

## 論文の内容の要旨

### Abstract

論文題目 Development of  $O(N)$  *Ab-initio* Molecular Dynamics that Exploits the Locality of Forces and its Acceleration through Machine Learning

(力の局所性を利用したオーダー $N$ ・第一原理分子動力学法の開発及び機械学習によるその高速化)

氏名 李 瀚

In the conventional research conducted by *ab-initio* calculations, the atomic structure of the target system is often unknown *a priori* and huge amount of the calculation time is spent on the determination of the stable atomic structure before the truly interesting investigation of the electronic structure. As the calculation cost of the conventional density functional theory (DFT/KS-DFT) grows as a cube of the target system size  $N$ , the scaling of the calculation is the bottleneck to extend its application to larger realistic systems. Thus, alternative methodologies to obtain the stable structures are desirable. Furthermore, due to the increase in the number of metastable structures as the target system grows, simple geometry optimization techniques such as conjugate gradient tend to be stuck to these local minima. Techniques such as simulated annealing work well even with those kinds of situations.

There are mainly three kinds of ways to tackle the computational scaling problem. While keeping the calculation *ab-initio*, methods exploiting the locality of the physical properties have been proposed. In these methods, the locality or nearsightedness of electron density matrix proposed by W. Kohn in 1995, is exploited and this is called the  $O(N)$  DFT. The methods are efficient for large systems and are able to describe electron transfer in a natural fashion but the short-coming is that these schemes require a special code and some unique parameters for calculations, making it hard to combine with other methods. The second type of approach is QM/MM, which stands for quantum mechanics and molecular mechanics. QM/MM combines

the ab-initio calculation with classical force fields to effectively generate molecular simulations. In the conventional setting of QM/MM, the target system is divided into a quantum mechanical part in which some chemical reactions take place and a molecular mechanical part which works as the medium. QM/MM is especially effective in biological and catalytically reaction system. The spatial replacement of ab-initio calculations with a certain approximated force field greatly reduces the computational time. The final approach is the Car-Parrinello molecular dynamics (CPMD). CPMD treats the Kohn-Sham orbitals from KS-DFT as classical objects and the time evolution takes place for atoms and wave-functions (KS orbitals) simultaneously. CPMD reduce the computational cost for time evolution by avoiding the recalculation of electron density through the well-known self-consistent field (SCF) calculation in KS-DFT.

Here I propose a new way of generation of molecular dynamics simulation with  $O(N)$  scaling by exploiting the locality of atomic forces to trade computational accuracy with computational speed. The propagation of the effect of the atomic forces is empirically known to be limited spatially, leading to the success of various classical force field containing spatial cutoffs. In the new method, the atomic forces are calculated from auxiliary subsystems, and the obtained forces are employed to perform the molecular dynamics simulation. The force error introduced into the system can be systematically reduced by increasing the radius of the subsystem sphere.

I have shown that with an appropriate hydrogen-termination treatment of the subsystem edge and some randomness in the subsystem selection, the forces can be obtained with good agreement to the conventional  $O(N^3)$  DFT and also a good influence on the conservational properties such as total energy. This can be intuitively explained by that without the randomness, the subsystem changes continuously thus inducing systematic error the atomic forces throughout the time evolution. The calculated phonon DOS of silicon by Fourier transforming the velocity autocorrelation function obtained from molecular dynamics with the proposed method, shows good agreement to the ones with conventional first-principles methods. Since unlike electron density or locally defined energy, the atomic forces are ascribed to each atom consisting the target system. This feature leads to one advantage of the proposed method that the method is mobile in the sense that it can be easily used with any other force fields. This enables an easily extension of QM/MM scheme in phase space where the quantum region and the molecular region can be mixed in both spatial and temporal space. Both classical force field and machine learning force field are considered to replace some parts of the ab-initio calculations to further reduce the computational time.

For our original motivation of the exploration of stable structures with the simulated annealing, the geometry optimization of oxidized SiC surface is conducted. The energy difference between the final structures can be well reproduced. Also, the systematic improvement of force accuracy with increasing subsystem size is shown. The proposed method works well with complex systems containing multiple kinds of elements and also surfaces.

The typical target system size for the crossover of computational time starts from several hundred atoms. It is shown that the proposed method can conduct the simulated annealing for the graphene/SiC interface system with around nine hundred atoms.

In summary, an efficient  $O(N)$  methods to conduct *ab-initio* molecular dynamics is developed. It exploits the locality of atomic forces to achieve  $O(N)$  scaling. The proposed method can systematically trade computational accuracy with computation cost. The simple division of the problem to obtain atomic forces allow simple hybridization of methods of various classical force field to further reduce computation time.