The Origin of Linear Scaling Phenomenon in Fock Matrix Calculation

Alexander V. Mitin
Center for Environmental Kinetics Analysis, The Pennsylvania State University, 2217 EES Building, University Park, PA 16802, USA

An application of fast multipole method\textsuperscript{1} and quantum chemical tree code\textsuperscript{2} in Fock matrix construction significantly extend a possibility of large-scale \textit{ab initio} calculations. This was reached because the Fock matrix can be constructed by these methods for time that scales significantly below than quadratic with respect to a problem size. In many cases it is close to the linear one.

The explanations of linear scaling phenomenon also were presented in works\textsuperscript{1,2}. However, they cannot be considered as convincing ones because both of them are based on estimation that a number of two-electron Coulomb integrals scales at least quadratically with respect to a problem size\textsuperscript{3}. But an estimation is not a proof. For this reason it cannot be excluded that a linear scaling phenomenon of Fock matrix construction observed in these methods is a consequence that a number of two-electron integrals linear scales with respect to a problem size.

To check this assumption the scaling property of a number of two-electron integrals has been investigated recently\textsuperscript{4}. It was analytically shown that asymptotic values of all multi-center two-electron integrals are equal to zero. Hence, at large distances between centers the only one-center two-electron integrals are nonzero. A number of such integrals linearly scales with a problem size. Therefore, a total number of nonzero two-electron integrals scales asymptotically linearly with respect to a problem size. Asymptotic curves of a number of nonzero two-electron integrals have been constructed by counting the nonzero integrals in large-scale calculations with different basis sets. The largest calculations with 6-31G basis included about 27000 contacted and 64000 primitive Gaussian functions. The calculations show that at $10^{-4}$ to $10^{-5}$ cutoff precision a number of two-electron integrals scales almost linearly while for higher precisions the scaling is below quadratic although is not yet linear one.

It has been noted also that all known linear scaling Fock matrix calculations in fact have been performed with delta density algorithm. In this connection an influence of this algorithm on Fock matrix scaling property has been investigated in the present study on an example of Fock matrix calculation from stored two-electron integrals. The calculations have been performed for a set of test molecules with different basis sets in large range of a number of basis functions. It has been demonstrated that the use of this algorithm indeed leads to linear scaling Fock matrix construction even at those cutoff precisions of two-electron integrals at which a number of two-electron integrals is still a not linear scaling function.

Examples of large scale \textit{ab initio} calculations with inclusion of all two-electron integrals and a number of contracted basis functions of about 10000 and more will be presented.

\textsuperscript{4} A. V. Mitin, \textit{Int. J. Quantum Chem.} (submitted)