by a rotation around either a single or a double bond, the former being non-reactive (not leading to a conical intersection) and the latter being reactive (leading to a conical intersection). On the other hand, if we perform a constrained geometrical optimization at the CASSCF level along the single bond (panel (c)), the system is unstable towards double bond rotation: the optimization for γ smaller than 40° results in a large double-bond rotation (θ ≈ 75°–90°), leading to the conical intersection region (results not shown). Only when γ is larger than 40°, we obtain a stable structure characterized by small values of the θ angle. Therefore, the CASSCF path presented in Fig. 3 is of minor chemical significance since it cannot be reached from the FC region.

Our analysis of the performance of TD-DFT for retinal relaxation will begin with a study of the in-plane excited-state minima of models PSB3(1), PSB4(1), and PSB5(1). Imposing planarity allows us to assess the description of the initial skeletal relaxation of the chromophore as also done in a recent TD-DFT study,[10] which however only investigated a very small subset of the functionals employed here. In particular, while a comparison with our planar reference structures permits us to rule out many functionals quickly, only the analysis of the out-of-plane relaxation along the single- and double-bond paths provides a definite indication of the actual ability of a theory to describe retinal relaxation. Such a benchmark study is not yet available in the literature and represents the core of this work.

Finally, we stress that, in analyzing the performance of a method to describe the excited-state PES of retinal, we always consistently employ the same method and functional to obtain both the excited-state geometries and energies. As we show in the supplementary material,[12] the procedure often used to evaluate the energies with one method with geometries obtained from a different method—for example, TD-DFT energies calculated using geometries from a CASSCF MEP as was done in Ref. 40—may lead to incorrect conclusions about the quality of some TD-DFT functionals.

### A. In-plane relaxation

We compute here the excited-state minima of models PSB3(1), PSB4(1), and PSB5(1) imposing planar (C_s) symmetry. To analyze the results, we focus on the BLA in the excited
state, which we define as the difference between the averages of formal single and double C–C bonds, where “formal” refers to the ground-state structure. Therefore, if $\text{BLA} < 0$ in the excited state, there is bond inversion with respect to the ground state since formal single bonds become double and vice versa. We expect that rotation out-of-plane should preferentially occur around formal double bonds if $\text{BLA} < 0$, and around formal single bonds if $\text{BLA} > 0$. If $\text{BLA} \approx 0$, we expect no preference and the rotation out-of-plane could proceed around either single or double bonds. We note that, in the BLA, we do not include the C–N bond, which is normally much shorter than the other double bonds.

The excited-state BLAs are presented in Fig. 4. All models show similar trends, so we do not distinguish between them in the discussion. As shown in panel (a), the CASSCF method yields a large negative BLA corresponding to a pronounced bond inversion while all higher-level methods, CC2, CASPT2, and CCSD, give a positive BLA and thus exhibit no bond inversion. In panel (b), we show GGAs and GHs, which present the well-known problem that they give an enhanced BLA compared to the ground state. The trend for the hybrids is also quite clear: the BLA monotonically decreases as the amount of HFX is increased and reaches values comparable to CASPT2 with M06-2X and M06-HF. If we compare to the BLA range spanned by the CASPT2 and CCSD values, the optimal amount of HFX appears to be somewhere between 54% and 100%, which is disturbingly high compared to the expected optimal theoretical value of 25%.102

The RSH (LRC) functionals are shown in panel (c) and give considerable smaller variations than the hybrids, with all values falling between the BLAs of M06-2X and M06-HF. The largest and smallest BLAs are given by CAM-B3LYP and LC-BLYP, respectively. This is consistent with the fact that CAM-B3LYP and LC-BLYP have the smallest and largest amount of exact exchange, respectively, while other functionals fall somewhere in-between. We find that LC-PBE, LC-M06-L, and LC-BLYP give exactly the same BLA and also the use of B3LYP and B3P86 gives very similar results (see Tables S14–S16 in the supplementary material).12 This indicates that, for retinal, the amount of HFX is the main factor in determining the bond lengths while the exact form of the pure DFT part (e.g., GGA versus meta-GGA) is not so important. This has been noted before for these models101 and we observe the same behavior for the vertical excitations as discussed in the supplementary material.12

B. Out-of-plane relaxation for the PSB4(1) model

We now lift planar symmetry in the excited-state relaxation of the PSB4(1) model. Since the initial in-plane skeletal relaxation results in a floppy chromophore which can follow single- and double-bond rotations, the relevant torsional angles are $\theta$ and $\gamma$ for the rotation around the formal double bond C11–C12 and the adjacent formal single bond C12–C13, respectively (see Fig. 2). We start the TD-DFT, CASSCF, and CASPT2 optimizations from the B3LYP, CASSCF, and CASPT2 ground-state geometry, respectively.

