COMMUNICATION

Efficient Implementation of Time-Dependent Density Functional-Based Tight-Bind Method on Multi-core and GPU System

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Abstract: This communication focuses on the implementation of the time-dependent density functional-based tight-bind (TD-DFTB) method on the Multi-core and GPU system to be used in excited state calculations of large system. Sparse matrix and OpenMP multithreading are used to speed up the program. The most time-consuming part of the DFTB ground state is implemented on the graphical processing units (GPUs) with double precision. The block Davidson algorithm is used for finding the lowest eigenvalue and eigenvector of the large time-dependent density-functional (TDDFT) matrix. Compared with the first-principle CIS and full TDDFT calculation, the implementation of the fast TD-DFTB code on serials of organic molecules shows that the fast TD-DFTB code can obtain reasonable result with a much cheaper computational requirement.

SCC-DFTB is derived using a Taylor series expansion of the DFT [1] total energy with respect to the charge density fluctuations around a given reference charge density. From the

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full Kohn-Sham DFT expressed on a local basis, SCC-DFTB undergoes several main approximations [2]. With the approximations the DFTB total energy and eigenvalue equation can be briefly written as: [3]
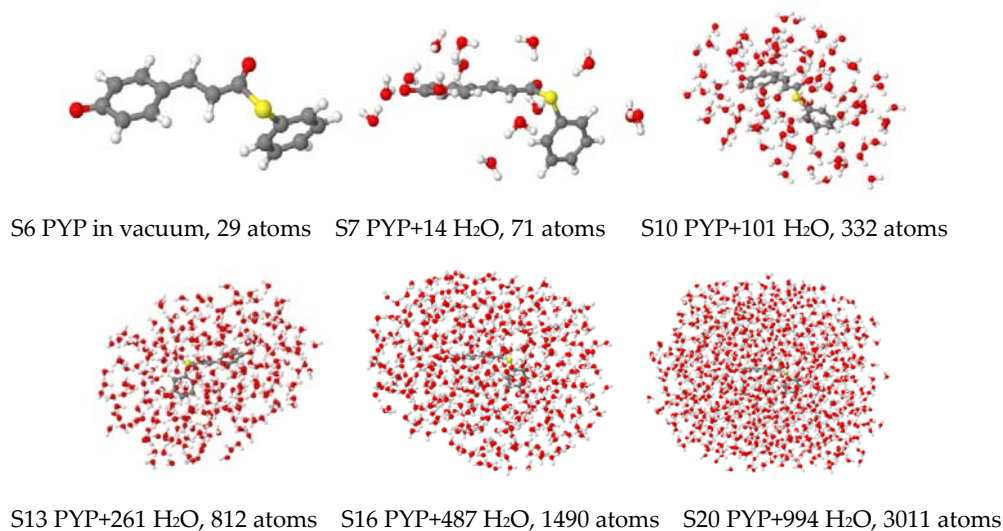
$$E = \sum_{i}^{occ} \sum_{\mu\nu} c_{\mu i}^{*} c_{\nu i} H_{\mu\nu}^{0} + \frac{1}{2} \sum_{AB} q_A \gamma_{AB} q_B + E_{rep}$$

$$\sum_{\nu} \left(H_{\mu\nu} c_{\nu i} - \epsilon_i S_{\mu\nu} c_{\nu i} \right) = 0 \tag{1}$$

The time-dependent liner response extension of DFT is used for the excited states. The resulting TDDFT eigenvalue equation is: [4, 5]

$$\sum_{jb} \left[\omega_{ia}^2 \delta_{ij} \delta_{ab} + 4\sqrt{\omega_{ia}} K_{ia,jb}^{\Sigma} \sqrt{\omega_{jb}} \right] F_{jb}^{I\Sigma} = \Omega_{I\Sigma}^2 F_{ia}^{I\Sigma} \tag{2}$$

To ignore the sophisticated integration, the same gamma approximation in the ground state is introduced to coupling matrix $K_{ia,jb}$ [6]. Eq. 2 is diagonalized to obtain the singlet and triplet excited state energies.

S6 PYP in vacuum, 29 atoms   S7 PYP+14 H_2O, 71 atoms   S10 PYP+101 H_2O, 332 atoms

S13 PYP+261 H_2O, 812 atoms   S16 PYP+487 H_2O, 1490 atoms   S20 PYP+994 H_2O, 3011 atoms

Figure 1: Structure of a PYP chromophore in vacuum (S6) and with an increasing number of solvated waters. Only five solvated PYP structure are shown (S7, S10, S13, S16, and S20).

The Hamiltonian matrix and the overlap matrix in Eq.1 are built and updated in a compressed sparse-row format. The OpenMP multi-thread technique is used to build up the sparse matrix. This reduces the computational cost of building the Hamiltonian matrix element into a small portion of the total ground-state procedure. The main computational time is then spent on the diagonalization of the eigenvalue Eq. 1. The MAGMA[7] library is a dense linear algebra library similar to LAPACK, but used for heterogeneous/hybrid