Impact Objectives

- Investigate how organic semiconductors have an intermediate property between band and hopping conduction
- Develop a novel method of modelling semiconductors

A new approach to conductivity

***Assistant Professor Hiroyuki Ishii** outlines his latest efforts to systematically understand the physical properties of electron movement and heat*

What sparked your interest in the field of physics?

From a young age, I have been interested in the question of how electrons and heat flow in a substance. Electrical conductivity is an unusual physical quantity in that it varies greatly by up to 20 orders of magnitude from 10^-15 S/m (insulator) to 10^5 S/m (metal). Consequently, many theories exist to try and explain this, but they have their limitations, and this hinders true systematic understanding. Two key contrasting theories – band theory and the hopping theory – can both describe aspects of electron movement. Despite discussing the same electrical conductivity, the calculated transport properties are completely different between the two. Several experiments have suggested that recently developed organic semiconductors with high mobilities have an intermediate property between band and hopping conduction. I am investigating this using the Schrödinger equation which underpins solid-state physics and by using as few approximations as possible. We have been developing a new method of electronic and thermoelectric simulation called Time Dependent-Wave Packet Diffusion (TD-WPD). The TD-WPD method handles important electron-phonon interactions in organic semiconductors without using perturbation theory. This allows us to systematically understand the physical properties of electron movement and heat current.

You have previously worked as a Postdoctoral Researcher at the National Institute of Advanced Industrial Science and Technology (AIST), The University of Tokyo. Can you talk a little about what you learnt in this role?

My role at The University of Tokyo and AIST was the foundation of my current research. My interest since my school days has been in the flow of electrons in certain substances. In the 2000s, the electrical properties of nanoscale materials were actively measured, and there had been reports on the quantisation of electrical conductance in ballistic conduction. A systematic understanding was not obtained because nanoscale ballistic conduction was discussed in the non-equilibrium Green's function method, and the macroscale diffusion conduction was discussed in the Boltzmann equation. Green's function can obtain the quantised conductance because it is based on quantum theory, but it cannot calculate the macroscale conduction because of the high calculation cost. The Boltzmann equation is semiclassical meaning the quantised conductance cannot be easily reproduced. My methodology aims to bridge the gap between these methods. This calculation method was applied to Carbon nanotube, and, for the first time, it was revealed how the change from ballistic conduction to diffusion conduction occurs as the carbon nanotube length increases.

You are working on analysing, understanding and predicting the electron transport properties of various materials. What is the purpose of this research?

The electron transport mechanism varies greatly depending on the material and there are many theories to explain these experimental results. I am aiming to establish a primary principle on electronic conduction that could systematically understand this. Through this work, I would like to deepen my understanding of the linear response theory, which will lead to further development of non-equilibrium physics in the future. Personally, I want to understand at an atomic level when and how energy is dissipated and settled into a non-equilibrium steady state when an electric field or temperature difference is applied. In terms of applications, the establishment of an improved electron transport theory can be used in various fields not only in academia but also in corporate material development.

How are you validating the findings from your studies?

With organic semiconductors, the physical properties of the material vary greatly if there are grain boundaries like polycrystals, making it difficult to compare with the calculation results. Therefore, we compared and studied the simulation results of single crystal organic transistors to validate the calculation method. We are also confirming that there are no contradictions with other theories by comparing our results with the existing ones. The real-world results were determined by Associate Professor Toshihiro Okamoto, a collaborating chemist.

New semiconductor calculations

*A team of physicists at the **University of Tsukuba** is looking to better model and understand the conductivity of semiconductors*

Physics is constantly evolving. It is a field that attempts to create calculations and theories capable of completely describing an observable phenomenon. Physics expert Assistant Professor Hiroyuki Ishii of the Faculty of Pure and Applied Physics at the University of Tsukuba in Japan, explains that typically, these theories work exceedingly well for the context in which they were discovered.