We first optimize the PSB4(1) model starting from the FC region and determine the optimal out-of-plane excited-state structure. We then focus on the rotational behavior of the B3LYP, CAM-B3LYP, and LC-BLYP functionals which are representative of a rather different TD-DFT behavior. While CAM-B3LYP has a more accurate in-plane BLA and a significantly larger adiabatic energy, B3LYP and CAM-B3LYP behave similarly with respect to single- and double-bond rotation and very differently from the LC-BLYP functional.
1. Out-of-plane minimum

For a large subset of representative TD-DFT functionals, we compare the out-of-plane optimal structure of the PSB4(1) model with the results of highly-correlated calculations in Table II. In line with what has been discussed above for the MEP, the CASPT2 optimal structure reachable from the FC region is characterized by a rotation mainly around a formal single bond, (C_{12}–C_{13}), with an angle \( \gamma = 43.6^\circ \). The system encounters then a small barrier to rotation of 0.03 eV beyond which one finds a second, lower minimum with \( \gamma = 112.7^\circ \). CC2 yields an optimal structure similar to CASPT2 but the rotation around \( \gamma \) is barrierless.

The DFT functionals give different excited-state minima depending on the value of BLA obtained in the excited-state planar relaxation and, as the planar BLA decreases, the optimal structure switches from a CASPT2- to a CASSCF-like minimum. BLYP and B3LYP are at one extreme with their significantly enhanced BLA with respect to the ground state, which is largely preserved in the rotation out of plane. The optimal BLYP and B3LYP structures are characterized by an angle \( \gamma \approx 85^\circ \), in reasonable agreement with CASPT2 and CC2, and an adiabatic excitation which is however significantly red shifted compared to the highly-correlated values. As the amount of HFX increases, the planar BLA decreases and the optimal structure changes character from a rotation around the C_{12}–C_{13} single bond to a rotation around the C_{11}–C_{12} double bond. At the other extreme of BLYP and B3LYP, the M06-HF functional yields the smallest in-plane BLA and a minimum close to a conical intersection with a rotation around the double bond, C_{11}–C_{12}, of \( \theta \approx 86^\circ \). This structure is similar to the CASSCF one.

The in-plane values of the BLA obtained with the different functionals allow us to categorize the corresponding out-of-plane behaviors. The functionals (M06-2X, CAM-B3LYP, and \( \omega \)B97XD) with an in-plane BLA > 0.025 Å give distortions around the formal single bond rather similar to BLYP and B3LYP but describe much better the optimal BLA and the adiabatic excitations. The functionals (\( \omega \)B97X, \( \omega \)B97, and LC-BLYP) with an in-plane BLA < 0.025 Å display a first excited-state minimum with much smaller rotation around the C_{12}–C_{13} single bond and an almost equal amount of rotation around the C_{11}–C_{12}, when the optimization is started from the B3LYP ground-state geometry. As one can also observe for the LC-BLYP functional in Fig. 6, there is a very small barrier of less than 0.08 eV at \( \gamma \approx 45^\circ \) for rotation to larger angles as we also encounter in the CASPT2 excited-state MEP. If we start the excited-state optimization from a structure beyond this barrier (e.g., for values of \( \gamma = 80^\circ \)), we obtain that the \( \omega \)B97X, \( \omega \)B97, and LC-BLYP functionals have rather similar excited-state minima as the other functionals, and adiabatic excitations which are a bit higher but in good agreement with the highly-correlated values. Furthermore, the excited-state energies for the \( \omega \)B97X, \( \omega \)B97, and LC-BLYP functionals do not decrease as much as for the other functionals, indicating that they have a flatter excited-state potential energy surface starting from the FC region, in general agreement with the CASPT2 results. We note that the use of different GGAs or meta-GGAs in the LC

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<th>In-plane</th>
<th>Out-of-plane</th>
<th>( \theta )</th>
<th>( \gamma )</th>
<th>( E_1 )</th>
<th>( E_{exc} )</th>
<th>( f )</th>
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\(^a\)Reference 56.
\(^b\)Optimization does not converge, approximate values.
\(^c\)CASSCF oscillator strengths.
\(^d\)Obtained starting at \( \gamma = 75.0^\circ \) (beyond barrier).
\(^e\)Obtained starting at \( \gamma = 80.0^\circ \) (beyond barrier).
Constrained geometrical excited-state optimization of the PSB4(1) model (C) for fixed torsional angle \( \theta \) (formal double-bond rotation) obtained within TD-DFT and CASPT2. We plot the BLA (panel (a)), the local BLA (panel (b)), the torsional angles \( \gamma \) for single-bond rotations (panel (c)), the ground- and excited-state energies (panel (d)), and the \( \Lambda \) values along the TD-DFT paths (panel (e)).

