Fast and highly-efficient quantum chemical calculations using pseudospectral methods

Keisuke Sawada

Computational Molecular Science Research Team, RIKEN Advanced Institute for Computational Science

A fast estimation of two-electron repulsive integrals (ERIs) is an important and imperative subject in any *ab-initio* quantum chemical calculations. Since the computational cost of the ERIs formally increases as N^4, where N is the number of basis functions, we often suffer from much time-consuming estimations in large molecular systems.

In order to address the tough problem, several methodologies have been developed to date. Among them, the pseudospectral (PS) method is a strong candidate for a quick and efficient evaluation of the ERIs. In the PS method, one analytical integral is replaced by a numerical summation consisting of discrete grid points and the computational cost is reduced from $O(N^4)$ to $O(MN^2)$, where M is the number of grid points. Because of the discretization of a continuous integral space, the PS method is not only a fast method for estimations of the ERIs but also suitable for recent massively parallel computations using numerous CPU cores. Nevertheless, *ab-initio* quantum chemical calculations with the PS method have never demonstrated in large molecular systems which contains more than 1,000 atoms.

In this study, we implement the PS and PS-GAP methods into our NTChem program and investigate the performances of these methods using the MPI/OpenMP hybrid parallelized code. The PS-GAP method is further accelerated method that the PS and Gaussian-and-plane-wave (GAPW) methods are combined. In large molecular system which includes more than 10,000 basis sets, we find that the PS and PS-GAP methods show a good scaling with respect to used CPU cores and become much faster than the analytic integral methods. Moreover, the PS-GAP method exhibits the low-dimensional scaling in terms of the number of basis sets and achieve less than $O(N^2)$ computational costs.