Newtonian physics, concerning the motion of large objects on Earth, works exceedingly well for describing just that – forces on a macroscale. Ishii says that it was only when particles at an atomic level and supermassive level were explored that Newtonian ideas no longer held. Physicists then reassessed and developed new theories and formulas that explain these phenomena. Einstein was able to find theories encompassing extremely large-scale objects and the physics of speeds approaching the speed of light. Quantum mechanics arose through the work of visionaries, such as Born, Heisenberg and Schrödinger, to describe the world at subatomic scales. This process does not simply stop. 'New observations are constantly being made that confound explanations through known theories and new models must be developed,' highlights Ishii.

The ability of various materials to conduct heat and electricity can vary wildly. Insulators can be 20 orders of magnitude less conductive than the best conductors. Everything in between, of course, is also possible. 'Conductivity is related to the creation of a material capable of providing free electrons for the transfer of a current through the material,' outlines Ishii. 'However, the current theories for the calculation of these conductive capacities have proven insufficient in the face of novel compounds, such as carbon nanostructures and organic semiconductors.'

Ishii is attempting to address this disparity with the support of a team of physicists based at the Faculty of Pure and Applied Physics, University of Tsukuba. He has developed a novel methodology for predicting and calculating the electrical conductivity that simulates the novel compounds using supercomputing technology. 'Our method can calculate electronic and thermal conductive properties and thermoelectric properties at a relatively high speed,' he highlights. 'Therefore, the physical properties of some candidate materials can be predicted before the experiment. In terms of semiconductor research, this simulation should be able to significantly reduce the time taken for real trial and error experiments.'

TIME FOR CHANGE

There are two main methods based on perturbation theory for calculating the conductivity of a material. Quantum theory tells us that free electrons have both particle nature and wave nature. 'In solid-state physics, covalent bonded material, such as silicon and carbon nanotubes, becomes a target of an investigation,' explains Ishii. 'Since strong electronic coupling between atoms are formed, electrons exist as waves extended uniformly in material.' He continues to explain that the relationship between the wavelength and the energy is known as band dispersion. When an external electric field is applied to the material, the electrons begin to move along the field. 'The movement of electrons are disturbed by thermally excited atomic vibrations (phonons), which is an origin of resistance of electric current,' he confirms. 'In general, the vibration amplitude is very small because covalent bonds are very tight interatomic bonds, thus the effect of disturbance becomes weak, resulting in realisation of high mobility. Band theory describes such a situation.'

Contrasting with the band theory of conductivity is the Marcus or hopping theory, which is often applied to molecular crystals such as organic semiconductors. This a more chemical-focused approach that looks to the transfer of electrons between molecules to explain conductivity. 'Usual organic semiconductors have no obvious electronic bond between molecules like covalent bond,' highlights Ishii. 'Molecules are condensed by weak van der Waals interactions. Electrons in such molecular crystal are basically localised in a molecule and can hop to neighbouring molecules as rare events.' Slight spatial overlap between molecular orbitals becomes the hopping path, therefore it had been believed that mobility of organic

semiconductors is much lower than that of covalent bonded materials. 'However, after 2000, the existence of some organic semiconductors with high mobility than amorphous silicon was reported,' he continues. 'In fact, experimentally observed mobilities exceed the upper limit of mobility predicted by conventional hopping theory. Such high-mobility organic semiconductors have the ideal packing structure optimised to maximise spatial overlap between orbitals.' As a result, the electron can be delocalised to some extent in the crystal. This result means that the wave nature of an electron begins to appear even in the molecular crystals.

Ishii poses the question about whether or not we can apply the conventional band theory to such molecular crystals. 'The answer is 'No', because band theory is applicable only in the case off weak electron-phonon interaction,' he says. 'Amplitude of the molecular vibrations of soft molecular crystals are much larger than that of covalent bonded materials. Ishii saw that a new method was required and set about creating an effective process for conducting such calculations.