**2. Double-bond rotation**

We summarize the results for the constrained rotation \( \theta \) around the double bond, \( C_{11}–C_{12} \), in Fig. 5. The B3LYP and CAM-B3LYP functionals give substantially different results from LC-BLYP and CASPT2 as the former are unstable towards single-bond rotations and, at small \( \theta \), yield large rotation around \( C_{12}–C_{13} \) single bond with absolute values of \( \gamma \) of about 90°. These values of \( \theta \) and \( \gamma \) correspond to the excited-state minima obtained in the unconstrained optimization (see Table II) and yield a decrease of about 0.7 eV and 1.5 eV in the CAM-B3LYP and B3LYP excited-state energies, respectively. Further increasing the value of \( \theta \) significantly raises the excited-state energies, which indicates that there is a large barrier for double-bond rotations.

LC-BLYP gives very different results and agrees for most part with CASPT2. There is no large single-bond rotation and the angle \( \gamma \) maintains a value of 20° along the constrained path, similar to the CASPT2 constrained path and the unconstrained LC-BLYP optimization. The LC-BLYP excitation energies are rather constant up to \( \theta = 45° \) and there seems to be no significant barrier for double-bond rotation while CASPT2 displays a small barrier of 0.06 eV.\(^5\) Then, for \( \theta \) between 45° and 50°, there is a sudden increase/decrease of the ground/excited-state energy, which brings the LC-BLYP excitation gap to almost zero. Therefore, the LC-BLYP constrained path leads to a conical intersection region similarly to CASPT2. Although the HOMO-LUMO gap is not zero, we encounter serious convergence difficulties for \( \theta \) beyond about 50°. Ground-state convergence difficulties are often associated with imaginary excitation energies in response theory calculations as explained in the supplementary material.\(^12\) While the Kohn-Sham gap is still large (about 5 eV) also at \( \theta = 50° \), we cannot converge the ground-state calculation and the corresponding LC-BLYP constrained optimization for larger values of \( \theta \) with the code employed here. We note that one difference of the LC-BLYP results compared to CASPT2 is that the global BLA remains positive for all values of \( \theta \). Nevertheless, a local BLA, defined only for the three bonds from \( C_{10} \) to \( C_{13} \) where the rotation occurs, shows that LC-BLYP is also characterized by bond-inversion around the \( C_{11}–C_{12} \) bond, although the value of the local BLA is considerably smaller. Even though the CASPT2 results presented in Fig. 5 display a regular behavior for \( \theta \) less than 60°, we note that the CASPT2 approach might encounter difficulties closer to the conical intersection.\(^3\)\(^8\)\(^9\)\(^10\)\(^4\)

We now wish to assess the degree of charge-transfer character along the reaction paths since we know that charge-transfer excitations typically improve with the amount of HFX in conventional or RSH hybrids.\(^76\) In particular, we also evaluate the \( \Lambda \) criterion\(^77\)–\(^76\) along the TD-DFT paths as illustrated in Fig. 5 (panel (e)) following the procedure described in Sec. II. The \( \Lambda \) values for the B3LYP and CAM-B3LYP functionals are very small (about 0.2) for all structures, indicating a charge-transfer excitation which is likely to be underestimated by B3LYP but whose underestimation may be corrected by the CAM-B3LYP functional. Interestingly, \( \Lambda \) is significantly larger along the LC-BLYP path, indicating a significantly different, and less problematic, nature of the excitation along this path (i.e., it is not of charge-transfer type for this functional). In this region, which continues up to about \( \theta = 45° \), we find the LC-BLYP results to be curiously similar to the CASPT2 results as regards excitation energy, pathway (angle \( \gamma \)), and BLA. Although it might seem that LC-BLYP is able to pull off the remarkable feat of including both static and dynamic correlation as does CASPT2, all is not rosy for the LC-BLYP functional as this functional is also the one
which displays the strongest triplet instability as shown in Table III. In fact, even the \( \theta = 0^\circ \) structure is characterized by a imaginary triplet excitation energy (traditionally represented as a negative real value), which signals that a closed shell Kohn-Sham description of the ground state is not adequate at this geometry.\(^6,105-108\) (see also the supplementary material\(^{12}\)). In such a case, we would usually expect the Tamm-Dancoff approximation (TDA)\(^{109}\) to improve the quality of the potential energy surfaces because of a pseudo-variational principle resulting from the close resemblance to configuration interaction singles.\(^8,105,108\) Results with and without the TDA are shown for TD-LC-BLYP excitation energies in Table IV. As expected, the TDA makes a dramatic difference for the triplet excitation energies along the original LC-BLYP path. Often (but not always) a triplet instability is associated with a “near singlet instability” in which (the square of) the corresponding singlet excitation also plummets when (the square of) the triplet excitation energy plummets. Remarkably, there is no notable near singlet instability seen in Table IV. This more dramatic collapse of the triplet excitation energies compared with singlet excitation energies has been noted before for the range-separated hybrid CAM-B3LYP functional.\(^{107}\) Instead, the TDA singlet values are a bit higher than the full values but not dramatically so compared to what happens with the triplet energies. Nevertheless, the structures obtained in the constrained optimization for fixed \( \theta \) angles with LC-BLYP in combination with the TDA parallel the CAM-B3LYP values and are therefore very different from the CASPT2 reference (see Table S4 and Fig. S11 in the supplementary material\(^{12}\)).

