

Extension of Frozen-orbital Analysis to the Tamm–Dancoff Approximation to Time-dependent Density Functional Theory

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(Received March 3, 2009; CL-090216; E-mail: nakai@waseda.jp)

Frozen-orbital analysis (FZO), which has been proposed in order to analyze excitations between degenerate orbitals, is extended to the Tamm–Dancoff approximation to time-dependent density functional theory (TDDFT/TDA). FZO for TDDFT/TDA with BLYP and B3LYP is applied to a CO molecule, and the difference between TDDFT/TDA and configuration interaction singles (CIS) is discussed.

Time-dependent density functional theory (TDDFT)¹ and the Tamm–Dancoff approximation (TDA) to TDDFT (TDDFT/TDA)¹ have become one of the most popular tools to calculate valence excitations owing to its low computational cost and reasonable accuracy in comparison with less accurate configuration interaction singles (CIS) based on Hartree–Fock (HF) method or computationally expensive correlated methods. However, it has been reported that TDDFT and TDDFT/TDA using conventional exchange–correlation functionals fail for core and Rydberg excitations. Remedies against the problems have been proposed by several groups recently.²

The difference between TDDFT/TDA and CIS has not been discussed in detail so far. For example, orbital energy difference $\Delta\epsilon$, which can be considered to be an approximate excitation energy, strongly depends on HF and DFT with conventional pure and hybrid functionals: the HF $\Delta\epsilon$ is generally larger than those of DFT with conventional pure and hybrid functionals. However, TDDFT/TDA and CIS provide excitation energies that do not exhibit as significant a difference as $\Delta\epsilon$. By comparing TDDFT/TDA with CIS, we can understand how excitation energies of TDDFT/TDA and CIS are estimated in terms of not only orbital energies but also two-electron integrals and exchange–correlation functionals. Frozen-orbital analysis (FZO),³ which considers only main configurations contributing to excitations, is a useful tool to qualitatively discuss the difference and provide a clear and intuitive picture about excitations among degenerate orbitals. So far, we have applied FZO to several molecules and obtained the following simple and clear general rules: (i) the highest transition is dipole-allowed out of excitations between degenerate orbitals, (ii) the energy gap between the highest (dipole-allowed) and second states is larger than the other gaps.

In this paper, we extend FZO to TDDFT/TDA and discuss the difference. We investigate excitations of CO from π to π^* orbitals by FZO for CIS and TDDFT/TDA with BLYP⁴ and B3LYP⁵ using the cc-pVDZ⁶ basis set. The SAC-CI⁷ calculations are also performed for comparison. The FZO for CO corresponds to the single excitations within the active space, consisting of highest occupied π and lowest unoccupied π^* orbitals. Necessary integrals for FZO are computed by the modified GAMESS program.⁸ The bond distance of C–O is 1.1283 Å.

The excitation energies in FZO are split into three terms as follows: $\Delta E = A + B + C$, where A is the orbital energy differ-

Table 1. FZO energy components of $\pi \rightarrow \pi^*$ excitation energies for CO

State	A	B	C
$^1\Sigma^+$	$(\epsilon_a - \epsilon_i)$	$(-c_{\text{HF}}J_{ia} + 2K_{ia} + (1 - c_{\text{HF}})K_{ia}^{\text{DFT}})$	$+[-c_{\text{HF}}(ab ij) + 2(ai jb) + (1 - c_{\text{HF}})(ai w_{xc} jb)]$
$^1\Delta$	$(\epsilon_a - \epsilon_i)$	$(-c_{\text{HF}}J_{ia} + 2K_{ia} + (1 - c_{\text{HF}})K_{ia}^{\text{DFT}})$	$-[-c_{\text{HF}}(ab ij) + 2(ai jb) + (1 - c_{\text{HF}})(ai w_{xc} jb)]$
$^1\Delta$	$(\epsilon_a - \epsilon_i)$	$(-c_{\text{HF}}J_{ja} + 2K_{ja} + (1 - c_{\text{HF}})K_{ja}^{\text{DFT}})$	$+[-c_{\text{HF}}(ab ij) + 2(aj ib) + (1 - c_{\text{HF}})(aj w_{xc} ib)]$
$^1\Sigma^-$	$(\epsilon_a - \epsilon_i)$	$(-c_{\text{HF}}J_{ja} + 2K_{ja} + (1 - c_{\text{HF}})K_{ja}^{\text{DFT}})$	$-[-c_{\text{HF}}(ab ij) + 2(aj ib) + (1 - c_{\text{HF}})(aj w_{xc} ib)]$

