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Finite-Field Spin-Flip Configuration Interaction Calculation of the Second Hyperpolarizabilities of Singlet Diradical Systems

Ryohei Kishi,*,[†] Masayoshi Nakano,*,[†] Suguru Ohta,[†] Akihito Takebe,[†]
Masahito Nate,[†] Hideaki Takahashi,[†] Takashi Kubo,[‡] Kenji Kamada,[§] Koji Ohta,[§]
Benoît Champagne,[||] and Edith Botek[||]

*Department of Materials Engineering Science, Graduate School of Engineering
Science, Osaka University, Toyonaka, Osaka 560-8531, Japan, Department
of Chemistry, Graduate School of Science, Osaka University, Toyonaka,
Osaka 560-0043, Japan, Photonics Research Institute, National Institute of Advanced
Industrial Science and Technology (AIST), Ikeda, Osaka 563-8577, Japan, and
Laboratoire de Chimie Théorique Appliquée, Facultés Universitaires Notre-Dame de
la Paix (FUNDP), rue de Bruxelles, 61, B-5000 Namur, Belgium*

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Abstract: Ab initio spin-flip configuration interaction (SF-CI) methods with the finite-field (FF) scheme are applied to the calculation of static second hyperpolarizabilities (γ) of several singlet diradical systems, i.e., the model H_2 molecule under dissociation, *p*-quinodimethane, *o*-quinoid five-membered ring, and 1,4-bis(imidazole-2-ylidene)cyclohexa-2,5-diene (BI2Y) models. The SF-CI method using the UHF reference wave function provides the qualitatively correct diradical character (*y*) dependence of γ in a wide range of a diradical character region for H_2 under dissociation and *p*-quinodimethane as well as *o*-quinoid five-membered ring models. For BI2Y, which is a real diradical system, a non-negligible spin contamination is found in the spin-unrestricted Hartree−Fock (UHF) triplet state, which results in overestimations (SF-CIS) or underestimations (SF-CIS(D)) of γ. Such deficiencies are significantly reduced when using the pure spin state, i.e., the restricted open-shell HF (ROHF) triplet wave function as the reference wave function. These results indicate the applicability of the FF-SF-CI method starting with a pure or a nearly pure high-spin state to provide qualitative or semiquantitative γ for large-size diradical systems. For selected systems, these SF-CI results are also compared to the SF equation of motion coupled cluster singles and doubles (SF-EOM-CCSD) and to SF time-dependent density functional theory (SF-TDDFT) schemes. In particular, large amounts of Hartree−Fock exchange in the functional are required to obtain qualitatively correct dependence of γ on *y* in the case of *p*-quinodimethane.

1. Introduction

There have been several guidelines for designing molecules presenting large first and second hyperpolarizabilities, β and γ, the molecular properties at the origin of the macroscopic second- and third-order nonlinear susceptibilities, $\chi^{(2)}$ and $\chi^{(3)}$.[1−11] For instance, π-conjugated systems with donor−acceptor substitutions[1−3] and charged compounds[4−9] as well as two- or three-dimensional supramolecular architectures[10,11] have been proposed as fundamental units to display high nonlinear optical (NLO) effects. In spite of such persistent pursuit, most candidates examined up to now have been restricted to closed-shell systems. In our previous studies, as a novel class of NLO systems, we have theoretically

* Corresponding author e-mail: rkishi@cheng.es.osaka-u.ac.jp (R.K.), mnaka@cheng.es.osaka-u.ac.jp (M.N.).
[†] Graduate School of Engineering Science, Osaka University.
[‡] Graduate School of Science, Osaka University.
[§] National Institute of Advanced Industrial Science and Technology (AIST).
[||] Facultés Universitaires Notre-Dame de la Paix (FUNDP).

proposed singlet diradical systems with intermediate diradical character, which exhibit significantly enhanced second hyperpolarizabilities relative to conventional closed-shell molecules.[12−18] Very recently, on the basis of these theoretical and computational studies, two-photon absorption (TPA) measurements have been performed on some of these diphenalenyl compounds, and it has been found that those are among the pure hydrocarbon systems with the largest TPA cross sections.[19]