Further investigation shows that the \( S_1 \) and \( T_1 \) excitations are a case where the singlet is dominated by the HOMO \( \rightarrow \) LUMO transition orbital but that the corresponding triplet involves this transition and a mixture of many more configurations. Thus, it is far from obvious that the triplet instability should necessarily signal problems with this singlet state in this case. In fact, our findings indicate otherwise as the \( S_1 \) results are surprisingly similar to those of our CASPT2 calculations. Finally, in Fig. 5, we also report the CC2 excited-state constrained path of double-bond rotation since this approach

<table>
<thead>
<tr>
<th>( \theta ) (°)</th>
<th>( S_1 )</th>
<th>( S_2 )</th>
<th>( T_1 )</th>
<th>( T_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>GS</td>
<td>3.67 (3.94)</td>
<td>5.67 (6.01)</td>
<td>0.69 (1.78)</td>
<td>2.94 (3.33)</td>
</tr>
<tr>
<td>0</td>
<td>3.41 (3.69)</td>
<td>5.37 (5.67)</td>
<td>-0.48 (1.55)</td>
<td>2.79 (3.16)</td>
</tr>
<tr>
<td>10</td>
<td>3.35 (3.63)</td>
<td>5.31 (5.59)</td>
<td>-0.56 (1.50)</td>
<td>2.76 (3.13)</td>
</tr>
<tr>
<td>20</td>
<td>3.27 (3.56)</td>
<td>5.29 (5.59)</td>
<td>-0.72 (1.42)</td>
<td>2.75 (3.12)</td>
</tr>
<tr>
<td>30</td>
<td>3.16 (3.46)</td>
<td>5.27 (5.58)</td>
<td>-0.90 (1.30)</td>
<td>2.76 (3.11)</td>
</tr>
<tr>
<td>40</td>
<td>2.97 (3.28)</td>
<td>5.22 (5.53)</td>
<td>-1.10 (1.10)</td>
<td>2.76 (3.09)</td>
</tr>
<tr>
<td>50</td>
<td>2.73 (3.06)</td>
<td>5.13 (5.44)</td>
<td>-1.21 (0.90)</td>
<td>2.74 (3.06)</td>
</tr>
<tr>
<td>60</td>
<td>2.52 (2.86)</td>
<td>5.04 (5.34)</td>
<td>-1.32 (0.79)</td>
<td>2.72 (3.04)</td>
</tr>
<tr>
<td>70</td>
<td>2.34 (2.62)</td>
<td>4.97 (5.24)</td>
<td>-1.43 (0.69)</td>
<td>2.70 (3.02)</td>
</tr>
<tr>
<td>80</td>
<td>2.17 (2.38)</td>
<td>4.91 (5.16)</td>
<td>-1.55 (0.59)</td>
<td>2.68 (3.00)</td>
</tr>
<tr>
<td>90</td>
<td>2.01 (2.15)</td>
<td>4.85 (5.08)</td>
<td>-1.67 (0.50)</td>
<td>2.66 (2.98)</td>
</tr>
</tbody>
</table>

**TABLE IV.** TD-LC-BLYP excitation energies in eV of the first two singlet (\( S_1 \) and \( S_2 \)) and triplet (\( T_1 \) and \( T_2 \)) excited states of the PSB4(1) model (C), along the corresponding constrained excited-state geometries optimized for fixed torsional angle \( \theta \), and without the TDA. Negative values in calculations without the TDA denote imaginary excitation energies (i.e., triplet instabilities) while a negative value in the TDA is a real-valued de-excitation.

