

Combined Self-Consistent-Field and Spin-Flip Tamm–Dancoff Density Functional Approach to Potential Energy Surfaces for Photochemistry

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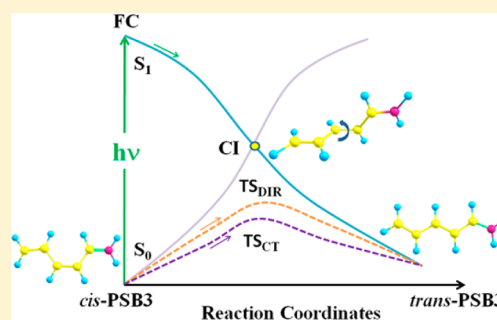
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S Supporting Information

ABSTRACT: We present a new approach to calculating potential energy surfaces for photochemical reactions by combining self-consistent-field calculations for single-reference ground and excited states with symmetry-corrected spin-flip Tamm–Dancoff approximation calculations for multi-reference electronic states. The method is illustrated by an application with the M05-2X exchange-correlation functional to *cis*–*trans* isomerization of the penta-2,4-dieniminium cation, which is a model (with three conjugated double bonds) of the protonated Schiff base of retinal. We find good agreement with multireference configuration interaction-plus-quadruples (MRCISD+Q) wave function calculations along three key paths in the strong-interaction region of the ground and first excited singlet states.

SECTION: Spectroscopy, Photochemistry, and Excited States



Density functional theory (DFT) has made great strides in treating ground-electronic-state chemistry,^{1,2} but an unconquered frontier is excited-electronic-state chemistry, which we will simply call photochemistry, where most DFT studies are carried out by adiabatic linear-response time-dependent density functional theory,³ here abbreviated as TDDFT. TDDFT has a number of well-known deficiencies for excited-state calculations,^{4,5} and it has been stated that⁵ “Even if the overall accuracy of these methods has improved much since the early times and its black-box applicability has slightly increased, it is still questionable whether they will ever have high accuracy and, especially, predictability, as required in photochemistry.” Wave function theory (WFT) in principle is systematically improvable, but the cost scales rapidly with system size, so similar accuracy questions remain for levels of WFT that are affordable for modeling the dynamics of large and complex systems. Thus there is great interest in improving and validating both kinds of electronic structure theory.

The isomerization paths of the PSB3 (penta-2,4-dieniminium cation⁶) model of the retinal protonated Schiff base chromophore of visual pigments is particularly challenging for DFT because, although it is a small enough system for benchmarks to be obtained, it includes more than one of the kinds of electronic structure that are very difficult for DFT to model. When the potential energy surface is computed at the complete-active-space self-consistent-field (CASSCF) level of multireference WFT, there are two kinds of low-energy thermal

paths for converting *cis*-PSB3 to *trans*-PSB3: one reaction path passing through a diradical transition state (TS_{DIR}), called the DIR path, has predominantly covalent or diradical character, and the other passing through a transition state (TS_{CT}), called the CT path, which has a predominant charge-transfer character.⁷ These paths are separated by a conical intersection (CI) between the ground state (S₀) and the first singly excited state (S₁) and thereby provide an illustration of a common motif⁸ of saddle points on the shoulder of a CI.

In the simplest terms, we can attribute the difficulty with modeling diradicals to the near-degeneracy (nondynamical or static) electron correlation in diradical states; this is hard to treat with Hartree–Fock exchange because Hartree–Fock exchange brings in static correlation error due to its origin in the exchange of a single Slater determinant. By contrast, charge-transfer states usually require high Hartree–Fock exchange to minimize self-interaction error. Previous work has shown that density functionals with percentages *X* of Hartree–Fock exchange between 25 and 60 represent the best compromise of these competing factors,⁹ but we ask: Can one find an approximate density functional that treats these paths in a balanced fashion?