Theoretical and computational analyses of the NLO properties of open-shell singlet systems in the sum-over-state (SOS) approach require the correct description of their ground- and excited-state electronic structures, which have to be described, in principle, by the multireference (MR) based electron correlation methods, e.g., the MR Møller−Plesset perturbation (MRMP) and MR coupled cluster (MRCC) methods if the high-order excitations involved in the single-reference spin-unrestricted CC (UCC) methods are contracted. Because these MR methods could not be applied to real large-size open-shell molecules due to their demanding computational resources, we need an alternative class of single-reference based methods, e.g., spin-projected methods using the spin-unrestricted solutions including low-order electron correlations such as the spin-projected UMP perturbation (PUMP) method.[20] Indeed, the PUMP methods reproduce well γ values for open-shell π-conjugated linear chain molecules calculated by the UCC method including the single, the double, and, perturbatively, the triple excitations [UCCSD(T)].[21,22] Still, these PUMP approaches are hardly applicable to large systems. On the other hand, the spin-unrestricted hybrid density functional theory (DFT) method employing a hybrid exchange-correlation functional with a large amount of HF exchange, in particular the BHandHLYP XC functional, is efficient to qualitatively describe the variation in static γ of the *p*-quinodimethane model as a function of the diradical character.[13] However, DFT methods based on conventional exchange-correlation functionals lead to catastrophic behavior when computing the linear and nonlinear responses of extended systems and therefore are not suitable to study the size effects on γ.[23] This failure has been related to the shortsightedness of the conventional XC functionals, which are not able to describe the ultranonlocality of the electronic response to electric fields. Nowadays, several solutions have been proposed and mostly correct the wrong behavior of the exchange component.[24] Although they are very promising, extensions are needed to include a balanced and consistent correlation term or to retrieve the computational advantages of DFT over high-order ab initio methods.[25]

In this paper, we address the potential of another single reference scheme, the spin-flip configuration interaction (SF-CI) method developed by Krylov,[26] which has been shown to describe the potential energy surface of the bond dissociation process with high precision in the single reference based theory.[26a] This foresees that the SF approach could be a reliable method to determine the properties including the second hyperpolarizabilities of diradical molecules. Then, compared to the conventional MRCI methods, in view of applications to large diradical systems, this method presents

the advantage of significantly reducing the need in computer resources. The reliability of the SF-CI method is examined here in combination with the finite-field (FF) approach. Four types of systems have been selected: the H_2 molecule under dissociation,[12a,17] the *p*-quinodimethane (PQM) model undergoing an aromatic-to-quinoid transformation,[13] *o*-quinoid five-membered ring models, and 1,4-bis(4,5-diphenylimidazol-2-ylidene)cyclohexa-2,5-diene (BI2Y).[14] The basis set dependence of these FF-SF-CI γ is also investigated for PQM and BI2Y. From the comparison of the FF-SF-CI results of γ to several conventional ab initio molecular orbital (MO) electron correlation and the DFT methods, we discuss the reliability and applicability of the FF-SF-CI method to determine the static γ of large-size singlet diradical molecules.

2. Calculation Methods

Within the FF approach, the longitudinal component of the static electronic γ_{iiii} (γ) is calculated using the fourth-order numerical differentiation expression[5b]

$$\gamma_{iiii} = \frac{1}{36(F^i)^4} \{ E(F^i) - 12E(F^i) + 39E(F^i) - E(0) +$$
$$39E(-F^i) - 12E(-2F^i) + E(-3F^i) \} \quad (1)$$

where $E(F^i)$ represents the total energy of a system in an electric field with an amplitude of F^i (the *i*th component of the field). The numerical stability on the derivatives was checked by using several values of F^i ranging from 0.0010 to 0.0360 au. The convergence on the total energy is fixed to 10^{-10} au. From these field amplitudes and the magnitudes of the total energies, the numerical errors of the FF method are estimated to be about 1% at most, except for the ROHF-SF-CIS(D)/6-31G*+*p* result of BI2Y (∼10%). Similar field amplitudes were already used in previous investigations.[13−18] The advantage of the FF method lies in the simplicity of the scheme, which only requires the evaluation of field-dependent energies, allowing its use with a broad range of methods including electron correlation and therefore the use of many program packages.

Details of the SF technique are presented in ref 26, so that we are restricted here to a brief explanation. In the SF single excitation CI (SF-CIS) method, the initial reference wave function is taken to be the open-shell Hartree−Fock (HF) triplet wave function, $|\cdots \phi_b\alpha\phi_a\alpha\rangle$, where ϕ_b and ϕ_a represent a pair of bonding (b) and antibonding (a) spatial orbitals, respectively. Allowing the spin-flipping operation, $\alpha \rightarrow \beta$, in the construction of single excitation configurations, the lowest spin-unrestricted CIS (UCIS) state corresponding to the ground state contains two configurations, $|\cdots \phi_b\alpha\phi_b\beta\rangle$ and $|\cdots \phi_a\alpha\phi_a\beta\rangle$, the latter being essential for describing the bond dissociation (singlet diradical state). This feature indicates that the SF-CIS method includes the static electron correlation in singlet diradical systems effectively within the single electron excitation scheme. The SF-CIS(D) method, which takes into account the double excitation effects in a perturbative manner, can correct for the lack of dynamical electron correlation. All (field-dependent) SF-CI calculations in this study were performed using the Q-CHEM 3.0 program package.[27]

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For comparison, we also apply the approximate spin-projection (AP) scheme based on the ab initio electron correlation methods. The APUHF and APUMPn low-spin (LS) energy of a $(2S+1)$ spin multiplet is given by[28]

$$^{LS}E_{APUX} = {}^{LS}E_{UX} + \frac{{}^{LS}\langle S^2 \rangle_{UX} - S(S+1)}{{}^{HS}\langle S^2 \rangle_{UX} - {}^{LS}\langle S^2 \rangle_{UX}}[{}^{LS}E_{UX} - {}^{HS}E_{UX}]$$

(2)

where HS represents the high-spin solution (a triplet for a diradical system) and X denotes the ab initio MO methods: HF, MPn ($n = 2, 4$), etc.

