I-O Electronic Structures of Polymers and Organic Molecular Crystals

In order to understand the electronic, optical, and magnetic properties of polymers and organic molecular crystals, we have investigated the electronic structures of these materials using various kinds of theoretical approaches, for examples, the density matrix renormalization group method for a model Hamiltonian, a first-principles pseudopotential method, and ab initio quantum chemical calculations. In particular, we have focused our attention mainly to phase transition phenomena accompanied by drastic changes of electronic and optical functions. The actual targets of our research are as follows: 1) Semiconductor-metal transition in doped conducting conjugated polymers, 2) Thermo- and photochromic phase transitions in polydiacetylene, 3) Neutral-ionic transition in tetrathiafulvalene-p-chloranil.

I-O-1 Charge Carriers and Semiconductor-Metal Transition in Doped Conducting Conjugated Polymers

SHIMOI, Yukihiro[1,2]; KUWABARA, Makoto[2,3]; ABE, Shuji[1]
([1]AIST; [2]IMS; [3]Kobe Univ.)

We have investigated how the configurations of charge carriers evolve in non-degenerated conjugated polymers when carrier concentration increases, putting emphasis on electron correlation effects and electron-lattice coupling. For this purpose, we have applied the density matrix renormalization group method to the one-dimensional extended Hubbard-Peierls model. We found out theoretically a new configuration of charge carrier, polaron-pair state, as an intermediate configuration between polaron and bipolaron. This configuration is possible under a relatively weak electron-lattice coupling. We have shown that gaps for charge and spin excitations become quite small at highly doping concentration. Comparing the non-interacting case, correlation effects suppress the gap, indicating the significant role of electron-electron interaction on semiconductor-metal transition of which mechanism is still open question.

I-O-2 First-Principles Study of Polydiacetylene

KATAGIRI, Hideki[1]; SHIMOI, Yukihiro[1,2]; ABE, Shuji[1]
([1]AIST; [2]IMS)

In order to elucidate the mechanism of thermo- and photochromic phase transitions in polydiacetylene (PDA), we have performed first-principles pseudopotential calculations for a typical theromochromic PDA, TCDU, (poly(5,7-dodecadiyne-1,12-diyl-bis-phenylurethane)). The calculated energy surface shows that the butatrinene conformation of backbone chain is not a metastable state in TCDU, in contrast to a hypotetical PDA where the side group is replaced by a hydrogen atom. This indicates that the side group has significant influence on the geometry of the backbone, consistent with experimental observations. We have investigated how the conformation of side group affects the energy surface and band gap in order to understand the interplay between the π-electronic structure at backbone and the configuration of side group more clearly.

I-O-3 Role of Intramolecular Charge Distribution on Neutral-Ionic Transition of Tetrathiafulvalene-*p*-Chloranil

KAWAMOTO, Tohru[1]; IIZUKA-SAKANO, Takako[1]; SHIMOI, Yukihiro[1,2]; ABE, Shuji[1]
([1]AIST; [2]IMS)

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We calculated the Madelung energies of both the ground state and excited states in tetrathiafulvalene-*p*-chloranil (TTF-CA) by taking into account intramolecular charge distribution. The distribution is found to be significant in the neutral-ionic (NI) transition. In the ionic phase, the Madelung energy depends more strongly on the intermolecular distance perpendicular to the π-stacking chains than on that along the chains. This indicates that simple single-chain models neglecting interchain electrostatic coupling are not adequate. The gain of the Madelung energy due to dimerization is concluded to be small compared with the other structural changes. We also calculated the formation energy of excited state domains, which appear in the initial process of the phase transition. A one-dimensional excited domain has the smallest energy among the possible domains with the same number of molecules, and the energy per molecule is considerably reduced in increasing the domain size. It is consistent with the experimental suggestion that a large number of excitations were generated by only one photon.