Prediction of photochemical properties has been increasingly common due to the advancement of time-dependent density functional theory (TD-DFT). Even with advancement in TD-DFT, the computational demanding is still a heavy burden for researchers who wish to investigate large systems. An alternative method is the density-functional tight-binding (DFTB) method. Here, we develop a formalism for the calculation of excitation energies and excited state gradients for the self-consistent-charge DFTB with the third-order contributions of a Taylor series of DFT energy with respect to the fluctuation of electron density, called TD-DFTB3.1

In computing excitation energies, the following non-Hermitian eigenvalue problem has to be solved,2,3

\[
\begin{pmatrix}
A & B \\
B & A
\end{pmatrix}
\begin{pmatrix}
X \\
Y
\end{pmatrix}
=
\omega
\begin{pmatrix}
1 & 0 \\
0 & -1
\end{pmatrix}
\begin{pmatrix}
X \\
Y
\end{pmatrix}
\]

where \(\omega\) is the excitation energy and matrix elements of A and B are defined as

\[
A_{ia\sigma,jb\tau} = \delta_{\sigma\tau} \delta_{ab} \delta_{ij} (\varepsilon_{a\sigma} - \varepsilon_{i\sigma}) + K_{ia\sigma,jb\tau}
\]

and

\[
B_{ia\sigma,jb\tau} = K_{ia\sigma,jb\tau}
\]

where \(\varepsilon_{i\sigma}\) is the eigenvalue of \(i\)-th molecular orbital, and the element of the coupling matrix \(K_{ia\sigma,jb\tau}\) is given as the second-order derivative of the total energy with respect to density matrix elements. For singlet-singlet excitation, the coupling matrix can be written as

\[
K_{ia\sigma,jb\tau} = \frac{1}{4} S_{\mu\nu} S_{\kappa\lambda} (\gamma_{AC} + \gamma_{BC} + \gamma_{AD} + \gamma_{BD}) + \frac{1}{6} S_{\mu\nu} S_{\kappa\lambda} [(\Gamma_{AC} + \Gamma_{AD}) \Delta q_A + (\Gamma_{BC} + \Gamma_{BD}) \Delta q_B \\
+ (\Gamma_{CA} + \Gamma_{CB}) \Delta q_C + (\Gamma_{DA} + \Gamma_{DB}) \Delta q_D \\
+ \sum_{E} (\Gamma_{AE} (\delta_{AC} + \delta_{AD}) + \Gamma_{BE} (\delta_{BD} + \delta_{BD})) \Delta q_E].
\]

Note that only the first term is necessary in the previous TD-DFTB2.3

Nuclear gradients can be obtained by solving Z-vector equations following the standard
TD-DFT approach. The third-order derivative of the total energy with respect to density matrix elements, defined as
\[
\hat{g}_{\mu\nu,\kappa\lambda,\phi(x)} = \frac{1}{12} S_{\mu\nu} S_{\kappa\lambda} S_{\phi(x)} \sum_{\ell} \left\{ \Gamma_{AE} (\delta_A C + \delta_A D) + \Gamma_{BE} (\delta_B C + \delta_B D) \right\} (\delta_{\phi E} + \delta_{\chi E}),
\]
is necessary in TD-DFTB3, and it is missing in the previous formulation for TD-DFTB2. A general equation for excitation energy gradient is finally given as
\[
\frac{\partial \omega}{\partial R_{ax}} = \sum_{\mu\nu\sigma} \frac{\partial H_{\mu\nu}^0}{\partial R_{ax}} P_{\mu\nu\sigma} - \sum_{\mu\nu\sigma} \frac{\partial S_{\mu\nu}}{\partial R_{ax}} W_{\mu\nu\sigma} + \frac{1}{2} \sum_{\mu\nu\sigma\kappa\lambda\tau} \frac{\partial K_{\mu\nu\sigma,\kappa\lambda\tau}}{\partial R_{ax}} \hat{f}_{\mu\nu\sigma,\kappa\lambda\tau}
\]
where \( P_{\mu\nu\sigma} \), \( W_{\mu\nu\sigma} \), and \( \hat{f}_{\mu\nu\sigma,\kappa\lambda\tau} \) are obtained as a solution of Z-vector equations. The presented method has been implemented in GAMESS-US, and the implementation may be available in a future release.

Because of the limit in length, only the computational efficiency is highlighted here. For demonstration, trans-polyacetylene (C\(_{400}\)H\(_{402}\)) which contained 2,002 basis functions had been chosen. Five lowest excitation energies were calculated, and the first excitation vectors were used in the gradient calculation. With TD-DFTB3, ground state SCF took 213.82 s, and the computation of excitation energies and gradient took 819.92 and 45.54 s with one CPU of Xeon E5-1620 v3 (3.50GHz). The additional computational cost for TD-DFTB3 compared to TD-DFTB2 is virtually negligible. These timings are probably one or two orders of magnitude faster than those of TD-DFT. It is therefore possible to apply TD-DFTB for medium-size molecules routinely. In the poster, calculated absorption and fluorescence energies of cresyl violet in explicit water molecules (~400 atoms) will be briefly discussed as well as the comparison of the performance of TD-DFTB2 and TD-DFTB3.

References