The diradical character y_i related to HOMO $- i$ and LUMO $+ i$ is defined by the weight of the doubly excited configuration in the multiconfigurational (MC)-SCF theory and is formally expressed in the case of the spin-projected UHF (PUHF) theory as[28,29]

$$y_i = 1 - \frac{2T_i}{1 + T_i^2}$$

(3)

where T_i is the orbital overlap between the corresponding orbital pairs (χ_{HOMO-i} and η_{HOMO-i}) and can also be represented by using the occupation numbers (n_i) of UHF natural orbitals (UNOs):

$$T_i = \frac{n_{HOMO-i} - n_{LUMO+i}}{2}$$

(4)

The diradical character y_i represents the instability of the chemical bond since the y_i amount to 0% and 100% for closed-shell and pure diradical states, respectively. The present calculation scheme using the UNOs is the simplest, but it reproduces the diradical characters calculated using highly correlated configuration interaction (CI) methods.[30]

3. Results and Discussion

3.1. H$_2$ Dissociation Model. For this simplest model, using the 6-31G**+sp ($\zeta_{s,p} = 0.0406$ on H atoms) basis set, the variations in γ are examined as a function of the diradical character y, while the reference triplet wave function is obtained at the UHF level. As shown in Figure 1(a), y remains equal to zero from the equilibrium bond distance ($r = 0.746$ Å at the CISD/6-31G**+sp level) to the triplet instability point[31] ($r = 1.2$ Å), where it starts to increase. As expected, it approaches 1.0 in the bond dissociation limit, i.e., the pure diradical state. Figure 1(b) sketches the variation curves of γ with y obtained at different levels of approximation. The reliability of the approximate methods is assessed by comparison to the full CI results, i.e., for a two-electron system, the CI singles and doubles (CISD) method. The full CI results show that γ increases with the increase of diradical character y, then it attains a maximum in the intermediate y region, and finally it decreases in the large y region. Due to triplet instability both the spin-restricted HF and low-order electron correlation methods, e.g., RMPn ($n = 2-4$), cannot reproduce the qualitative diradical character dependence of γ, whereas both the UHF and UMPn ($n = 2-4$) methods provide incorrect behavior of γ for the diradical character unless removing the spin contamination.[13] The APUHF and
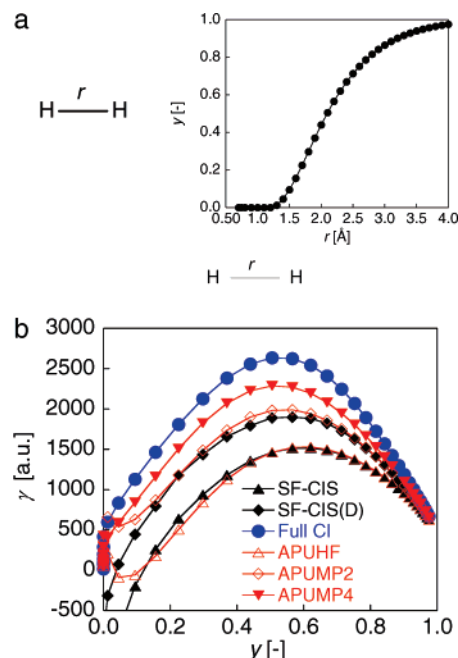

Figure 1. Diradical character (y) versus bond distance r [Å] for an H$_2$ dissociation model calculated from the UNOs using the 6-31G**+sp basis set (a) and evolution of the longitudinal γ [au] with y. The SF-CIS, SF-CIS(D), APUHF, and APUMPn ($n = 2, 4$) results are shown as well as the full CI results using the 6-31G**+sp basis set.