**FIG. 6.** Constrained geometrical excited-state optimization of the PSB4(1) model (C) for fixed torsional angle \( \gamma \) (formal single-bond rotation) obtained within TD-DFT. The CASPT2 MEP as a function of the torsional angle \( \gamma \) is also shown. We plot the BLA (panel (a)), the torsional angles \( \theta \) for double-bond rotations (panel (b)), and the ground- and excited-state energies along the paths (panel (c)), and the \( \Lambda \) values along the TD-DFT paths (panel (d)).
has been recently employed to benchmark TD-DFT structures of in-plane retinal models.\textsuperscript{10} We find that CC2 behaves very similarly to CAM-B3LYP, displaying a significant increase in the excited-state energy and, consequently, a large barrier to double-bond rotation. Therefore, while CC2 describes satisfactorily in-plane relaxation and yields an out-of-plane optimal structure with a large \( \gamma \) angle compatible with the second CASPT2 minimum (see Table II), this method cannot reproduce the richer potential energy surface of retinal, being unstable towards single-bond rotation.

### 3. Single-bond rotation

The results for the rotation around the \( C_{12}-C_{13} \) formal single bond are shown in Fig. 6. The differences among the functionals are mainly in the energies along the constrained path while the behavior is rather similar regarding values taken by the angle of rotation around the double bond and the BLA. The rotation around the \( C_{11}-C_{12} \) double bond is characterized by small angles which approach zero with increasing single-bond rotation. The BLA changes only slightly along the constrained path and has always the same ordering with B3LYP having the largest and LC-BLYP the smallest BLA. B3LYP and CAM-B3LYP have no barrier for single-bond rotation in the excited state and display a minimum corresponding to the one obtained in the unconstrained optimization. LC-BLYP behaves differently as the excited-state energy does not decrease but stays rather constant. This behavior compares rather favourably to the CASPT2 MEP which proceeds mainly along a rotation around the single bond and maintains an excited-state energy rather constant along the whole MEP as also shown in Fig. 6. Therefore, even though CAM-B3LYP is expected to be less plagued by charge-transfer problems and therefore more reliable than B3LYP, the two functionals behave rather similarly, being both unstable towards single-bond rotations. LC-BLYP displays a small barrier to single-bond rotation, beyond which it yields a minimum in line with CAM-B3LYP. Comparing to CASPT2, more accurate results are clearly obtained with LC-BLYP also for single-bond rotation.

An analysis of the TD-DFT paths with the \( \Lambda \) criterion (panel (d)) reveals that the sequence of B3LYP, CAM-B3LYP, and LC-BLYP yields large values of \( \Lambda \) for an increasingly wider range of \( \gamma \) angles. Both B3LYP and CAM-B3LYP have a minimum for large values of \( \gamma \), where \( \Lambda \) becomes small, of the order of 0.2. LC-BLYP maintains instead a satisfactory \( \Lambda \) values up to the first minimum but \( \Lambda \) drops to small values in correspondence of the second minimum, similar to B3LYP and CAM-B3LYP. We find it very significant that the degree of agreement between (TD-)DFT and CASPT2 energies [panel (c)] continues to correspond remarkably well to the regions with large values of \( \Lambda \).

As we recall from Table II above, two other functionals, \( \omega B97 \) and \( \omega B97X \), behave like LC-BLYP in the unconstrained optimization, yielding an excited-state minimum with a rather similar amount of rotation around the double and the single bond. To investigate how far this similarity holds, we also perform a constrained geometrical optimization with these functionals and show the results in Figs. S12 and S13 in the supplementary material.\textsuperscript{12} For rotation around the double bond, the \( \omega B97 \) functional behaves very similarly to LC-BLYP and yields a constrained path that leads to conical intersection region, while the \( \omega B97X \) functional behaves like CAM-B3LYP and is unstable towards single-bond rotations. For rotation around the single bond, the \( \omega B97 \) and \( \omega B97X \) functionals exhibit a behavior in-between LC-BLYP and CAM-B3LYP as they have almost no barrier for single-bond rotation in the excited-state, while the excited-state energies do not decrease as much as for CAM-B3LYP. The different out-of-plane behaviors of these RSH functionals can be rationalized by looking at the relevant functional parameters: CAM-B3LYP displays a high degree of correspondence of the second minimum, similar to B3LYP and CAM-B3LYP, for large values of \( \gamma \).

