Generation Scheme of Effective Models Based on Symmetry-Adapted Multipole Basis and Clarification for Universal Properties of Chiral Materials

Academic Year 2022
Graduate School of Science and Technology
Resume of Doctoral Dissertation

Generation Scheme of Effective Models Based on Symmetry-Adapted Multipole Basis and Clarification for Universal Properties of Chiral Materials

Major: Physics Program

Name: Rikuto Oiwa

1 Research goal

Various theoretical approaches have been developed to elucidate the hidden order parameters characterizing unusual physical phenomena in solids, such as the group theoretical arguments, electronic multipole theory, and density functional theory (DFT). Although these approaches have been successful in some aspects, they still need to be improved to reveal the microscopic representation of the order parameter and the microscopic understanding of its related physical phenomena. From these circumstances, it is highly desirable to develop a systematic prescription for clarifying the quantum-mechanical operator corresponding to the order parameter and quantitatively evaluating it. In particular, the order parameter for molecule and crystal chirality, i.e., the electric toroidal monopole, G_0, has not fully been understood at the microscopic level. Clarifying the microscopic description of chirality, i.e., G_0, is essential for unveiling the heart of chirality and achieving absolute enantioselection in chiral materials.

In this thesis, we develop a systematic generation scheme of a DFT-based tight-binding (TB) model based on the symmetry-adapted multipole theory. First, we construct a complete orthonormal symmetry-adapted multipole basis (SAMB) that enables us to express any electronic degrees of freedom in molecules and crystals. The Hamiltonian is expressed as the linear combination of SAMB, in which the weights correspond to the model parameters. We construct the DFT-based TB model by optimizing the weights to reproduce the DFT band dispersion. Using this systematic generation scheme, we can unveil hidden electronic multipole degrees of freedom and their quantum-operator expressions explicitly in molecules

and crystals. Moreover, by optimizing the weights, we can also evaluate their contributions quantitatively. Using the generation scheme, we investigate the microscopic description of chirality and its related responses.

2 Summary of the chapters

In Chap. 1, we give an introduction, outline, and organization of this thesis.

In Chap. 2, we clarify the advantages and disadvantages of using a de facto standard DFT-based tight-binding model based on the Wannier functions and atomic orbitals. In particular, the Wannier TB model is superior in its quantification, whereas the required symmetry is not taken into account in the model construction process. On the other hand, the Slater-Koster approach based on the atomic orbitals partially considers the symmetry, however, essential parameters would often be lost in the TB model owing to the lack of the effect from the surrounding environment around the bond of the electron hopping.

In Chap. 3, we develop the systematic generation scheme of SAMB. First, we decompose the electronic degrees of freedom into orbital/spin and the sublattice parts which are described by the atomic and site/bond-cluster multipole bases, respectively. By combining the atomic and site/bond-cluster multipole bases, we construct complete orthonormal SAMB set in the given Hilbert space. Using SAMB, we can describe any electronic degrees of freedom in the isolated and periodic multi-site systems, such as molecules and crystals.

In Chap. 4, we demonstrate a systematic generation scheme of the DFT-based symmetry-adapted TB model given by the linear combination of SAMB. We optimize the model parameters, i.e., the weights of each SAMB, so as to reproduce a given DFT band dispersion. To efficiently optimize the weights, we utilize machine learning techniques and introduce a deep neural network (DNN) where the SAMB plays a role of a neuron in the network, which we call DNN-SAMB. Using DNN-SAMB, we can perform highly efficient and accurate optimization with less initial guess dependence of the model parameters. We demonstrate our method for graphene, $SrVO_3$, and monolayer MoS_2. We achieve accuracy of less than 10^{-4} of the mean squared error between the normalized energy eigenvalues of the optimized TB model and that of the DFT or DFT-based Wannier calculation. Most remarkably, we obtain highly accurate optimized TB model although our TB model contains fewer model parameters than the Wannier TB model. Since the proposed method refers only to the energy eigenvalues, there is no guarantee to reproduce the orbital dependence of the electronic states in the reference bands. Nevertheless, the optimized TB Hamiltonian well reproduces the orbital

dependence of the electronic states of $SrVO_3$ because of the use of the SAMB, which imposes strong constraints by symmetry. It should be emphasized that our method is applicable to any crystallographic structure within 230 space group. Furthermore, DNN-SAMB could be useful in various fields such as materials informatics.

In Chap. 5, we elucidate the microscopic description of chirality, i.e., G_0, by taking elemental Te crystal as the simplest example of chiral crystals. Based on the systematic generation scheme introduced in Chap. 4, we construct the DFT-based realistic tight-binding Hamiltonian of Te and elucidate that the local and itinerant G_0 are the most dominant contributions in the Hamiltonian. Furthermore, we clarify that the itinerant G_0 is the crucial element to realize the possible electric-field induced static rotational lattice deformation.

Lastly, we propose a possible experimental approach to realize the absolute enantioselection in chiral materials by means of the conjugate field of chirality, such as simultaneously applying electric and rotation fields, or a magnetic field and electric current, and so on. The sign of the combined field controls the preferred handedness during the crystallization process. It should be emphasized that this generic approach is applicable to any chiral material. Since a larger coupling magnitude between G_0 and its conjugate field is favorable for achieving an absolute enantioselection, quantitative experimental observation of the responses related to the coupling is essential in future development.