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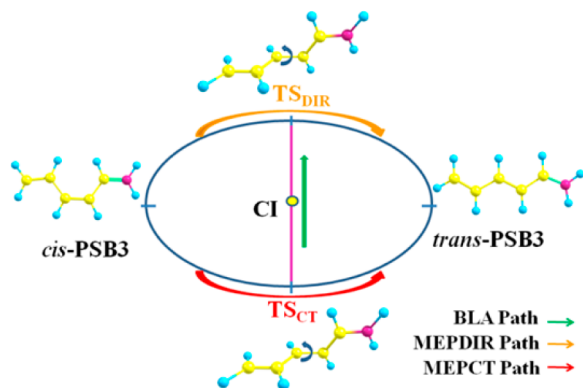
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From another point of view, the interaction of the S_0 and S_1 states of the retinal chromophore exposes a different difficulty of DFT, namely, the challenge of treating ground and excited states on a consistent footing. DFT was originally a ground-state theory, but it can find excitation energies by locating the poles of the response of the ground state to a periodic electric-field perturbation. This yields TDDFT,³ but TDDFT is unstable near state intersections.⁴ This instability can be alleviated but not completely removed⁴ by making the Tamm–Dancoff approximation^{10,11} (TDA), but neither TDDFT nor TDDFT-TDA based on the ground-state Kohn–Sham (KS) self-consistent-field (SCF) reference function can represent the partial doubly excited character of the open-shell excited state with diradical character. Some progress can be made by using spin-flip (SF) TDDFT-TDA to model the diradical state as a spin flip from the T_1 state.¹² All these approaches, though, can suffer potential inaccuracies due to representing electronic states via the linear response of SCF states rather than as variationally optimized SCF states in their own right.

Recent work has used multireference WFT to include both near-degeneracy correlation energy and dynamic correlation in the treatment of the S_0 and S_1 states of PSB3 along the minimum energy DIR (MEPDIR) reaction path, the minimum energy CT (MEPCT) reaction path, and a bond length alternation path, called the BLA path, from one saddle point to the other through the CI.⁷ These paths are illustrated in Scheme 1, where the bottom portion of the scheme

Scheme 1



corresponds to CASSCF wave functions with CT character, and the top portion corresponds to CASSCF wave functions with DIR character. In PSB3, the dynamic correlation energy introduced by the multireference configuration interaction-plus-quadruples (MRCISD+Q) method shifts the CI position so much toward the top of the scheme (with respect to the original CASSCF position) that the DIR path does not have a diradical character anymore but rather has charge transfer character, because along the BLA path in Scheme 1 it is located at a position slightly below the intersection. As a consequence, both CT and DIR paths (that were computed⁷ at the CASSCF level) span regions in which the MRCISD+Q ground-state wave functions has closed-shell π^2 character.

The paths in Scheme 1 present a challenge; can one model the energies along these paths in the vicinity of the conical intersection in a reasonable way with DFT? This question is particularly interesting in light of previous work¹³ that showed that the popular equations-of-motion coupled cluster method with single and double excitations (EOM-CCSD, a single-

reference WFT method that is already much more expensive than DFT) cannot describe these energies well, and one must use even more expensive WFT methods such as MRCISD+Q (which is the most accurate level considered in either ref 7 or ref 13) or spin-flip EOM-CCSD with a perturbative account of triple excitations derived from the diagonal of the similarity transformed Hamiltonian (EOM-SF-CCSD(dT)). We will show here, by comparison to MRCISD+Q results, that one can obtain a consistent representation of S_0 and S_1 by using single-reference density functional methods, in particular, a high-exchange density functional (M05-2X¹⁴ with the percentage X of Hartree–Fock exchange equal to 56) along with a treatment that combines the SCF treatments of the single-reference ground and excited states and multireference singlet states with a collinear SF-TDDFT-TDA treatment of the singlet–triplet splitting. (In the Supporting Information, we show that we can also get qualitatively correct results with three other high-exchange density functionals, namely, M06-2X¹⁵ with $X = 54$, M08-HX¹⁶ with $X = 52.23$, and M08-SO¹⁶ with $X = 56.79$. We show M05-2X in the article itself because it happens to be slightly more accurate in the present case. The results are less accurate with M11, which has X equal to only 42.8 for small interelectronic separation.) For the BLA path, we will also compare to two single-reference WFT methods, equations-of-motion coupled cluster singles and doubles (EOM-CCSD)¹⁷ (also considered previously¹³ as mentioned above), and symmetry adapted cluster/configuration interaction (SAC-CI).¹⁸

