First-principles prediction of stability and functionality of complex materials

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In recent years, considerable progress has been made in predicting material properties using the density functional theory (DFT) simulations and the DFT-based model simulations. In our group, we have developed a scheme to construct the exchange-correlation (xc) functional of the Kohn-Sham DFT by machine-learning the many-body wave function of small molecules [1,2]. In our prior study [1], small molecular systems were simply used as the learning set, but the success was limited to molecular systems only; problems remain in crystalline systems. To overcome this problem, physical conditions applicable to general materials were introduced into the learning process, and the resulting xc functional within the meta-GGA format was found to significantly improve the applicability [2]. The improved xc functional was implemented to an electronic structure calculation package VASP and is ready to distribute to supercomputer users. For further progress, we focused on techniques for the DFT for classical systems (classical DFT) and, in this case, low-density approximation of the n-particle density was found to be effective [3]. We consider that applying this method to electronic systems will also be effective not only for electronic systems but also the hybrid solvation models that we have long been studying.

In view of ability of meta-GGA in describing the Mott insulators, this functional was used for our study on exotic materials such as the solid oxygens in the high-pressure phases and the Hg-cuprate ($HgBa_2Ca_{n-1}Cu_nO_{2n+2+x}$) [4]. We found that the lattice parameters and the bandgaps become consistent with experiments with this functional, indicating that we are now at the start line of quantitative research.

One of the open problems of DFT-based simulation is to incorporate the nuclear quantum effect. Although the path integral molecular dynamics (PIMD) simulation is an established first-principles scheme, it becomes difficult to reduce the statistical fluctuation as the temperature is reduced and thus different scheme is needed. To overcome this problem for the hydrogen diffusion on metal surfaces, we have reformulated the quantum transition state theory that is based on a semi-classical approximation using an apparently full-quantum formulation. The fluctuation effect was found to be significantly reduced with the new method

[5].

We have also investigated the effect of nuclear quantum motion on the bandgap of insulators. This was done using the Allen-Heine-Cardona (AHC) theory and its extensions [6]. Herein the Debye-Waller terms of AHC was reformulated using the momentum operator, by which some of the electron-phonon coupling terms can be added to infinite order.

The description of electrochemical interfaces is a challenging problem of first-principles simulations, on which our group has long been studying. The difficulty of the simulation is due to existence the electric dipole layer (EDL) that can extend macroscopically. The thickness of EDL, however, is reduced to several nm when the ions are densely distributed as in strong acidic/alkaline solutions, but methods for the simulation has been developed only for the solution side. Therefore, EDL existing in the solid side of the interface remains to be a challenge; this is the case when semiconducting electrode is used. To simulate the ZrO_xN_{2-x} electrode, which is a candidate for Pt-free electrode of the next-generation fuel-cells, we have applied the first-principles Monte Carlo simulation with abICS [7] and then sped it up with the help of a machine-learned model potential. By the simulation, we could successfully obtain the distribution of oxygen vacancies and the nitrogen impurity atoms, and the result was used to describe the EDL. We further investigated efficiency of the oxygen reduction reaction occurring thereon and considered the effect of liquid water as well. These results were shared with experimentalists and helped them in planning the electrode development.

References

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