ence $\Delta\epsilon$ and the B and C terms consist of $\{J_{ov}, K_{ov}$, and $K_{ov}^{\text{DFT}}\}$ and $\{(oo'|vv'), (ov|o'v')$, and $(ov|w_{xc}|o'v')\}$, respectively. J_{ov} , K_{ov} , and K_{ov}^{DFT} represent $(oo|vv)$, $(ov|ov)$, and $(ov|w_{xc}|ov)$, respectively. w_{xc} represents the second derivative of exchange–correlation functionals with respect to the density. The indexes $\{o, o'\}$ and $\{v, v'\}$ represent general occupied and virtual orbitals. The B and C terms originate in diagonal and off-diagonal elements of Slater determinant, respectively. Specifically, Table 1 shows the FZO energy expressions of the A , B , and C terms of CO for CIS and TDDFT/TDA with BLYP and B3LYP in a unified way. c_{HF} represents a portion of HF exchange. For example, $c_{\text{HF}} = 1.0$ for the CIS method, whereas c_{HF} of B3LYP and BLYP are set to 0.2 and 0.0, respectively. Note that two orbitals $\{i, a\}$ and $\{j, b\}$ of $\{\pi, \pi^*\}$ are located on xz and yz planes, respectively, where the CO bonding axis is z axis.

Figure 1 illustrates the energy splitting of $^1\Sigma^+$, $^1\Delta$, and $^1\Sigma^-$ by FZO for CIS and TDDFT/TDA with BLYP and B3LYP. The left energy levels estimated by the A term are the orbital energy differences $\Delta\epsilon$ between π and π^* orbitals. As mentioned above, TDDFT/TDA and CIS provide the significantly different energy levels. As a portion of HF exchange increases, $\Delta\epsilon$ also increases. The two energy levels with about 4–6-eV gap are obtained by considering not only the A but also B terms for all methods. The three energy levels on the right are reproduced by $A + B + C$. The large gap between the highest and second states is observed: the dipole-allowed highest excited state is well separated from the other excited states, which is consistent with the general rule obtained in ref 3.

Next, we examine the behavior of Figure 1 in greater detail. Table 2 lists the values of A , B , and C of CO estimated by FZO

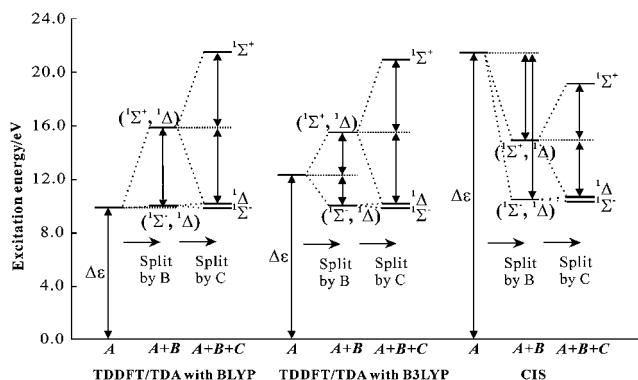
**Figure 1.** Schematic picture of excitation-energy splitting of CO.