THEORETICAL METHODS

All calculations are based on the 6-31G* basis set¹⁹ because this basis set was used^{7,13} for mapping the effect of dynamical correlation on the potential energy surfaces in previous studies. Although this basis set is insufficient for quantitative accuracy, it is adequate for testing the ability of DFT to yield qualitatively correct potential energy surfaces.

We will use the MRCISD+Q²⁰ wave function calculations of ref 7 as reference WFT data to test DFT. In brief, these WFT calculations are based on a two-level treatment. The first level, denoted CASSCF,²¹ is an equal-weight, two-root, state-averaged complete active-space SCF wave function for six electrons in six active π orbitals. The second level, denoted MRCISD+Q, is a multireference configuration interaction with all single and double excitations out of the CASSCF wave function treated variationally and with quadruple excitations approximated by a multireference Davidson correction. The three paths are found at the CASSCF level, but all energies in this Letter are single-point MRCISD+Q (or, below, DFT, EOM-CCSD, and SAC-CI) calculations along the CASSCF paths. For further details of the CASSCF and MRCISD+Q calculations, please see ref 7.

For the DFT calculations, we designed a computational strategy that uses SCF methods for single-reference states (closed-shell ground states and states well represented by a high-spin single Slater determinant) with SF TDDFT calculations in the TDA to obtain energy differences of open-shell multireference singlets from SCF states. We label the highest occupied molecular orbital (HOMO) as π and the lowest unoccupied molecular orbital (LUMO) as π^* . The dominant configurations in the states of interest here are π^2 and $\pi\pi^*$.

The conventional singlet ($\langle \hat{S}^2 \rangle = 0$) restricted and triplet ($\langle \hat{S}^2 \rangle = 2$, $M_S = +1$) unrestricted KS SCF calculations are

Table 1. The Energies (kcal/mol) of the Ground and First Vertical Excitation Singlet States at *cis*-PSB3, *trans*-PSB3, TS_{CT}, and TS_{DIR} Structures Relative to That of the *cis*-PSB3 Ground State As Calculated by Various Methods

method ^a	<i>trans</i> -S ₀	TS _{CT} -S ₀	TS _{DIR} -S ₀	<i>cis</i> -S ₁	<i>trans</i> -S ₁	TS _{CT} -S ₁	TS _{DIR} -S ₁
SCF	−3.0	45.6	51.4				
SF2				97.7	97.8	56.2	52.4
TDA				110.7	111.6	54.3	50.8
TDDFT				101.9	101.9	54.0	52.7
SAC-CI	−2.9	58.7	65.0	99.3	98.9	73.0	69.2
EOM-CCSD	−3.0	46.6	52.5	102.3	101.9	63.3	59.4
MRCISD+Q	−3.1	48.7	54.3	101.4	101.3	59.0	54.9

^aThe M05-2X functional is used for the SCF, TDDFT, TDA, and SF2 calculations.

performed first. The singlet restricted SCF energy is taken as the energy of the state dominated by the closed-shell π^2 configuration. The $M_S = +1$ triplet state obtained from the unrestricted SCF calculation is represented by a $|\pi\alpha\pi^*\alpha\rangle$ single Slater determinant. The SF-TDDFT-TDA takes it as a reference wave function and excites and flips one α spin into a β spin to get spin-flipped states with $M_S = 0$. The target $\pi\pi^*$ singlet state is a linear combination of $|\pi\alpha\pi^*\beta\rangle$ and $|\pi\beta\pi^*\alpha\rangle$ determinants. Due to the spin incompleteness, the SF solutions are not pure spin eigenfunctions for the $\pi\pi^*$ singlet state,²² and this introduces spin contamination with $\langle\hat{S}^2\rangle \sim 1$ as a result of a singlet–triplet mixing. We use Yamaguchi's approximate spin projection (AP) formula²³ to convert the energy of this unphysical mixed spin-symmetry $\pi\pi^*$ state (E_{mix}) obtained from the SF-TDDFT-TDA calculation to the energy of pure $\pi\pi^*$ singlet state (E_S). The energy of the final open-shell $\pi\pi^*$ singlet state is thereby calculated as

