Chemical Physics Letters 622 (2015) 115–119

Contents lists available at ScienceDirect

Chemical Physics Letters

journal homepage: www.elsevier.com/locate/cplett

Vertical excitation energies of linear cyanine dyes by spin-flip time-dependent density functional theory

Noriyuki Minezawa

Fukui Institute for Fundamental Chemistry, Kyoto University, Sakyo-ku, Kyoto 606-8103, Japan

ARTICLE INFO

Article history:
Received 31 October 2014
In final form 19 January 2015
Available online 23 January 2015

ABSTRACT

Vertical excitation energies of linear cyanine dyes are examined using the spin-flip time-dependent density functional theory. The Hartree–Fock exchange (HFX) plays an essential role in predicting the absorption spectra, and the best values are obtained by the combination of collinear approximation and hybrid functionals with ~50% HFX. The non-collinear approach with pure density functionals underestimates the excitation energy severely. The significant error is due to low excitation energy from the reference triplet to first excited singlet state. The excitation energy decomposition gives small orbital energy difference term and large negative non-collinear kernel.

1. Introduction

Accurate prediction of excitation energies is of critical importance not only for designing new molecular materials but for analyzing the photochemical processes after light absorption. Computing the absorption energies of linear cyanine dyes (Figure 1), which forms π-conjugation along the chain, is challenging to theoretical methods. The observation is surprising because the lowest excited-state is described as the excitation from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). Several benchmark studies have been reported using various methodologies including multi-reference perturbation theory, many-body perturbation theory, coupled cluster, diffusion Monte Carlo (DMC), and density functional theory [1–6].

The linear-response time-dependent density functional theory (LR-TDDFT) [7] is a promising approach to simulate the excitation energies for large molecules with modest computational cost. A large number of benchmark studies have been reported to investigate the performance of LR-TDDFT and to propose new density functionals [8]. The previous studies on linear cyanine dyes show the LR-TDDFT method overestimates the excitation energy [2–4]. Grimme and Neese found that the double hybrid functional yields the better result [9]. These authors argued the difference of electronic correlation between the ground and excited states is partially accounted for by the correlation energy of the second-order Møller–Plesset perturbation theory (MP2) and the configuration interaction singles with doubles correction. The notorious charge-transfer problem that is inherent in the LR-TDDFT is not severe for these molecules; the range-separated functional does not improve the results [10].

This Letter reports the computational study on the excitation energy of linear cyanine dyes by using the spin-flip TDDFT (SF-TDDFT) [11–19]. This approach has been successfully applied to describe the conical intersections of ethylene, butadiene, and the model chromophore of protonated Schiff base retinal [20–23]. Thus, it is interesting to examine the accuracy by applying the SF-TDDFT to linear cyanine dyes. Furthermore, one expects that the SF-TDDFT can take into account the correlation energy contribution of LUMO explicitly because the reference triplet state is $(\mathrm{HOMO})^1(\mathrm{LUMO})^1$. Very recently, Filatov and Huix-Rotllant have investigated linear cyanine dyes using the ensemble DFT, LR-TDDFT, SF-TDDFT and ΔSCF (self-consistent field) methods [24]. In the SF-TDDFT computation, these authors employed exclusively the hybrid functional with ~50% Hartree–Fock exchange (HFX) in conjunction with the collinear approximation. This work introduces various functionals including local density approximation (LDA), semi-local generalized gradient approximation (GGA), hybrid GGA, and meta-GGA functionals. In addition, a comparison is made between the collinear and non-collinear approaches implemented in the program package GAMESS [25,26]. The latter formulation is general and applicable to any functionals while the collinear approximation allows only the hybrid functionals.

