3P114

三次の展開項を用いた時間依存密度汎関数強束縛法(TD-DFTB3)

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Time-Dependent Density-Functional Tight-Binding Method with the Third-Order Expansion of Electron Density (TD-DFTB3)

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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]

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

where ω is the excitation energy and matrix elements of **A** and **B** are defined as

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

and

$$B_{ia\sigma,jb\tau} = K_{ia\sigma,bj\tau} \quad .$$

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

$$\begin{aligned} K_{ia\sigma,bj\tau} = {} & \frac{1}{4}S_{\mu\nu}S_{\kappa\lambda}(\gamma_{AC} + \gamma_{BC} + \gamma_{AD} + \gamma_{BD}) + \frac{1}{6}S_{\mu\nu}S_{\kappa\lambda}[(\mathit{\Gamma}_{AC} + \mathit{\Gamma}_{AD})\mathit{\Delta} q_A + (\mathit{\Gamma}_{BC} + \mathit{\Gamma}_{BD})\mathit{\Delta} q_B \\ & + (\mathit{\Gamma}_{CA} + \mathit{\Gamma}_{CB})\mathit{\Delta} q_C + (\mathit{\Gamma}_{DA} + \mathit{\Gamma}_{DB})\mathit{\Delta} q_D \\ & + \sum_E \{\mathit{\Gamma}_{AE}(\delta_{AC} + \delta_{AD}) + \mathit{\Gamma}_{BE}(\delta_{BD} + \delta_{BD})\}\mathit{\Delta} q_E]. \end{aligned}$$

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.[4] The third-order derivative of the total energy with respect to density matrix elements, defined as

$$\hat{g}_{\mu\nu\sigma,\kappa\lambda\tau,\phi\chi\upsilon} = \frac{1}{12} S_{\mu\nu} S_{\kappa\lambda} S_{\phi\chi} \sum_{E} \{\Gamma_{AE}(\delta_{AC} + \delta_{AD}) + \Gamma_{BE}(\delta_{BC} + \delta_{BD})\}(\delta_{\phi\in E} + \delta_{\chi\in E}),$$

is necessary in TD-DFTB3, and it is missing in the previous formulation for TD-DFTB2.[5] A general equation for excitation energy gradient is finally given as

$$\frac{\partial \omega}{\partial R_{\alpha x}} = \sum_{\mu\nu\sigma} \frac{\partial H^{0}_{\mu\nu}}{\partial R_{\alpha x}} P_{\mu\nu\sigma} - \sum_{\mu\nu\sigma} \frac{\partial S_{\mu\nu}}{\partial R_{\alpha x}} W_{\mu\nu\sigma} + \frac{1}{2} \sum_{\mu\nu\sigma\kappa\lambda\tau} \frac{\partial K_{\mu\nu\sigma,\kappa\lambda\tau}}{\partial R_{\alpha x}} \hat{\Gamma}_{\mu\nu\sigma,\kappa\lambda\tau}$$

where $P_{\mu\nu\sigma}$, $W_{\mu\nu\sigma}$, and $\hat{\Gamma}_{\mu\nu\sigma,\kappa\lambda\tau}$ 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

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