APUMPn ($n = 2, 4$) results reproduce semiquantitatively the full CI results except in the small y value region ($y < 0.2$),[13] where the AP scheme leads to an incorrect behavior owing to the lack of ionic configuration in the UHF spin-polarized solution. Indeed, as discussed in ref 32, the resonating HF method including ionic configurations in addition to the UHF spin polarized configurations is known to better reproduce the multireference based results in the whole region of y. Moreover, the SF-CIS and SF-CIS(D) curves nearly coincide with the APUHF and APUMP2 results, respectively, except in the small y region. This good agreement originates in the fact that the PUHF ($\sim$APUHF) ground-state wave function eliminating the triplet component from the singlet UHF is expressed by the UNO CASCI(2,2) form, whose configurations correspond to the dominant configurations included in the SF-CIS method. Therefore, the APUMP2 and SF-CIS(D) methods, which include the dynamical correlation effects at the second-order level, provide nearly the same behaviors of γ. The APUMP4 method, which involves the fourth-order correlation effects, further improves the amplitudes of γ and makes them closer to the full CI results.

The y value associated with the maximum in γ is slightly smaller when going from the SF-CIS ($\approx$ APUHF) to the full CI: $y_{max} = 0.621$ [SF-CIS($\approx$ APUHF)], $y_{max} = 0.566$ [SF-CIS(D)($\approx$APUMP2)], $y_{max} = 0.505$ (APUMP4 and full CI). On the other hand, the maximum γ value (γ_{max}) increases when going from the SF-CIS ($\approx$ APUHF) to the full CI: $\gamma_{max} = 1514$ (57%) [SF-CIS($\approx$ APUHF)], $\gamma_{max} = 1889$ (72%) [SF-CIS(D)], $\gamma_{max} = 1989$ (75%) (APUMP2), $\gamma_{max} = 2288$ (87%) (APUMP4), and $\gamma_{max} = 2635$ (100%) (full CI). In the pure diradical regions ($y \approx 1$), all methods give similar γ values since the static correlation is dominant.
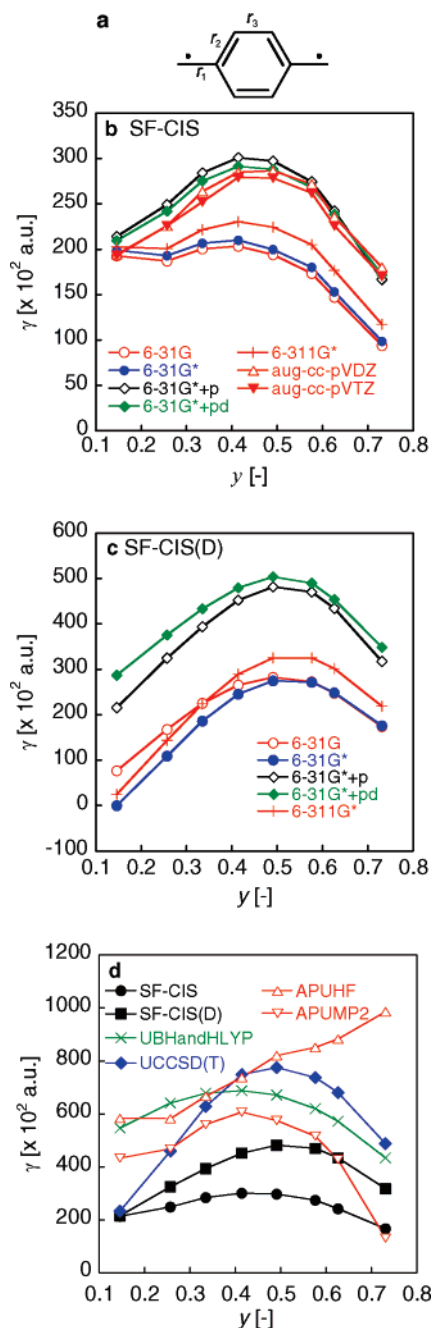
Figure 2. Key geometrical parameters of the *p*-quinodimethane (PQM) model (a) and basis set dependence of the longitudinal γ [$\times 10^2$ au] at the SF-CIS (b) and SF-CIS(D) (c) levels of approximation as well as the relationship between γ [$\times 10^2$ au] of PQM and its diradical character as determined using the SF-CIS, SF-CIS(D), UBHandHLYP, UCCSD(T), APUHF, and APUMP2 methods and the 6-31G*+p basis sets (d).

In summary, these results suggest that the FF-SF-CIS(D) scheme effectively includes the static and dynamic electron correlation effects on γ like the PUMPn schemes.

3.2. *p*-Quinodimethane Model. *p*-Quinodimethane (Figure 2(a)) is one of the simplest π-conjugated singlet diradical systems. In a previous study,[13] the variation in γ was monitored as a function of stretching the r_1 C−C bond length from 1.35 to 1.7 Å while constraining $r_2 = r_3 = 1.4$ Å.