2. Method

2.1. Non-collinear SF-TDDFT method

In this work, the non-collinear SF-TDDFT method [12–19] is developed within the Tamm–Dancoff approximation. The

---

E-mail address: minezawa@fukui.kyoto-u.ac.jp

http://dx.doi.org/10.1016/j.cplett.2015.01.033
0009-2614/

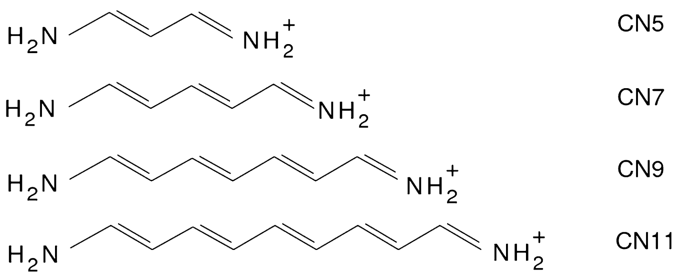

Figure 1. Molecular structure of cyanine dyes.

SF-TDDFT employs the triplet state with two unpaired alpha electrons as the reference, and the response states are described by alpha-to-beta spin-flip excitations. The transition amplitude **X** and excitation energy Ω are obtained by solving the Hermitian matrix equation:

$$\mathbf{AX} = \Omega\mathbf{X} \tag{1}$$

The coupling matrix **A** is

$$A_{i\bar{a},j\bar{b}} = (\varepsilon_{\bar{a}} - \varepsilon_i)\delta_{ij}\delta_{\bar{a}\bar{b}} + f^{\text{ncol}}_{i\bar{a},j\bar{b}} - c_x(ij|\bar{a}\bar{b}) \tag{2}$$

As usual, $i, j, \ldots$ label the occupied orbitals and $a, b, \ldots$ the virtual orbitals. The bar symbol denotes the beta spin. ε is the orbital energy, and c_x is the mixing weight of HFX. Mulliken notation is adopted for the two-electron integral. The second term of Eq. (2) is the non-collinear kernel:

$$f^{\text{ncol}}_{i\bar{a},j\bar{b}} = \int d\mathbf{r} \frac{(\delta E^{\text{xc}}/\delta n_\alpha(\mathbf{r})) - (\delta E^{\text{xc}}/\delta n_\beta(\mathbf{r}))}{n_\alpha(\mathbf{r}) - n_\beta(\mathbf{r})} \psi_i(\mathbf{r})\psi_j(\mathbf{r})\bar{\psi}_a(\mathbf{r})\bar{\psi}_b(\mathbf{r}) \tag{3}$$

The numerator is the difference between the exchange potential, and the denominator is the spin density of the reference state, i.e., the triplet state with two unpaired alpha electrons.

Shao et al. [11] have developed the collinear approximation by neglecting the non-collinear kernel ($\mathbf{f}^{\text{ncol}}$). In this case, only the HFX term contributes the off-diagonal elements of the coupling matrix. Thus, one must employ the functionals with a fraction c_x of HFX. Otherwise, the coupling matrix is diagonal and gives the orbital energy difference as the excitation energy.

For the non-collinear calculations, three approaches are considered here. The first method (NCOL0) computes Eq. (3) rigorously. Using the partial integration, Li and Liu [16] evaluate this term as the second functional derivatives ($\delta^2 E^{\text{xc}}/\delta n \delta n$) and the second derivatives of electron density ($\nabla\nabla n$). This formulation yields nearly zero excitation energy for the response ($M_S = 0$) triplet states. The drawback is severe numerical instability as pointed out in Ref. [16]. The second approach (NCOL1) can eliminate the instability entirely by setting the terms stemming from the density derivative (∇n) and kinetic energy density (τ) to be zero

$$\frac{(\delta E^{xc}/\delta n_\alpha(r)) - (\delta E^{xc}/\delta n_\beta(r))}{n_\alpha(r) - n_\beta(r)} \rightarrow \left[\frac{(\partial E^{xc}/\partial n_\alpha(r)) - (\partial E^{xc}/\partial n_\beta(r))}{n_\alpha(r) - n_\beta(r)}\right]_{\nabla n = \tau = 0} \tag{4}$$

Note the change from the functional derivative to the density derivative. Li and Liu call this approximation ALDA0 and show that this replacement can provide numerically stable results even for GGA functionals [16]. The last approach (NCOL2) replaces the functional derivative by the derivative with respect to explicit density but keeps the density derivative and kinetic energy density

$$\frac{(\delta E^{\text{xc}}/\delta n_\alpha(\mathbf{r})) - (\delta E^{\text{xc}}/\delta n_\beta(\mathbf{r}))}{n_\alpha(\mathbf{r}) - n_\beta(\mathbf{r})} \rightarrow \frac{(\partial E^{\text{xc}}/\partial n_\alpha(\mathbf{r})) - (\partial E^{\text{xc}}/\partial n_\beta(\mathbf{r}))}{n_\alpha(\mathbf{r}) - n_\beta(\mathbf{r})} \tag{5}$$

In contrast to NCOL1, this approximation encounters numerical instability when n_α approaches n_β. The numerator does not always converge to zero due to the density derivative and the kinetic energy density.