$$E_S = E_T - \frac{2(E_T - E_{\text{mix}})}{\langle\hat{S}^2\rangle_T - \langle\hat{S}^2\rangle_{\text{mix}}} \quad (1)$$

E_T in eq 1 is the energy of the triplet $\pi\pi^*$ reference state obtained from the unrestricted SCF calculations, and $\langle\hat{S}^2\rangle_T$ and $\langle\hat{S}^2\rangle_{\text{mix}}$ are, respectively, expectation values of the triplet $\pi\pi^*$ reference state and of the spin mixed $\pi\pi^*$ state obtained by SF-TDDFT-TDA calculations. This combined SCF and SF-TDDFT-TDA method with eq 1 to remove spin contamination of the $\pi\pi^*$ singlet state will be denoted as SF2. For comparison, the energies of the open-shell $\pi\pi^*$ singlet state along the three paths are also calculated using the conventional TDDFT and TDDFT-TDA methods (the latter abbreviated as TDA) based on the ground-state reference function. Along the BLA path, the two states of interest are also calculated by two high-level single reference WFT methods: EOM-CCSD and SAC-CI.

The TDDFT-TDA and SF-TDDFT-TDA calculations are performed using the GAMESS²⁴ program; the TDDFT and SAC-CI calculations are performed using Gaussian;²⁵ EOM-CCSD is performed with the Molpro²⁶ package.

Table 1 lists the energies of the S₀ and vertical S₁ states at the *cis*-PSB3, *trans*-PSB3, TS_{CT}, and TS_{DIR} equilibrium geometries relative to the S₀ energy of *cis*-PSB3. The energy profile of the open-shell $\pi\pi^*$ singlet state along the BLA path, MEPCT path, and MEPDIR path calculated by the newly presented SF2 and by the conventional TDDFT and TDA methods with the M05-2X functional are shown respectively in Figures 1a, 2 and 3, compared to the reference MRCISD+Q results. The dashed curves in those figures are for the state with π^2 as the dominant configuration, and they correspond to the restricted M05-2X SCF calculation (labeled as SCF in the figures) and to the MRCISD+Q calculation. The energy profiles of the two states

of interest along the BLA path obtained by EOM-CCSD and SAC-CI methods are shown in Figure 1b.

The data in Table 1 indicate that all the single-reference methods (EOM-CCSD, SAC-CI, and the restricted M05-2X SCF calculation) give an accurate ground-state relative energy of equilibrium structures *trans*-PSB3 and *cis*-PSB3 with errors less than or equal to 0.2 kcal/mol as compared to the reference MRCISD+Q results. Single-reference methods also do reasonably well (errors less than or equal to 3.5 kcal/mol) for the excited-state calculations of the *cis* and *trans* equilibrium structures, except TDA, which overestimates the energy of the S₁ state by 9.3 kcal/mol. At the TS_{CT} and TS_{DIR} geometries, where static correlation energy is not negligible, the M05-2X SCF and EOM-CCSD methods predict the energy of the S₀ state, which is closed-shell π^2 state, reasonably well with errors of 2.1–2.9 kcal/mol, while SAC-CI gives worse results with errors of 10.0 to 10.7 kcal/mol; for the more difficult open-shell S₁ states, only the SF2 method agrees reasonably with the MRCISD+Q results.