Indeed, varying the geometry in this way leads to variations in the diradical character from 0.146 to 0.731. Since the choice of basis set is important for calculating γ, we first examined the basis set dependence of γ values of PQM at the FF-SF-CI level of approximation. Figure 2(b) shows the SF-CIS γ values calculated using the 6-31G, 6-31G*, 6-31G*+p, 6-31G*+pd ($\zeta_{p,d} = 0.0523$ on C atoms), 6-311G* and aug-cc-pVDZ and aug-cc-pVTZ basis sets as a function of y. The results using the double-ζ basis sets including diffuse functions, 6-31G*+p and 6-31G*+pd, are almost the same as those obtained with the aug-cc-pVDZ and aug-cc-pVTZ basis sets, though the latter ones provide slightly smaller γ values than the former ones: when increasing y, γ increases, attains a maximum for intermediate diradical character, and then decreases. Similarly, the γ values and their variations with y are quasi identical when employing the standard 6-31G, 6-31G*, and 6-311G* basis sets, where the triple-ζ basis set only slightly increases the γ values compared to double-ζ basis sets. On the other hand, the γ values are smaller than those using basis sets containing diffuse functions, except for $y = 0.146$ (equilibrium geometry). The SF-CIS(D) methods (Figure 2(c)) display a more pronounced diradical character dependence of γ than the SF-CIS scheme though the results with and without diffuse functions show similar differences. Judging from these results, the 6-31G*+p basis set is adopted for assessing the reliability of the FF-SF-CI schemes in comparison with other methods.

The most reliable and therefore reference results are obtained at the UCCSD(T) level, which significantly removes the spin contamination in the UHF solution. At this level, the behavior of γ with y mostly resembles the y-dependence of γ in the H_2 model (Figure 1(b)). In ref 13, it was found that all the spin-restricted-based post-HF and DFT methods cannot reproduce the UCCSD(T) results due to triplet instability in the intermediate and large y regions, whereas the UHF and UMPn ($n = 2-4$) methods provide an incorrect variation in γ, i.e., a monotonous decrease with y. On the other hand, the APUMP2 and the UBHandHLYP methods reproduce at least qualitatively the variations in γ except for small values of y where the γ values overshoot the reference values (see Figure 2(d)). The SF-CIS method also qualitatively reproduces the correct behavior of γ with y though the γ values are significantly underestimated, e.g., $\gamma_{max} = 30\,090$ au (39%) at $y = 0.414$ (SF-CIS) vs $\gamma_{max} = 77\,540$ au (100%) at $y_{max} = 0.491$ [UCCSD(T)]. The SF-CIS(D) method improves the γ estimate in the intermediate y value region, which amounts to 62% (48 150 au at $y_{max} = 0.491$). In contrast to the H_2 dissociation model, the SF-CIS(D) and APUMP2 results are different, and the same is true for SF-CIS and APUHF. In the intermediate y value region, the APUMP2 γ values are closer to the UCCSD(T) γ values than the SF-CIS(D), the feature of which suggests the more effective inclusion of the dynamical electron correlation by the APUMP2 method. For small values of y, the variations of γ are better described by the SF-CIS(D) method than using APUMP2. The APUHF scheme does not reproduce the behavior of γ with the diradical character. Thus, considering PQM, the SF-CI methods are able to describe the diradical

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Table 1. Comparison of CPU Times (s) for Single Point Calculations on PQM Using the SF-CIS, SF-CIS(D), and UCCSD(T) Methods

basis set	6-31G	6-31G*	6-31G*+p
number of basis functions	88	136	160
CPU times : SF-CIS [s]	11	60	180
CPU times : SF-CIS(D) [s]	111	731	1501
CPU times : UCCSD(T) [s]	5669	37253	85025

character dependence of γ, at least at a comparable level to the APUMP2 and UBHandHLYP methods.

As shown in Table 1, the CPU time required to perform SF-CIS(D) calculations are 1−2 orders of magnitude smaller than for UCCSD(T) calculations, and the computational efforts for SF-CIS calculations are further reduced by about a factor of 10. These CPU times correspond to single point calculations (at equilibrium geometry) performed on Pentium D 3.6 GHz workstation using the Q-CHEM 3.0 program package. Furthermore, the CPU time scaling, estimated by considering larger basis sets, is also smaller for SF-CIS(D) than for UCCSD(T).

The SF concept has also been applied to several other calculation methods, e.g., the SF equation of motion CCSD (SF-EOM-CCSD)[33] and the SF time-dependent DFT (SF-TDDFT),[34] and was then combined here with the FF method to estimate γ values. Figure 3(a) shows the SF-EOM-CCSD γ values as a function of y in comparison with the SF-CIS, SF-CIS(D), UCCSD, and UCCSD(T) results. The SF-EOM-CCSD γ values are in good agreement with those of the UCCSD method, though the maximum in γ is displaced toward large y values, while in the small and intermediate y regions, they tend to undershoot the UCCSD(T) γ values.