\begin{table}[h]
\centering
\begin{tabular}{|l|c|c|c|c|c|c|}
\hline
 & In-plane & Out-of-plane & \( \theta \) & \( \gamma \) & \( E_1 \) & \( E_{\text{exc}} \) & \( f \) \\
\hline
CASPT2 & 0.034 & 0.035 & -11.4 & 26.5 & 2.79 & 2.62 & 1.20\textsuperscript{a} \\
2nd min.\textsuperscript{b} & 0.034 & 0.034 & 5.6 & 115.3 & 2.71 & 2.26 & 0.26\textsuperscript{a} \\
B3LYP & 0.080 & 0.060 & -2.2 & 85.5 & 1.57 & 0.60 & 0.00 \\
CAM-B3LYP & 0.035 & 0.039 & -1.7 & 85.7 & 2.37 & 1.48 & 0.00 \\
\( \omega B97XD \) & 0.030 & 0.037 & -1.5 & 87.0 & 2.43 & 1.59 & 0.00 \\
\( \omega B97X \) & 0.024 & 0.024 & -16.3 & 14.0 & 3.08 & 2.93 & 1.33 \\
2nd min.\textsuperscript{b} & 0.024 & 0.029 & -1.4 & 86.3 & 2.81 & 1.92 & 0.00 \\
\( \omega B97 \) & 0.021 & 0.021 & -18.9 & 13.3 & 3.08 & 2.90 & 1.33 \\
2nd min.\textsuperscript{b} & 0.021 & 0.025 & -1.1 & 86.8 & 3.00 & 2.09 & 0.00 \\
LC-BLYP & 0.019 & 0.020 & -19.0 & 12.7 & 3.09 & 2.95 & 1.37 \\
2nd min.\textsuperscript{b} & 0.019 & 0.021 & -0.6 & 87.1 & 3.10 & 2.24 & 0.00 \\
\hline
\end{tabular}
\caption{Out-of-plane torsional angles (\( ^\circ \)) of the PSB5(1) model (D) optimized in the excited state with various methods. We list the excited-state energy relative to the ground-state energy at the corresponding ground-state geometry (\( E_1, \text{eV} \), the B3LYP geometry is used for all TD-DFT functionals), vertical excitation energy (\( E_{\text{exc}}, \text{eV} \)), oscillator strength (\( f \)), and the out-of-plane BLA (\( \Lambda \)) at the excited-state minimum. The planar BLA obtained in a constrained \( C_\alpha \) symmetry is shown for comparison.}
\end{table}
is the only RHS functional considered here with only 65% HFX at long range while ωB97X has a smaller damping factor ω than either LC-BLYP or ωB97. Therefore, a requirement for a good TD-DFT description of retinal relaxation seems to be that the RHS functional converges quickly to a long-range limit of 100% HFX.

C. Out-of-plane relaxation for the PSB5(1) model

To investigate the general validity of the relaxation picture emerging from the PSB4(1) calculations, we consider here the out-of-plane behavior of the larger chromophore, PSB5(1). For this model, the computation of the CASPT2 MEP starting from the FC region is too costly and we therefore restrict our CASPT2 analysis to the out-of-plane minimal structures and to the geometries optimized at constrained angles of rotation θ around the formal double bond, C11–C12. As shown below, these reference data are sufficient to establish that the PSB5(1) model behaves in a qualitatively similar manner to the smaller PSB4(1) at all levels of theory.

The parameters of the out-of-plane minima of PSB5(1) obtained with CASPT2 and a set of representative TD-DFT functionals are listed in Table V. As in the case of PSB4(1), CASPT2 displays a first out-of-plane minimum characterized by a small angle θ and a more pronounced angle γ, and a second, lower-energy structure with a significantly larger value of γ. Also the behavior of TD-DFT parallels very closely to the one observed in the PSB4(1) model. B3LYP, CAM-B3LYP, and ωB97XD agree in yielding a minimal structure with an angle γ ≈ 86° in reasonable agreement with the second CASPT2 minimum with CAM-B3LYP and ωB97XD giving a BLA and adiabatic excitation energy in better agreement with the correlated values. Characterized by a smaller in-plane BLA, the RSH ωB97, ωB97, and LC-BLYP functionals display instead two out-of-plane minima, a first minimum with a smaller rotation around the C12–C13 angle and a deeper second minimum which is structurally rather similar to the one obtained with the CAM-B3LYP and ωB97XD functionals but with a larger adiabatic excitation energy in better agreement with the CASPT2 value.