QUANTUM MECHANICS

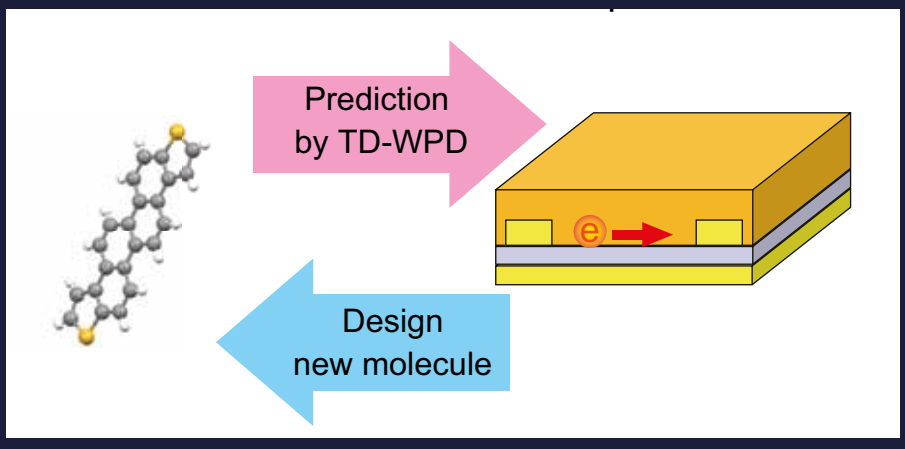
Ishii's approach, known as Time Dependent-Wave Packet Diffusion (TD-WPD), is designed to calculate the interaction between phonons and electrons in a material. 'The electronic transport properties are obtained from the wavepacket dynamics based on quantum theory,' he outlines. 'Wavepacket can describe wave nature and particle nature simultaneously based on quantum theory. We introduced the interaction between electron and phonon by wavepacket dynamics simulation combined with the molecular dynamics simulation. Using this nonperturbative approach with respect to electron-phonon coupling, we succeeded to investigate systematically the transport properties of the solid covalent bonded crystals and soft molecular crystals.'

The TD-WPD method can calculate conductivity of macrostructures based on changes at the molecular level, because a super high-speed algorithm is employed for calculations of wavepacket dynamics. His research also took advantage of the growing power and availability of supercomputing technology. 'The methodology calculates the electronic properties of macroscale systems based on quantum theory,' outlines Ishii. 'This makes it possible to evaluate the conductive properties of aggregates of up to about 100 million atoms or molecules by performing ultrafast calculations of electron wave packet dynamics.' Ultimately, this means that the method can be applied to non-single-crystal materials, such as polymer semiconductors with amorphous structures and poly-crystalline materials, which existing transport theories based on quantum mechanics are hard to apply.

> *The methodology calculates the electronic properties of macroscale systems based on quantum theory*

MAKING WAVES

Ishii's novel method has bountiful theoretical and academic applications. Novel combinations and shapes of organic compounds can be probed for the conductivity under different conditions. This will help advance semiconductor research, which, of course, underpins all modern electronics. In addition, the TD-WPD method can be used directly in applied electronics. 'In conversations with a chemical company, we estimate that the performance of a candidate material can be predicted within two to three days. This means one can judge whether the candidate is promising or not prior to expensive experimentation,' he confirms. TD-WPD can therefore be used in the actual material development.'



Device performance prediction and Material development

Project Insights

FUNDING

• JSPS KAKENHI Grant Number JP18H01856, 'Development of thermoelectric simulation methodology based on density functional theory and application to organic materials', Kakenhi Grant-in-Aid for Scientific Research (B) (https://kaken.nii.ac.jp/en/grant/KAKENHI-PROJECT-18H01856/)
• JSPS KAKENHI Grant Number JP17H03104, Kakenhi Grant-in-Aid for Scientific Research (B) (https://kaken.nii.ac.jp/en/grant/KAKENHI-PROJECT-17H03104/)

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科研費 KAKENHI

University of Tsukuba