Abstract

Gallium Nitride (GaN) is significant for our lives as it is widely used for the electrical device such as Light Emitting Diode (LED) and solar cells. GaN is a direct transition type semiconductor, in which the bandgap is defined as the difference between Valence Band Maximum (VBM) and Conduction Band Minimum (CBM) at the same wavenumber. Some distinguishable properties of GaN are derived from its *d*-electron. *d*-electron, also referred to as semicore electron, has characters of both valence electron and core electron. For compounds of elements that do not have a semicore electron, it is sufficient to calculate the physical properties by considering only the valence electrons that contribute to chemical bonding. However, in the case of elements with a semicore electron, it is arbitrary whether the semicore electron should be treated as a valence electron or a core electron. In particular, since the bandgap is defined as the difference between the VBM and the CBM, the predicted value of the bandgap is expected to change significantly depending on the treatment of the semicore electron. Furthermore, it is nontrivial how the semicore electron affects the prediction of cohesive properties of the ground state like lattice constant and bulk modulus. As such, gap prediction is far more nontrivial as it requires the excited state quantities.

Density Functional Theory (DFT) is widely used for calculating bandgap. Although DFT can calculate many physical properties precisely, it suffers from an underestimation of the bandgap, as the self-interaction of the electron cannot be canceled in the typical functional such as Local Density Approximation (LDA) and Generalized Gradient Approximation (GGA).

On the other hand, the Quantum Monte Carlo (QMC) is developed as an *ab initio* method that adopts a different approach from DFT. In the QMC framework, time appears in Schrödinger equation is replaced with imaginary time. The wave function is then developed with time using Monte Carlo simulation. After a sufficient time elapses, ground state energy is estimated using the final wave function. Unlike DFT, QMC does not suffer from an insufficient cancelation of self-interaction, as it directly samples the value of the wave function at each point. Therefore, QMC is expected to be suitable for accurately evaluating the bandgap.

In the large core pseudopotential, *d*-electrons are treated as the core electrons, while *d*-electron is treated as valence electron in the small core pseudopotential. We calculated the energy difference between the ground state and the first excited state as the bandgap. The wave function for the first excited state was so constructed that one of the Kohn-Sham orbitals was replaced with CMB orbital. We used CASINO for the package code of QMC. Quantum Espresso was used for the package code of DFT for generating the trial wave function.

DMC results showed that large and small pseudopotentials both overestimate the bandgap than the experimental value (3.39 eV). We also found that large core pseudopotential overestimates the bandgap than the small core one by about 1.2 eV. As the result, we found that treating the *d*-electron as the core electron functions as a bias that widen the bandgap.

At the conventional DFT level, quantum many-body interactions cannot be well described, which leaves the unexplored area open where one cannot decide whether the prediction is underestimated or overestimated. In this study, we revealed the effects of the semicore electrons on the bandgap prediction by using *ab initio* QMC method by running it on massively parallel computing. Specifically, we found that the bandgap was overestimated within the large core pseudopotential than within the small core one, as the large core pseudopotential cannot incorporate the quantum dynamics of the semicore electrons. Moreover, overestimation of bandgap within the large core pseudopotential can be explained by insufficient incorporation of the semicore electrons in the *pd* hybridation and shielding effect, as well as energy shift of valence band due to the fewer valence electrons.

Keywords:
ab initio calculation, bandgap, quantum Monte Carlo, Density Functional Theory, semiconductor