

Electronic Structure

In this part we restrict to the following groups of materials, i.e., TTF-TCNQ, $(\text{TMTSF})_2\text{X}$, BEDT-TTF salts, BO-salts, BETS-salts. The references are not complete and the following contents are mostly form

[R1] T. Mori, Bull.Chem.Soc.Jpn.71, 2509(1998); 72, 2011 (1999).

[R2] T. Mori, H. Mori, and S. Tanaka, Bull.Chem.Soc.Jpn.72, 2509(1998).

[R3] T. Ishiguro and K. Yamaji, Organic Superconductors (Springer-Verlag, 1990).

The present author thanks the invaluable support from Prof. T. Mori and Dr. T. Miyazaki.

I. TIGHT-BINDING CALCULATIONS

The electronic structures in organic conductors mentioned above are very well reproduced by the tight binding model taking into account only the HOMO of the donor molecules. Then the values of the transfer integrals are the main issue, the calculation of which and the resulting band dispersions and Fermi surfaces are reviewed here. The overlap integral depends strongly on the relative position of two molecules. For example, when two parallel molecules are considered, the relative position is characterized by θ and D shown in Fig.G1 [R1]. The θ and D dependence of the overlap are shown in Fig.G2(a) and (b) [R1], respectively. Here RA and RB means Ring-over-atom and Ring-over-bond configurations, respectively. These two configurations are important because they often appear in the crystal structures of ET-salts. It also happens that two molecules are not parallel to each other. Fig.G3 [R2] shows the dependence of the overlap on the angle ϕ . Fig.G4 [R1] shows the genealogy of the crystal structures of ET-salts seen from the molecular long axis. Fig.G5 [R1] shows the stacking patterns of $(\text{TMTSF})_2$, TTF-TCNQ, and β -phase ET-salts seen from the molecular short axis. In addition to these types, there is another important type called β' -type ET-salts. Fig.G6 [R2] shows the donor sheets viewed along the molecular long axis. In this structure, the dimerization is the important feature. The references for various materials are listed in Table 1, and the band dispersion and Fermi surfaces for several representative materials are shown

in Figs. 1-14.

II. FIRST-PRINCIPLES CALCULATION AND ELECTRON CORRELATIONS

It has been recognized that the shape of the Fermi surface is not so sensitive to the electron-electron interaction. One reason for this is the Luttinger theorem for Fermi liquid saying that the volume surrounded by the Fermi surface does not change. Therefore the Fermi surfaces observed by dHvA oscillation agree well with the tight-binding calculation reviewed in Section I. However other quantities, such as the bandwidth, Fermi velocity etc., are sensitive to the electron-electron interactions. Furthermore various phase transitions and long range orderings occur in real materials. Then the first-principles calculations and the treatment of the Coulomb interaction in the Hubbard like models become important when one goes into the detailed discussion of the physical quantities.

First-principles band calculations have been done for $-(\text{BEDT-TTF})_2\text{Cu}[\text{N}(\text{CN})_2]\text{Br}$ [60,61] and $\text{DCNQI}-(\text{Cu,Ag,Li})$ [62,63,64]. These calculations are based on the local density approximation (LDA), which is supposed to take into account the electron-correlation effect to a certain degree. The most difficult part of these calculations is that there are many orbitals in the unit cell. For $-(\text{BEDT-TTF})_2\text{Cu}[\text{N}(\text{CN})_2]\text{Br}$, some differences from the Hückel-type tight binding calculations have been reported [60]. Among them the most important is that the bandwidth is reduced to about half of the Hückel-type calculations.

Based on these first-principles calculations, several people determine the parameters appearing in the effective Hubbard-type model for ET-salts [65,66,67]. Further simplification has been proposed, where the model donor structure in Fig. G7 is considered [68]. The interaction b_1 controls dimerization while b_4 controls the band width and band overlap. These two interactions are identified to be the most important ones to understand the variety of ET-salts in a unified way. Based on this band structure, the phase diagram has been determined in the mean field approximation for the on-site Hubbard interaction U [68].