Table 2. FZOA energy components of CO $\pi \rightarrow \pi^*$ excitation energies by CIS, TDDFT/TDA with BLYP and B3LYP with cc-pVDZ in eV

	State	A				B				C				Excitation energy		
		$\Delta\mathcal{E}$	$c_{\text{HF}}J_{ov}$	K_{ov}	K_{ov}^{DFT}	Total	$c_{\text{HF}}(ab ij)$	$(ov o'v')$	$(ov w_{xc} o'v')$	Total	FZOA	Full	Exptl			
TDDFT/TDA with BLYP	$^1\Sigma^+$	(9.90)	(0.00)	(3.72)	(-1.47)	(5.96)	(0.00)	(3.01)	(-0.35)	5.67	21.53	14.71				
	$^1\Delta$									-5.67	(10.20)	(10.20)	(10.23)			
	$^1\Delta$		(0.00)	(0.35)	(-0.56)	(0.15)		(0.35)	(-0.56)	0.15						
	$^1\Sigma^-$									-0.15	9.90	9.90	9.88			
TDDFT/TDA with B3LYP	$^1\Sigma^+$	(12.28)	(2.69)	(3.55)	(-1.12)	(3.28)	(0.09)	(2.87)	(-0.28)	5.37	20.93	15.09				
	$^1\Delta$									-5.37	(10.19)	(10.17)	(10.23)			
	$^1\Delta$		(2.52)	(0.34)	(-0.42)	(-2.26)		(0.34)	(-0.42)	0.17						
	$^1\Sigma^-$									-0.17	9.85	9.83	9.88			
CIS	$^1\Sigma^+$	(21.47)	(12.29)	(2.86)	(0.00)	(-6.56)	(0.38)	(2.31)	(0.00)	4.23	19.13	14.75				
	$^1\Delta$									-4.23	(10.68)	(10.53)	(10.23)			
	$^1\Delta$		(11.52)	(0.28)	(0.00)	(-10.97)		(0.28)	(0.00)	0.18						
	$^1\Sigma^-$									-0.18	10.33	9.99	9.88			

for CIS and TDDFT/TDA with BLYP and B3LYP. The values of the A term are in the order of CIS, B3LYP, and BLYP: $\Delta\mathcal{E}$ of BLYP and B3LYP are 9.90 and 12.28 eV, respectively, which are significantly smaller than 21.47 eV of CIS. As regards the B term, the balance of J_{ov} and K_{ov} determines an overall trend since K_{ov}^{DFT} is relatively small. In general, the lower states for all methods are determined by the main contributions of $-c_{\text{HF}}J_{ja}$ and the higher states are lifted from the lower states by 4–6 eV through the main contributions of $2K_{ia} - c_{\text{HF}}J_{ia}$. Let us examine the details: For BLYP, the lower state is not affected significantly in spite of the consideration of the B term since $-c_{\text{HF}}J_{ja}$ is missing and K_{ja} and K_{ja}^{DFT} are relatively small. The reason for the small contribution is ascribed to the spatial distance between two orbitals $\{j, a\}$. The higher state is lifted by 5.81 eV from the lower one by the consideration of the B term. For B3LYP, the lower state is lowered by 2.26 eV, which mainly comes from $-c_{\text{HF}}J_{ja}$ term, while the higher state is lifted by 3.28 eV. The gap between the two states is 5.54 eV. For CIS, the lower state is lowered by 10.97 eV, which mainly comes from $-c_{\text{HF}}J_{ja}$ term. The higher state is lowered by 6.56 eV. Both states are decreased by the consideration of the B term and their gap is 4.41 eV. It is intriguing that the gap between the lower and higher states gradually decreases as the portion of HF exchange increases. After consideration of the A and B terms, the energy levels are close to each other although $\Delta\mathcal{E}$ are significantly different between CIS and TDDFT/TDA with BLYP and B3LYP. This originates in the following facts that (i) for the lower states, $\Delta\mathcal{E} - c_{\text{HF}}J_{ja}$ less depends on the methods since $\Delta\mathcal{E}$ increases and $-c_{\text{HF}}J_{ja}$ decreases with respect to HF exchange portions; (ii) for the higher states, in addition to (i), K_{ia} less depends on the methods.