Turning to the SF-TDDFT scheme, several exchange-correlation functionals have been considered: B3LYP (20% HF + 8% Slater + 72% Becke88 for exchange, 19% VWN + 81% LYP for correlation), the BHandHLYP functional (50% HF + 50% Becke88 for exchange, 100% LYP for correlation), and a series of modified BHandHLYP functionals including 60, 70, and 80% of HF exchange (60, 70, 80% HF + 40, 30, 20% Becke88 for exchange, 100% LYP for correlation) (see Figure 3(b)). Using the traditional BHandHLYP functional, the diradical character dependence of γ is similar to the UB3LYP results, while the SF-TDDFT-B3LYP data display negative γ values for small diradical character and then a rapid increase with y. Similar shifts of maximum point were reported at the AP-UBHandHLYP level for the H_2 dissociation model, and this was related to overprojection judging from the fact that the spin contaminations at the level of DFT are significantly smaller than those at the level of UHF based approximations. Similarly, one can relate the PQM γ overestimation at the SF-TDDFT-BHandHLYP level to this overprojection as well as to shortsightedness of the DFT exchange functional.[35] Indeed, successive increase of the HF exchange leads to qualitative and quantitative improvement in the description of the variations in γ as a function of y. Nevertheless, when the percentage of HF exchange is large (80%), this approach leads to negative γ values at equilibrium geometry.
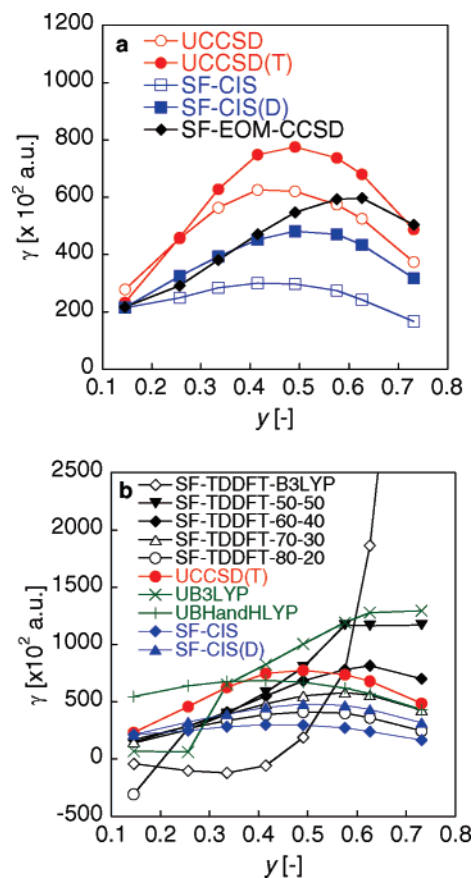

Figure 3. Diradical character dependence of longitudinal γ [× 10^2 au] of PQM for the SF-EOM-CCSD (a) and the SF-TDDFT (b) level of approximations. For SF-TDDFT, we employ the B3LYP (20% HF + 8% Slater + 72% Becke88 for exchange, 19% VWN + 81% LYP for correlation), the BHandHLYP functional (50% HF + 50% Becke88 for exchange, 100% LYP for correlation), and a series of modified BHandHLYP functionals including 60, 70, and 80% of HF exchange (60, 70, 80% HF + 40, 30, 20% Becke88 for exchange, 100% LYP for correlation). These are represented by SF-TDDFT-B3LYP, −50−50, −60−40, −70−30, and −80−20, respectively.

3.3. *o*-Quinoid Five-Membered Ring Models. To further investigate the reliability of the FF-SF-CI calculation, the γ values of two *ortho*-quinoid five-membered ring structures were evaluated. Model compounds A and B are built from a pyrrole or thiophene ring bearing two methylene groups in the β position, respectively (Figure 4(a)). Following UB3LYP/6-31G** geometry optimization, the y values calculated by the UHF/6-31G*+p method amount to 0.487 for model A and 0.694 for model B. Thus, y increases when the ring aromaticity decreases, starting from $y = 0.146$ for PQM (benzene ring). Despite their larger y values, models A and B present smaller γ values than PQM, at least when considering the direction connecting the radical sites (corresponding to the horizontal axis in Figure 4(a)). This is most probably associated with their smaller extent−and therefore electron delocalization−in this direction.