The good performance of the SF2 method is further validated by Figure 1a. Along the BLA path, the energy profile of the open-shell $\pi\pi^*$ state obtained by the SF2 method intersects with the potential curve of the closed-shell π^2 state obtained by restricted SCF calculations at a position similar to that obtained by the MRCISD+Q method. As shown in Figure 1a, the conventional TDDFT method fails to predict the energies of the open-shell $\pi\pi^*$ states around the region of the conical intersection due to the triplet instability problem (symmetry breaking in the ground state⁴). The TDA method gives a much improved energy curve of the $\pi\pi^*$ state compared to TDDFT: it yields a position of the crossing with the π^2 state that is a little early as compared to the MRCISD+Q reference and the SF2 method, as a result of underestimating the energies of the $\pi\pi^*$ state along the BLA path.

Figure 1b shows that the EOM-CCSD and SAC-CI single-reference WFT methods both fail to predict a crossing of the two states of interest along the BLA path. The EOM-CCSD method can predict the energy of the closed-shell π^2 state fairly well, but it largely overestimates the energy of the $\pi\pi^*$ state. The SAC-CI method gives even worse results, and it seriously overestimates the energies for both states of interest. Therefore, only the DFT methods are compared for the other two paths: MEPCT and MEPDIR.

Figures 2 and 3 show that, as a result of underestimating the energy of the $\pi\pi^*$ state in the vicinity of the saddle points (TS_{CT} and TS_{DIR}), both TDDFT and TDA methods give wrong shapes and energetics for energy curve of the $\pi\pi^*$ state along MEPCT and MEPDIR paths, as compared to MRCISD+Q results. However, combining the SCF calculations for the π^2 state and SF2 calculations for the $\pi\pi^*$ state, one gets

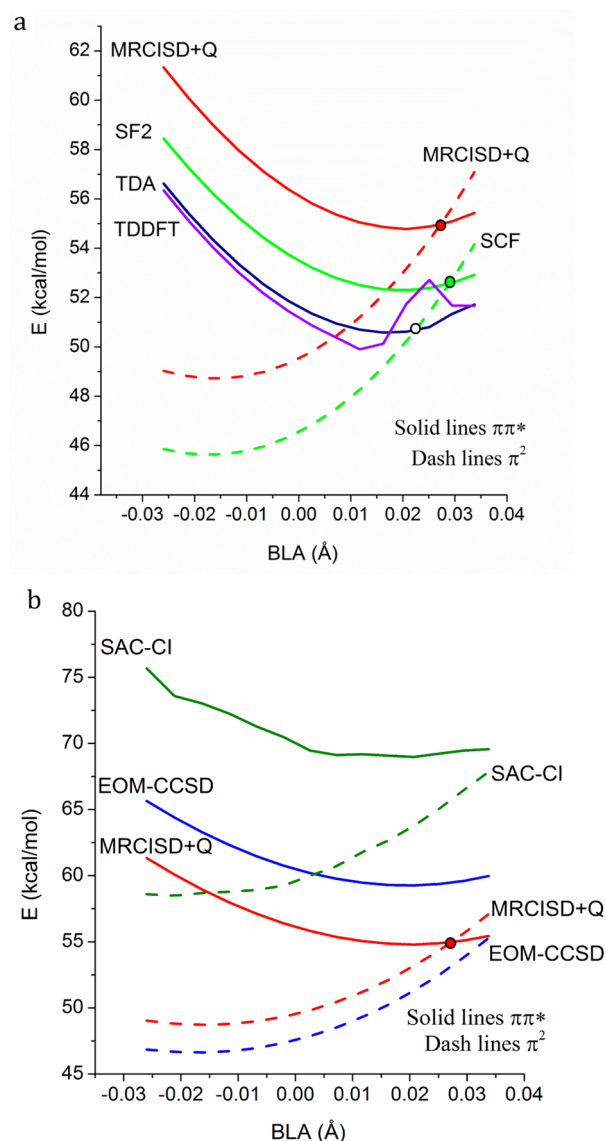


Figure 1. (a) The energy profile (solid lines) of the open-shell $\pi\pi^*$ singlet state along the BLA path as calculated by the newly suggested SF2 method and by conventional TDDFT and TDA methods with the M05-2X functional compared to the reference MRCISD+Q results. The energies for the state with π^2 as the dominant configuration as calculated by the restricted M05-2X SCF (labeled as SCF) and MRCISD+Q methods are shown using dashed lines for comparison and for showing the positions of conical intersections obtained by various methods. (b) The energy profiles of $\pi\pi^*$ singlet state and π^2 state calculated by EOM-CCSD and SAC-CI (three singlet excited states are calculated at the same time). Energy is relative to the *cis*-PSB3 ground state.

qualitatively correct energy profiles of the two states using the M05-2X functional.

