Correction to An On-the-Fly Surface-Hopping Program JADE for Nonadiabatic Molecular Dynamics of Polyatomic Systems: Implementation and Applications

Likai Du and Zhenggang Lan*

In eq 13 of page 1363, there is a typographical mistake:

$$\sigma_{ji}\left(t + \frac{\Delta t}{2}\right) = \frac{\langle \varphi_i^*(t)|\varphi_j(t+\Delta t)\rangle - \langle \varphi_i^*(t+\Delta t)|\varphi_j(t)\rangle}{2\Delta t} \tag{13}$$

It should instead read as follows:

$$\sigma_{ji}\left(t + \frac{\Delta t}{2}\right) = \frac{\langle \varphi_j(t)|\varphi_i(t+\Delta t)\rangle - \langle \varphi_j(t+\Delta t)|\varphi_i(t)\rangle}{2\Delta t} \tag{13}$$

Also, in the Supporting Information, eq S1

$$\sigma_{ji} = \langle \Psi_i^*(t)|\frac{\partial}{\partial t}|\Psi_j(t)\rangle \tag{S1}$$

should be

$$\sigma_{ji} = \langle \Psi_j(t)|\frac{\partial}{\partial t}|\Psi_i(t)\rangle \tag{S1}$$

and Supporting Information eq S2

$$\sigma_{ji}\left(t + \frac{\Delta t}{2}\right) = \frac{\langle \Psi_i^*(t)|\Psi_j(t+\Delta t)\rangle - \langle \Psi_i^*(t+\Delta t)|\Psi_j(t)\rangle}{2\Delta t} \tag{S2}$$

should be

$$\sigma_{ji}\left(t + \frac{\Delta t}{2}\right) = \frac{\langle \Psi_j(t)|\Psi_i(t+\Delta t)\rangle - \langle \Psi_j(t+\Delta t)|\Psi_i(t)\rangle}{2\Delta t} \tag{S2}$$

Furthermore, in Supporting Information eq S6, one should note that the superscripts α and β are not referred to a specfic spin state, and they are just used to distinguish two Slater determinants.

$$\langle \Phi^\alpha(\mathbf{r}; \mathbf{R}(t))|\Phi^\beta(\mathbf{r}; \mathbf{R}(t+\Delta t))\rangle = \det\{\langle \phi_k(t)|\phi'_{k'}(t+\Delta t)\rangle\} \tag{S6}$$

It should be more readable, if other superscripts were adopted; for example,

$$\langle \Phi^a(\mathbf{r}; \mathbf{R}(t))|\Phi^b(\mathbf{r}; \mathbf{R}(t+\Delta t))\rangle = \det\{\langle \phi_k(t)|\phi'_{k'}(t+\Delta t)\rangle\},$$
$$a, b \in \alpha, \beta \tag{S6}$$

Equation 15 of page 1363 is only one approximated option to obtain the expansion coefficients for the excited state K:

$$c_{i,a}^K = \sqrt{\frac{\varepsilon_a - \varepsilon_i}{\omega_K}} (\mathbf{X} + \mathbf{Y})_{i,a}^K \tag{15}$$

And eq 15 should be corrected to

$$c_{i,a}^K = \sqrt{\frac{\varepsilon_a - \varepsilon_i}{\omega_K}} \mathbf{Z}_{i,a}^K \tag{15}$$

$\mathbf{Z}_{i,a}^K$ represents the solution of the TDDFT pseudoeigenvalue problem.[1,2] In eq 15, ε_a, ε_i are the energies of virtual and occupied molecular orbitals, respectively. And ω_K is the corresponding excitation energy. A few variations to approximate the expansion coefficients $(c_{i,a}^K)$ have been reported;[3−10] i.e.,

$$c_{i,a}^K \approx \sqrt{\frac{1}{\varepsilon_a - \varepsilon_i}} (\mathbf{X} + \mathbf{Y})_{i,a}^K$$

$$c_{i,a}^K \approx (\mathbf{X} + \mathbf{Y})_{i,a}^K$$

$$c_{i,a}^K \approx (\mathbf{X})_{i,a}^K$$

$\mathbf{X}$ and $\mathbf{Y}$ represent the solutions of the TDDFT/RPA or TDHF eigenvalue problem.[1] Our JADE code may select any of preceding assignments by swiching via a particular keyword. Please note that some previous work also included the additional prefactor that does not change the preceding assignment due to normalization. For the case of TDDFT/TDA and CIS, only the $\mathbf{X}$ vector is available, and one can simply take the $\mathbf{X}$ vector. Recently, we also noted further discussions of the pseudo wavefunction description of time-dependent Hartree−Fock (TDHF) states by Subotnik and co-workers.[11,12] In practice, although different approximated assignment ways were made, the numerical test gave very similar and consistent results, possibly owning to the small $\mathbf{Y}$ amplitudes. And some numerical test examples with different assignment ways can be found in the Supporting Information (SI).

■ REFERENCES

(1) Casida, M. E. Time-Dependent Density Functional Response Theory for Molecules. *Recent Advances in Density Functional Methods*; World Scientific: Singapore, 1995; Vol. 1, Chapter 5, pp 155− 192, DOI: 10.1142/9789812830586_0005.

(2) Dreuw, A.; Head-Gordon, M. Single-Reference Ab Initio Methods for the Calculation of Excited States of Large Molecules. *Chem. Rev.* 2005, 105, 4009−4037.

(3) Tapavicza, E.; Tavernelli, I.; Rothlisberger, U. *Phys. Rev. Lett.* 2007, 98, 023001.

(4) Werner, U.; Mitrić, R.; Suzuki, T.; Bonačić-Koutecký, V. *Chem. Phys.* 2008, 349, 319−324.

(5) Tavernelli, I.; Tapavicza, E.; Rothlisberger, U. *J. Mol. Struct.: THEOCHEM* 2009, 914, 22−29.

(6) Tapavicza, E.; Tavernelli, I.; Rothlisberger, U.; Filippi, C.; Casida, M. E. *J. Chem. Phys.* **2008**, *129*, 124108.

(7) Tavernelli, I.; Tapavicza, E.; Rothlisberger, U. *J. Chem. Phys.* **2009**, *130*, 124107.

(8) Wohlgemuth, M.; Bonacic-Koutecky, V.; Mitric, R. *J. Chem. Phys.* **2011**, *135*, 054105.

(9) Plasser, F.; Crespo-Otero, R.; Pederzoli, M.; Pittner, J.; Lischka, H.; Barbatti, M. *J. Chem. Theory Comput.* **2014**, *10*, 1395−1405.

(10) Zhang, X.; Li, Z.; Lu, G. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2011**, *84*, 235208.

(11) Alguire, E. C.; Ou, Q.; Subotnik, J. E. *J. Phys. Chem. B* **2015**, *119*, 7140−7149.

(12) Ou, Q.; Alguire, E. C.; Subotnik, J. E. *J. Phys. Chem. B* **2015**, *119*, 7150−7161.