2.2. SF-TDDFT excitation energies

The SF-TDDFT excitation energies are calculated using the three approaches [18,19]. The first method (SF1) computes the energy as follows:

$$\begin{aligned} \Delta E^{\text{SF1}} &= E^{\text{SF}}(\text{S}_1) - E^{\text{SF}}(\text{S}_0) \\ &= \Omega(\text{S}_1|\text{T}_1) - \Omega(\text{S}_0|\text{T}_1) \end{aligned} \tag{6}$$

where $\Omega(\text{S}_1|\text{T}_1)$ denotes the excitation energy from the reference triplet T_1 to singlet S_1 state. Similarly, $\Omega(\text{S}_0|\text{T}_1)$ is the transition energy from the reference T_1 to ground state S_0. Both $\Omega(\text{S}_0|\text{T}_1)$ and $\Omega(\text{S}_1|\text{T}_1)$ are obtained by the standard SF-TDDFT calculation. The SF1 method is simple and yields the excitation energy by a single energy calculation. Moreover, the S_0 and S_1 states can be treated on an equal footing.

The second method (NSF2) [18,19] uses the ground-state Kohn–Sham (KS) DFT energy instead of $E^{\text{SF}}(\text{S}_0)$,

$$\Delta E^{\text{NSF2}} = E^{\text{SF}}(\text{S}_1) - E^{\text{KS}}(\text{S}_0) \tag{7}$$

The NSF2 method is intended to correct the closed-shell ground state on the assumption that the KS-DFT energy gap is more accurate than the SF-TDDFT $\Omega(\text{S}_0|\text{T}_1)$. Eq. (7), however, may introduce some bias due to two different methods employed.

The last method (SF2) [18,19] uses Yamaguchi's spin projection formula [27] to eliminate the spin contamination of the S_1 state,

$$\Delta E^{\text{SF2}} = \Delta E^{\text{NSF2}} - \left[\Omega(\text{S}_1|\text{T}_1) - \frac{2\Omega(\text{S}_1|\text{T}_1)}{\langle S^2\rangle_{\text{T}_1} - \langle S^2\rangle_{\text{S}_1}}\right] \tag{8}$$

where $\langle S^2\rangle$ is the spin expectation value of $\hat{S}^2$ for the unrestricted KS T_1 state or the spin-flipped S_1 state.

2.3. Computational details

The developed codes were interfaced with the program package GAMESS [25,26]. Geometries at the MP2/cc-pVQZ level were taken from Ref. [4]. The linear cyanine molecules have C_{2v} symmetry, and the excitation from the ground (A_1) to the lowest (B_2) singlet state was considered. Unrestricted KS-DFT was used to describe the reference B_2 triplet state, in which two singly occupied π orbitals have b_1 and a_2 symmetries. The functionals examined in this work are LDA (SVWN [28,29]), semi-local and hybrid GGA (BLYP [30,31], B3LYP [32–34], BHHLYP [30,31], PBE [35,36], PBE0 [35–37], PBE50 [17]), range-separated CAMB3LYP [38], and meta-GGA (M06 [39], M06-2X [39], M06-HF [40]). The basis set employed was TZVP [41,42], and the deviation of excitation energy is 0.02 eV compared to the largest basis set (see Table S1 in the Supplementary material). The numerical integration was performed using 96 radial points and 590 Lebedev's angular grid. The collinear approach requires the non-zero HFX, and thus pure density functionals are not applicable. Also, the NCOL0 approach is not available for meta-GGA because it is difficult to develop the rigorous integration of kinetic energy density.