The present results indicate that in the vicinity of the conical intersection, although the π^2 state involves charge transfer as compared to the equilibrium ground state, its closed-shell character allows it to be predicted well by a restricted SCF calculation with the M05-2X functional. Furthermore, it can be described reasonably well by any of the single-reference methods that include enough dynamic correlation. The open-shell $\pi\pi^*$ state has diradical character in the region we investigate, and it has significant static correlation. That is why

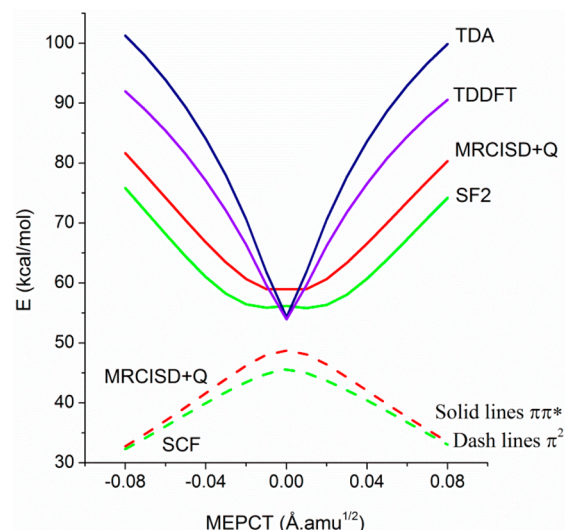


Figure 2. The energy profile (solid lines) of the open-shell $\pi\pi^*$ singlet state along the MEPCT path calculated by the new SF2 method and by the conventional TDDFT and TDA methods with the M05-2X functional compared to the reference MRCISD+Q results. The energy profile of the state with π^2 as the dominant configuration, as calculated both by restricted M05-2X SCF (labeled as SCF) and by MRCISD+Q methods, is shown using dashed lines for comparison. All energies are relative to the *cis*-PSB3 ground state.

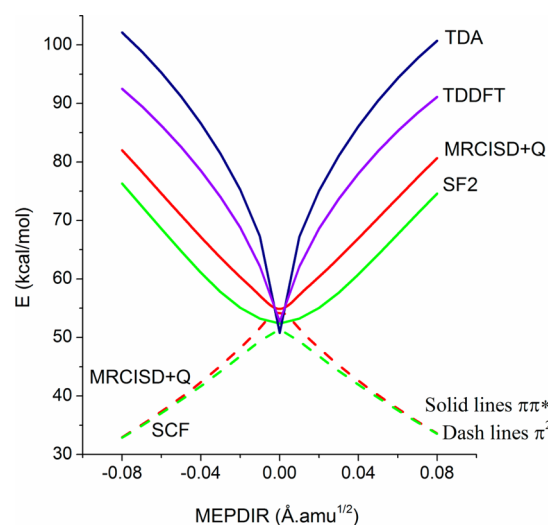


Figure 3. The energy profile (solid lines) of the open-shell $\pi\pi^*$ singlet state along the MEPDIR path calculated by the new SF2 method and by the conventional TDDFT and TDA methods with the M05-2X functional compared to the reference MRCISD+Q results. The energy profile of the state with π^2 as the dominant configuration, as calculated both by restricted M05-2X SCF (labeled as SCF) and by MRCISD+Q methods, is shown using dashed lines for comparison. All energies are relative to the *cis*-PSB3 ground state.