As shown in Fig. 7, also the constrained optimization of PSB5(1) for fixed torsional angle θ does not yield surprises. After an initial plateau extending from the FC to an angle of γ ≈ 25°, the CASPT2 ground/excited-state energy begins to increase/decrease and the system approaches a conical intersection region characterized by BLA inversion. The B3LYP and CAM-B3LYP functionals are instead unstable against single-bond rotation, yielding a structure with a large angle γ, similar to the minimal one of Table V. For larger values of the angle θ, we observe a steady increase of the excited-state energy of both functionals, indicating the presence of a large barrier to double-bond rotation. Also for PSB5(1), the behavior of LC-BLYP is clearly superior, since, similarly to CASPT2, the ground- and excited-state LC-BLYP energies are rather flat at small θ and the gap drops to zero only after a certain angle, which is however larger than the corresponding highly-correlated value (45° versus 25°). Beyond this angle, the local BLA of the LC-BLYP structures becomes slightly negative. The Λ criterion computed along the TD-DFT paths (panel (e)) supports the reliability of the LC-BLYP energies up to the conical intersection region since Λ is rather large for all angles less than about θ = 45°. This must be contrasted to the Λ values computed along the B3LYP and CAM-B3LYP paths, which are systematically and significantly lower. Finally, we report the TD-DFT paths obtained in a constrained optimization around the formal single-bond γ in Fig. S14 of the supplementary material, which are also in qualitative agreement with the behavior observed for the smaller PSB4(1).

We stress that, in this section and Secs. III A and III B, we have always consistently employed the same method and...
out-of-plane torsional angles (°) and BLA (Å) of the PSB3(0) model (A) for the excited-state minimum and transition state between this minimum and the conical intersection region, obtained with CASPT2 and LC-BLYP. We list the excited-state energy relative to the ground-state energy at the CASPT2 or the B3LYP ground-state geometry (E1, eV), the vertical excitation energy (Eexc, eV), and the oscillator strength (f). The LC-BLYP results are obtained with the cc-pVTZ basis set.

<table>
<thead>
<tr>
<th></th>
<th>Out-of-plane BLA</th>
<th>θ</th>
<th>γ</th>
<th>E1</th>
<th>Eexc</th>
<th>f</th>
</tr>
</thead>
<tbody>
<tr>
<td>Minimum</td>
<td>CASPT2</td>
<td>0.045</td>
<td>3.7</td>
<td>73.0</td>
<td>3.75</td>
<td>2.08</td>
</tr>
<tr>
<td></td>
<td>LC-BLYP</td>
<td>0.036</td>
<td>1.8</td>
<td>76.4</td>
<td>3.87</td>
<td>2.45</td>
</tr>
<tr>
<td>TS</td>
<td>CASPT2</td>
<td>0.024</td>
<td>−23.9</td>
<td>21.7</td>
<td>3.98</td>
<td>3.54</td>
</tr>
<tr>
<td></td>
<td>LC-BLYP</td>
<td>0.034</td>
<td>−6.5</td>
<td>32.7</td>
<td>4.25</td>
<td>3.70</td>
</tr>
</tbody>
</table>

aCASPT2/6-31G* results from Ref. 41.
bCASSCF oscillator strengths.

functional to obtain both the excited-state geometries and energies. As discussed in the supplementary material, the computation of TD-DFT excited-state energies on the CASPT2 structures as done for instance for the smaller PSB3(0) model would have lead us to the incorrect conclusion on the performance of CAM-B3LYP: the functional would have been tested on a path which is of minor relevance, since it is inconsistent with the use of CAM-B3LYP in obtaining the geometries and would not be reached from the FC region.

D. Out-of-plane relaxation for the PSB3(0)

We conclude the out-of-plane section with the smaller PSB3(0) model for which the CASPT2 MEP has also been mapped out between the first minimum in the single-bond rotation pathway and the conical intersection region in Ref. 41. For this model, we only investigate the performance of the LC-BLYP functional, which has outperformed all other functionals in Secs. III A–III C. In Table VI, we compare the LC-BLYP minimum and TS geometries and the corresponding energies with the CASPT2 values. The comparison is rather satisfactory, in particular, for the minimum geometry, while, at the TS state, LC-BLYP predicts a smaller θ angle of double-bond rotation.

IV. DISCUSSION AND CONCLUSIONS

In this paper, we have presented a thorough investigation of the performance of TD-DFT for describing the excited-state relaxation of retinal PSB models. We considered a large set of functionals which cover almost the entire range of relevant functional parameters and tested them against recent ab initio benchmark results, which we here expanded with CASPT2 calculations for the larger PSB5(1) model. We also employed quality measures internal to TD-DFT such as the Λ criterion or the presence of triplet and near singlet instabilities.