Figure 4(b) compares the γ values calculated at the SF-CIS, SF-CIS(D), UBHandHLYP, and UCCSD(T) levels of approximation using the 6-31G*+p basis set. The

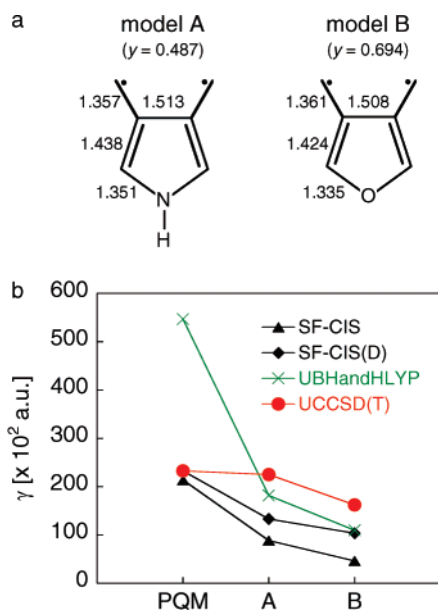**1704** *J. Chem. Theory Comput., Vol. 3, No. 5, 2007*

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Figure 4. Optimized geometries of *o*-quinoid five-membered ring models involving NH (model A) and O (model B) (a) and calculated γ (along the horizontal axis) [$\times$ 10^2 au] of these models in comparison with that of PQM at equilibrium geometry (b).
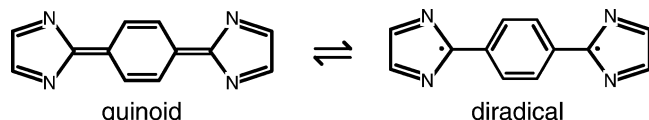

Figure 5. Resonance structures (quinoid and diradical forms) of BI2Y.

Table 2. Longitudinal γ Values [$\times$ 10^2 au] of BI2Y[a]

method	6-31G	6-31G*+p
UHF	1736	2002
UMP2	9387	9962
UMP3	7747	–
UMP4SDTQ	7484	–
PUHF ($l = 3$)	−862	–
PUMP2 ($l = 3$)	6944	–
PUMP3 ($l = 3$)	4682	–
UCCSD	4474	–
UCCSD(T)	5244	–
UBHandHLYP	4844	6534
UHF-SF-CIS	6278	5709
ROHF-SF-CIS	3570	3370
UHF-SF-CIS(D)	2681	2594
ROHF-SF-CIS(D)	4370	60 × 10^2

^{a} γ calculations at the UMP3, UMP4SDTQ, PUHF($l = 3$), PUMP2($l = 3$), PUMP3($l = 3$), UCCSD, and UCCSD(T) levels of approximation could not be performed due to storage needs exceeding our computer capabilities.

UCCSD(T) γ decreases in the following order: PQM (233 $\times$ 10^2 au) > model A (225 $\times$ 10^2 au) > model B (162 $\times$ 10^2 au). Compared to UCCSD(T), the UBHandHLYP method significantly overshoots the difference of γ value for PQM (547 $\times$ 10^2 au; 245%), while it gives similar values for the *o*-quinoid models A (181 $\times$ 10^2 au; 80%) and B (109 $\times$ 10^2 au; 67%). This can be understood by the fact that the latter two models lie in the intermediate *y* region, where the UCCSD(T) γ is well reproduced by the UBHandHLYP γ, whereas the PQM lies in the small *y* region, where UBHandHLYP method overshoots the UCCSD(T) γ (see Figure 2(d)). The SF-CIS method underestimates the UCCSD(T) values, model A (89 $\times$ 10^2 au; 40%) and model B (46 $\times$ 10^2 au; 28%), while adding dynamical electron correlation effects at the SF-CIS(D) level improves the agreement with the reference data: model A (133 $\times$ 10^2 au; 59%) and B (103 $\times$ 10^2 au; 64%). In summary, the SF-CIS and the SF-CIS(D) methods can describe at least qualitatively the variations of γ due to changing the nature of the aromatic ring of diradical species.

3.4. 1,4-Bis(imidazole-2-ylidene)cyclohexa-2,5-diene. In order to assess the applicability of the SF-CI method to systems of practical interest, we examined the γ value of BI2Y (Figure 5), a thermally stable π-conjugated diradical molecule.[36] We use the geometry of ref 14, which was optimized under the constraint of D_{2h} symmetry by the B3LYP/6-31G** method. This molecule displays an inter-mediate diradical character [$y = 0.4227$ as calculated by the UHF/6-31G*+p ($\zeta = 0.0523$ for C atoms and 0.0582 for N atoms)] in the singlet ground state. Table 2 further addresses the basis set dependence of γ at the UHF, UMP2, UBHandHLYP, SF-CIS, and SF-CIS(D) levels of approximation. Because the $<S^2>$ values of the UHF triplet states of BI2Y are relatively large, 2.36 (6-31G) and 2.28 (6-31G*+p), SF-CI calculations based on the UHF triplet reference state are expected to give a spin contaminated ground state. Indeed, the $<S^2>$ values of the SF-CIS ground state are 0.80 (6-31G) and 0.69 (6-31G*+p), which lead to the significant over- or underestimation of γ values. Therefore, we also consider another type of reference state having no spin contamination, i.e., the restricted open-shell HF (ROHF) triplet state. We perform the SF-CI calculations starting with the restricted open-shell HF (ROHF) triplet wave function as the reference state (ROHF-SF-CI) in addition to those using the UHF triplet one (UHF-SF-CI) in order to examine the spin contamination effects on SF calculations.

