論文の内容の要旨

First-principles and machine learning study of anharmonic vibration and dielectric properties of materials

(物質の非調和振動と誘電特性の第一原理および機械学習による研究)

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This thesis aims to develop computational methods to predict the dielectric properties of materials. Dielectric properties describe the response of a material to an electric field and are important in physics and practical applications. Infra-red spectroscopy has been widely used to study the structure and dynamics of crystals and molecules. In industry, dielectric materials are used in various fields, such as pigments, capacitors, optical coatings, and optical fiber. In recent years, low-dielectric materials for high-speed communications have also attracted attention. Prediction of dielectric properties by theoretical calculation is an important issue, both for analyzing experimental spectra and for developing new dielectric materials.

To accurately calculate the dielectric function, the classical static charge is often insufficient, and the Born effective charges or the mass center of the Wannier function (Wannier center) are required to describe the dipole moments of a system. There are two main methods for simulating dielectric properties. One is to calculate the dielectric properties of crystals using anharmonic phonons, and the other is to calculate the dielectric properties of liquids using molecular dynamics (MD) simulations. In this thesis, we addressed those two methods.

The anharmonic phonon method requires an accurate estimation of the phonon self-energies. Especially in the case of strongly anharmonic materials, the usual perturbation theory breaks down, and the self-energy must be treated self-consistently. Furthermore, the frequency dependence of the self-energy and the effect of the four-phonon scattering process, which is usually neglected, on the dielectric properties have not been fully investigated. Therefore, in this thesis, we propose a method to calculate the dielectric properties of crystals with strong anharmonicity using the modified self-consistent phonon (SCPH) theory, including third-order anharmonicity as well as fourth-order anharmonicity. We applied our method to calculate the lattice dielectric function of strongly anharmonic rutile TiO_2. The resulting optical phonon frequencies and linewidths at

the Γ point much better agree with experimental measurements than those from a perturbative approach. We show that the four-phonon scattering process contributes as much as the third-order anharmonic term to phonon linewidths of some phonon modes. Furthermore, incorporating the frequency dependence of phonon linewidth reveals that experimentally known but unidentified peaks of the dielectric function are due to the two-phonon process. This work emphasizes the importance of the self-consistent approach in predicting the optical properties of highly anharmonic materials.

In the MD method, the dipole moment is calculated by computing the Wannier centers at each step of MD, and the dielectric properties are calculated from the dipole autocorrelation function. The method is computationally time-consuming. In this thesis, we aimed to improve the computational efficiency by using machine learning (ML) techniques to calculate the dipole moments. So far, ML models of molecular dipole moments have focused primarily on the centroid of the Wannier funcitons of each molecule. However, this method is difficult to apply when the size of the molecules increases. Therefore, we develop a scheme that assigns Wannier centers to chemical bonds and makes predictions on a chemical bond basis. This method can be applied to larger molecules. Also, ML models are potentially applicable regardless of molecular species, as we build them for each chemical bonds. We apply this method to calculate the dielectric properties of methanol and ethanol. The ML model successfully predicted the dipole moments of molecules in the liquid phase with an accuracy of the root mean square error (RMSE) of 0.1 D. Furthermore, we show that in combination with classical MD and first-principles MD, the calculated dielectric constant and dielectric function reproduce experimental data well. We also show that the dipole moment and dielectric constant are significantly increased in liquid due to the electronic polarization of the WCs of O lone pairs and OH bonds. We also apply our method to propylene glycol (PG), its dimer (PG2), and a much larger molecule, the 14-mer (PPG725). Our models predict the dipole moment of PPG725 with high accuracy. Also, when we train the ML model using only PG2 as training data, the model predicts the dielectric function of PPG725 in good agreement with experimental values.

We expect that both methods we develop will be applied to other materials to further elucidate the physical mechanisms that contribute to dielectric properties and to develop new dielectric materials.