Importantly, while we have revisited “routine” calculations of vertical excitation energies or in-plane minima, the focus of our TD-DFT investigation is on a larger and much more relevant part of the potential energy surface, namely, the out-of-plane relaxation with its distinct single- and double-bond rotational pathways. Thus, while some previous TD-DFT studies of retinal have used our CASPT2 in-plane structures to focus on the initial skeletal behavior, we showed here that the in-plane restriction only allows the rejection of a subset of functionals. In particular, while we can safely rule out almost all global hybrid functionals solely on the in-plane results, this criterion is insufficient for choosing between different RSH functionals. It is only by going further, as we have done in this study, to consider the out-of-plane behavior that we obtain a much more challenging test for TD-DFT functionals and one which is closer to the CASPT2 photoreaction pathway itself. In fact, an in-plane study of retinal can even mislead one in choosing the reference method for retinal: the CC2 method, for instance, performs reasonably well for the initial stretching of the system but cannot reproduce the complexity of retinal relaxation as described by CASPT2.

Consistently with previous studies, the principal conclusion one can draw from the analysis of the vertical excitation energies (see the supplementary material) is that the main factor influencing the excitation energy is the amount of HFX in the functional. The dependence of the excitation energy on the ground-state geometry is instead a better measure of the performance of TD-DFT for retinal and confirms the inadequacy of GGAs and hybrids with low percentage of HFX: these functionals wrongly predict a decrease in excitation with increasing BLA, consistent with the fact that they yield incorrect excited-state minima with increased BLA with respect to the ground state. Thus, it is not surprising that a functional like B3LYP severely underestimates the blue shift with respect to the gas phase when a negative point charge is placed close to the protonated Schiff base as is known to happen in rhodopsin, since the presence of the charge leads to a ground-state geometry with increased BLA. Consequently, the use of hybrids with low percentage of HFX in opsins is to be discouraged. In contrast, all RSH functionals considered here display the correct behavior as the BLA increases along this sequence of geometries or in the presence of a counter-ion.

Focusing on the out-of-plane behavior, we found that the value of BLA obtained in plane gives a good indication of what excited-state minimum the functional will yield. As the planar BLA decreases, the out-of-plane minimum switches from a CASPT2-like (single-bond rotation) to a CASSCF-like structure (double-bond rotation). Among the functionals which
display a minimum characterized by single-bond rotation, we identified three classes of behavior with B3LYP, CAM-B3LYP, and LC-BLYP as representatives. While CAM-B3LYP has a more accurate in-plane BLA and a significantly larger out-of-plane adiabatic energy, B3LYP and CAM-B3LYP behave rather similarly with respect to single- and double-bond rotation, being unstable towards single-bond rotation and displaying a high barrier to double-bond rotation. As also validated by the larger values of $\Lambda$ along a longer stretch of the rotation pathways, the LC-BLYP functional is found to be superior to either B3LYP or CAM-B3LYP. The LC-BLYP behavior with respect to single-bond rotation is qualitatively similar to CASPT2, and the LC-BLYP constrained path for double-bond rotation is rather flat like the CASPT2 one, quickly approaching a conical intersection region after a certain angle. Overall, considering the relative accuracy of the CASPT2 approach itself, the qualitative agreement between CASPT2 and LC-BLYP is quite satisfactory but surprising. Given the well-known importance of the role of HFX in the functional, one might conclude that the success of LC-BLYP as compared to CAM-B3LYP should be attributed to the higher percentage of HFX in the former. However, a comparison with other RSH functionals indicates that, to describe the complex relaxation of retinal in the excited state, one needs RSH functionals which converge rather quickly (large damping factor $\omega$) to their long-range limit of 100% HFX.

This paper has assessed functionals which are readily available for the TD-DFT description of an important photochemical reaction. The analysis has been restricted to what happens around the FC region because this is where TD-DFT is expected to work best. However, it seems appropriate to end this conclusion by noting that the extension of TD-DFT well-beyond the FC region has become an increasingly intense area of current research. Most of the new DFT-based approaches that may take us closer to an accurate description of the conical intersection region are now only in development versions of programs which are not yet available to the larger public. However, these will most likely become available in the next few years to a broader community of users. Thus, there is plenty of reason to remain optimistic that TD-DFT’s importance in the photochemical modeler’s toolbox will continue to grow in the future.

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12See supplementary material at dx.doi.org/10.1063/1.4916354 for additional results and analysis.