It is found that the 6-31G results are smaller than the 6-31G*+p results: 87% (UHF), 94% (UMP2), and 74% (UBHandHLYP). For the SF-CI approach, the 6-31G results are slightly larger than the 6-31G*+p results: 110% (UHF-SF-CIS), 103% (UHF-SF-CIS(D)), and 106% (ROHF-SF-CIS), except for the 73% of the ROHF-SF-CIS(D) results. As a result, the 6-31G basis set was further used for semiquantitatively examining the dependence of γ on the applied calculation methods. Similarly to the PQM model, the UMPn ($n = 2-4$) methods tend to overshoot the UCCSD(T) γ value, while the UBHandHLYP result ($\gamma = 4844$ au; 92%) is very close (see Table 2). The PUMP2 ($l = 3$) ($\gamma = 6944$ au; 132%) and PUMP3 ($l = 3$) ($\gamma = 4682$ au; 89%), which use the *l*-fold spin-projection scheme by Löwdin,[20] well reproduce the UCCSD(T) γ value. The UHF-SF-CIS method ($\gamma = 6278$ au; 120%) seems to be a good approximation to the UCCSD(T) γ values, whereas the UHF-SF-CIS(D) ($\gamma = 2681$ au) undershoots these by a factor of 2. This deficiency of the SF-CIS(D) results is due to the spin contamination described above. Indeed, it is significantly

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improved by using the ROHF triplet reference as the initial wave function. Using the 6-31G basis set, the ROHF-SF-CIS and -CIS(D) approaches reproduce about 68% and 84% of the UCCSD(T) γ value. These ROHF-SF-CIS/UCCSD(T) and ROHF-SF-CIS(D)/UCCSD(T) ratios are even better than for the H_2 model system (53 and 70% for $y = 0.44$) and PQM (40 and 60% for $y = 0.41$) models. The ROHF-SF-CIS(D) results are also very similar to the UBHandHLYP results for both basis sets.

4. Concluding Remarks

The SF-CI approach has been employed to evaluate the static second hyperpolarizability of diradical systems covering a wide range of diradical character, and these results have been compared to those of reference ab initio methods as well as of hybrid DFT schemes. For the H_2 molecule under dissociation, the SF-CIS and SF-CIS(D) methods provide similar γ values to the APUHF and APUMP2 methods, respectively, while they reproduce qualitatively or semi-quantitatively the variation in γ with the diradical character obtained by reference high-level electron correlation methods. These conclusions further extend to γ of the model of the *p*-quinodimethane molecule of which the diradical character is externally modified by stretching as well as to the trend in γ among related quinoid compounds, *p*-quinodimethane and *o*-quinoid five-membered ring models. In the case of *p*-quinodimethane, these SF calculations have been extended to the EOM-CC and TDDFT levels of approximation. Though the SF-EOM-CCSD approach reproduces qualitatively the *y*-dependence of γ obtained at the UCCSD level of approximation, the SF-TDDFT approach only provides qualitatively correct results when the exchange-correlation functional contains a large (>70%) percentage of Hartree−Fock exchange. In the case of *p*-quinodimethane, a basis set investigation has shown the need for including a set of *p* diffuse functions, particularly at the SF-CIS(D) level.

Treating the BI2Y molecule, a larger system of practical interest, has evidenced other phenomena. Indeed, the *usual* UHF triplet reference presents a non-negligible spin contamination, which transfers to the SF-CI ground state as shown by $<S^2>$ values larger than 0.6 at the SF-CIS level of approximation. This leads to an underestimation of the SF-CIS(D) γ value, whereas the SF-CIS result is in better agreement. On the other hand, by employing the spin contamination-free ROHF method to define the reference wave function, the SF-CIS(D) γ value gets in good agreement with the reference UCCSD(T) result. Since the ROHF-based SF-CIS and SF-CIS(D) approaches also perform well for the H_2 and PQM model, they turn out to be promising calculation schemes, especially when dealing with large compounds presenting diradical character, such as diphenalenyl compounds. This reliability has also to be contrasted with the difficulties of conventional DFT methods, i.e., without long-range corrections, to address size-dependence effects on γ. Future investigations will concern the determination of both geometries and hyperpolarizabilities of diradical species since the γ values of conjugated systems are sensitive to the geometry and particularly to the bond length alternation along the conjugated backbone. Indeed,

very recently, the importance of spin-projection was highlighted for geometry optimization at the UDFT level of approximation,[37] whereas the SF-TDDFT approach was also shown to reproduce highly correlated MO methods in the case of singlet diradical systems. Further investigations will also tackle the efficiency of the SF-TDDFT approach as a function of the nature of the exchange-correlation functional.

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