Molecular Electrostatic Potential Evaluation with the Fragment Molecular Orbital Method

Abstract

The molecular electrostatic potential (MEP) is a useful tool to analyze intramolecular electrostatic interactions and the properties of the chemical system. The most accurate way to compute MEP is to use quantum mechanical (QM) methods, but it is too expensive for large systems. The typical way to reduce computational cost is the fragment molecular orbital (FMO) method, which is to divide a molecular system into fragments and calculate the MEP on each fragment. The fundamentals of the recent advances in X-ray, synchrotron microscopy, NMR, and mass-spectrometry techniques for resolution of atomic structures and dynamics will be reviewed. This talk is to use two main scaling GMT methods, the fragment molecular orbital (FMO) method. The major problems are accurate computation of MEP on the molecular system’s atomic density and electron distribution, and complexity of the surface for defining the molecular surface. In this talk, we will show that the FMO method is much faster than the typical QM method. It was found that the new fragment cube code (FCC) produces accurate potential in a fraction of the cost.

Supercomputer Challenge

ACCD Supercomputer (Maia Blue Gene)
- 1.694 nodes per rack
- 16 processors
- 16 GB of memory
- 40 racks (768,000 cores)
- 54 total nodes of IBM
- performance of 10 teraflops
- 288 GB of memory
- 2.4 GHz processor
- 499 GB of memory/node

A challenge for quantum chemistry codes such as GAMESS is to efficiently use the enormous number of cores which require well parallelized and scalable algorithms. For example, in this work a number of parallelization of algorithms were attempted for efficient parallelization of MEP code.

Molecular Electrostatic Potential (MEP) method

There are two ways to compute MEP:

1. Solvated Potential Evaluation
2. Fragment Molecular Orbital Method

Fragment Molecular Orbital (FMO) method

In FMO, a molecular system is divided into fragments and the total properties, such as the energy or its gradient, are obtained from those of the fragments and FMO total energy is computed in the final step. The gradient of the FMO total energy is obtained from the local energy gradient in each fragment. The principal difference between TCM and FOM is the way the potential and electron density arrays are calculated. TCM computes the potential and density as by summing contributions for the entire molecule and an extra space of grids, meaning that the contribution due to fragments is added to the potential and density calculated for the molecule. FMO divides the cube into fragments and it calculates the contributions of each fragment independently of the others, and then sums the contributions to obtain the potential and density for the system as a whole. The total energy can be written as:

\[ \sum_{\text{all fragments}} \left( \sum_{\text{all grid points}} \phi \right)^2 \]

where \( \phi \) is the nuclear charge of Atom A, \( \mu \) and \( \nu \) are atomic orbital basis functions.

The difference between FCM and FOM is in the storage of cubes. A separate cube is created for each fragment by constructing a cube around it and calculating the potential and density in that fragment. The fragmentation methods, such as by summing contributions for the entire molecule, is used to calculate the potential and density for the system as a whole. The total energy can be written as:

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FMO MEP Algorithms

There are two ways to calculate MEP in FMO: the total cube method (TCM) and the fragment cube method (FCM). It is important to note that all calculations are done with FMO, there are no QM derivative calculations. The TCM is the standard method for large systems and the FCM is more suitable for small systems. The FCM is more efficient because it only performs energy gradient calculation on those atoms in the fragment and it also takes into account the fragmentation change transfer.

Total Cube Method (TCM)

The whole system is put into a cube by limiting on some points that are around the atom. For each atom, \( \phi \) is a window of the atom and \( \phi \) is an extra space of \( \phi \) around it. Then, the total data are accumulated by computing across the surface of the fragments, whose windows located in different fragments.

Fragment Cube Method (FCM)

The algorithm for computing MEP in the cube method is implemented in DOE’s scatter runs by using FMO. The difference between TCM and FOM is in the storage of cubes. A separate cube is created for each fragment by constructing a cube around it and calculating the potential and density in that fragment. The fragmentation method, such as by summing contributions for the entire molecule, is used to calculate the potential and density for the system as a whole. The total energy can be written as:

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Results

The calculations have been done on 64-core node Grids for a small tripeptide chain (FOM cube) using FMO (with NOV and 6-31G* basis set).

Conclusions

In this work, we developed and parallelized two new algorithms to compute and store MEP of large chemical systems which can be compared with FMO. We found that FMO is a more scalable solution and also possible the demand to be reduced to compare with TCG-Base TCM. FOM and significantly improves performance over existing TCM implementations, and it is also more accurate than TCM compared with ARPS.