As regards the C term, $(ia|jb)$ are large contributions to the higher state: 3.01 eV for BLYP, 2.87 eV for B3LYP, and 2.31 eV for CIS, respectively. Thus, the higher states are considerably split by the C term. This means that the interaction between different singly excited configurations plays an important role in determining energy splittings. On the other hand, the lower states are varied less significantly since $(ab|ij)$, $(ja|ib)$, and $(ja|w_{xc}|ib)$ are relatively small contributions. Thus, TDDFT/TDA and CIS obtain the similar energy levels to the case of the $A + B$ terms because the main contribution $(ia|jb)$ is less dependent on HF exchange portions and takes similar values. The excitation energies of the dipole-allowed $^1\Sigma^+$ state by the FZOA method are calculated to be 21.53, 20.93, and 19.13 eV for

TDDFT/TDA with BLYP, B3LYP, and CIS, respectively. The other states range from 9.85 to 10.68 eV, which are relatively close to those of experimental values² and SAC-CI.

Let us summarize here. This letter extends the FZOA to TDDFT/TDA and compares it with the conventional CIS-based FZOA. The A and B terms strongly depend on the portions of HF exchange. However, the addition of the A and B terms reduces the dependence on the portion of HF exchange. On the other hand, the C term, which less strongly depends on the portions of HF exchange, makes a small difference in the splittings among the TDDFT/TDA and CIS methods. Thus, in spite of the big differences of $\Delta\mathcal{E}$, close excitation energies are obtained.

This study was partially supported by a Grant-in-Aid for Scientific Research on Priority Areas “Molecular Theory for Real Systems” “KAKENHI 18066016” from the Japanese Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan; a Grant-in-Aid for Young Scientists (Start-up) “KAKENHI 19850027” from Japanese Society for the Promotion of Science (JSPS); and Nanoscience Program in the Next Generation Super Computing Project of MEXT. We are also grateful to Global Center Of Excellence (COE) “Practical Chemical Wisdom” from MEXT, Japan.

References

- 1 a) E. Runge, E. K. U. Gross, *Phys. Rev. Lett.* **1984**, 52, 997. b) S. Hirata, M. Head-Gordon, *Chem. Phys. Lett.* **1999**, 314, 291.
- 2 a) Y. Tawada, T. Tsuneda, S. Yanagisawa, T. Yanai, K. Hirao, *J. Chem. Phys.* **2004**, 120, 8425. b) A. Nakata, Y. Imamura, T. Otsuka, H. Nakai, *J. Chem. Phys.* **2006**, 124, 094105. c) A. Nakata, Y. Imamura, H. Nakai, *J. Chem. Phys.* **2006**, 125, 064109.
- 3 a) H. Nakai, H. Morita, H. Nakatsuji, *J. Phys. Chem.* **1996**, 100, 15753. b) H. Morita, H. Nakai, H. Hanada, H. Nakatsuji, *Mol. Phys.* **1997**, 92, 523. c) H. Nakai, H. Morita, P. Tomasello, H. Nakatsuji, *J. Phys. Chem. A* **1998**, 102, 2033. d) T. Baba, Y. Imamura, M. Okamoto, H. Nakai, *Chem. Lett.* **2008**, 37, 322. e) H. Nakai, *Progress in Theoretical Chemistry and Physics*, submitted.
- 4 a) A. D. Becke, *Phys. Rev. A* **1988**, 38, 3098. b) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, 37, 785.
- 5 A. D. Becke, *J. Chem. Phys.* **1993**, 98, 5648.
- 6 T. H. Dunning, Jr., *J. Chem. Phys.* **1989**, 90, 1007.
- 7 a) H. Nakatsuji, K. Hirao, *J. Chem. Phys.* **1978**, 68, 2053. b) H. Nakatsuji, *Chem. Phys. Lett.* **1978**, 59, 362. c) H. Nakatsuji, *Chem. Phys. Lett.* **1979**, 67, 329.
- 8 M. W. Schmidt, K. K. Baldrige, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. Su, T. L. Windus, M. Dupuis, J. A. Montgomery, *J. Comput. Chem.* **1993**, 14, 1347.