the single-reference WFT methods, EOM-CCSD and SAC-CI, fail. Density functional exchange does not bring in static correlation error to the extent that Hartree–Fock reference functions, as used in EOM-CCSD and SAC-CI, do; however, the triplet instability as a result of the mixing of the two states of interest in the strong interaction region makes the conventional TDDFT method unstable for predicting the energy of the $\pi\pi^*$ state. TDA predicts an improved energy curve for the $\pi\pi^*$ state along the BLA path as compared to

TDDFT, but it still cannot represent the partial doubly excited character of the diradical, it underestimates the energy of the diradical state near saddle points, and it leads to the wrong shape of the energy profile along the MEPCT and MEPDIR paths. The SF-TDDFT-TDA method avoids the instability, and at the same time it includes the double excitation for the diradical state; unfortunately, though, it introduces serious spin contamination due to spin incompleteness. The new SF2 method successfully removes spin mixing in the SF-TDDFT-TDA calculations to get a pure $\pi\pi^*$ state, and the SF2 method with the M05-2X functional treats the $\pi\pi^*$ state better than the other single-reference methods. At the same time, it is also applicable for the excited state calculations in the equilibrium structure region. Just as we showed above, the combination of an SCF calculation for π^2 state and an SF2 calculation for $\pi\pi^*$ state yields qualitatively good energy profiles along all three paths (BLA, MEPCT, and MEPDIR).

The present SF-TDDFT-TDA calculations are based on a collinear approximation, and only the Hartree–Fock exchange part of exchange–correlation (XC) kernel is responsible for the spin-flip transitions.²⁷ Consequently, high Hartree–Fock exchange, for example X larger than ~ 50 , seems to be required for a reasonable estimation of spin-flip excitation energies. Therefore the popular B3LYP functional with $X = 20$ is not suitable for the suggested SF2 method, whereas M05-2X, M06-2X, M08-HX, and M08-SO, which are all broadly accurate high- X functionals, all give reasonable potential energy surfaces for the PSB3 model with the SF2 method. In addition, the need for high- X of this system is probably in part because of the charge-transfer character.

Another point we want to emphasize is that the combination of SCF for a closed-shell π^2 state and SF2 for an open-shell $\pi\pi^*$ state does much better than the CASSCF method, which only considers nondynamical correlation. In the present isomerization case, the CASSCF even gives wrong energy profiles because it ignores the important dynamic correlations as ref 7 shows. Due to the computational cost, many studies have been performed using the CASSCF method to investigate multi-reference electronically nonadiabatic systems; however, dynamic correlation could change the final conclusions. The method suggested here of combining SCF and SF2 calculations employing DFT is less expensive and easier than CASSCF (in general, single-reference calculations are much easier than multi-reference ones), it includes both the dynamic and static correlations, and it yields results of comparable accuracy to the very expensive MRCISD+Q method.

A combined DFT method for calculating potential energy surfaces of photochemical systems is suggested, in particular to perform restricted SCF KS calculations for the single-reference ground state, and to do spin-flip TDA calculations in a collinear approximation for multi-reference singlet excited states with a single-reference triplet KS calculation as reference. Yamaguchi's formula is used to remove the spin contamination due to spin incompleteness in the spin-flip calculations. This combined method, using the high- X functional M05-2X (alternatively M06-2X, M08-HX, or M08-SO as shown in the Supporting Information) yields potential energy profiles comparable with MRCISD+Q for the retinal chromophore model PSB3 along three key paths (BLA, MEPCT, and MEPDIR) in the vicinity of a conical intersection. In this system, the two electronic states of interest have quite different correlation energies such that both dynamic and nondynamical (static) correlation effects have to be considered. The new combined method, called SF2,

treats the two states on a consistent footing, and does much better than the conventional TDDFT or TDDFT-TDA methods or even than the much more expensive SAC-CI and EOM-CCSD single-reference methods or the multi-reference CASSCF method. We believe that this may provide a route toward using DFT more constructively for photochemical applications like the one considered here.

■ ASSOCIATED CONTENT

■ Supporting Information

Additional figures showing results for the M06-2X, M08-HX, and M08-SO density functional and EOM-SF-CCSD(dT)/ROHF methods. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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