# Orbital degeneracy in $\pi$ molecular conductors: A target in the next decade

Masafumi Tamura

Condensed Molecular Materials Laboratory, RIKEN

The characteristics and limitations of the  $\pi$  molecular conductors are pointed out. Introduction of orbital degeneracy is proposed to be efficient to rise above the limitations by taking account of the intramolecular degrees of freedom. Simple models to realize the orbital degeneracy are shown.

# Physical characteristics of the $\pi$ -molecular conductors: Advantage and limitation

By the end of the 20th century, the research of electromagnetic behavior of  $\pi$ -electrons in organic crystals made several outstanding achievements. Since 50's, the epoch-making finding appeared every decade: enhanced conductivity in halogen complexes of aromatic hydrocarbons<sup>1)</sup> (1954), highly conductive radical salts of a  $\pi$ -acceptor TCNQ<sup>2)</sup> (1960), a charge transfer complex TTF-TCNQ with quasi-one-dimensional metallic behavior  $^{3)}$  and charge density waves (CDW) (1973), the organic superconductors (TMTSF)<sub>2</sub>X and spin density waves  $(SDW)^{(4)}$  (1980), the first purely organic ferromagnet  $\beta$ -p-NPNN<sup>5)</sup> and superconductivity in C<sub>60</sub> salts<sup>6)</sup> (1991). In 2001, superconductivity induced by strong magnetic field<sup>7)</sup> and those induced by carrier injection into an organic FET  $^{\rm 8)}$ were reported. Almost all the basic phases in solid state physics have been, thus, established in organic crystals. This doubtlessly owes much to the developments of synthetic chemistry providing new molecular designs and to the many efforts to control molecular arrangements in crystals.

Various physical techniques using low temperature, high magnetic field or high pressure have been efficiently applied to the  $\pi$  molecular conductors. In this way, some attracting features of conduction electrons in the low-dimensional systems have been revealed very clearly in these materials, as shown in the variety of Fermi surface studies using the quantum oscillation analyses, for instance. It turned out that high quality crystals suitable for detailed physical studies can be grown in not a few cases by crystallization processes of usual room temperature chemistry in organic solvents. The  $\pi$  conductors have thus closely concerned the basic advances in condensed matter physics.

The good quality of the  $\pi$  conductors is owing to the anisotropy of structure and cohesive mechanism in the crystals. Most  $\pi$  molecular conductors are two-component systems and have layered structures of alternating piling of anion and cation sheets; the crystals have ionic character for the directions perpendicular to the layers. The conduction electrons are moving within either sheet, in which the van der Waals and charge-transfer (partially covalent) interactions are operating. In such a layered salt structure, the position, size, orientation, and charge of the molecule are regulated rather strictly. Since a  $\pi$  molecule, usually with a flat shape, has its own unique size and geometry, the pack-

ing of the molecules in the ionic layers efficiently eliminates impurities and defects. In fact, the  $\pi$  molecular crystals are not plastic in most cases, unlike polymers and conventional metals. This is a remarkable difference between the  $\pi$  conductors and the conventional inorganic conductors made of single atoms. This enables us to observe clear behavior of clean low-dimensional electron systems. On the other hand, the doping technique, which is used widely for the inorganic conductors in order to control the carrier concentration, is quite difficult to apply for most  $\pi$  conductors. Attempts to incorporate dopants into molecular crystals often result in poor quality.

Another significant feature in the  $\pi$  conductors is the simplicity of the electronic structures. Since the intermolecular charge transfer interactions are much smaller than the intramolecular level spacing, only one frontier molecular orbital (HOMO for a donor molecule and LUMO for an acceptor) can contribute to the conduction. This gives a useful viewpoint for the molecular and crystal design, and simple models for systematic analyses of physical properties.<sup>9)</sup> Although the unit cell may contain two or more molecules, similar discussion holds for a combination of the frontier orbitals, e.g., the anti-bonding one of a dimer. The physics of the conduction electrons is thus described by the band width (corresponding to the intermolecular transfers), lattice deformation and the on-site and inter-site Coulomb repulsions, which have brought about several classes of interesting materials and phenomena so far.

However, this single MO situation restricts the variety of electronic properties. The conduction electrons have only the charge and spin (1/2) degrees of freedom on each molecule. Although organic molecules themselves have many degrees of freedom, such as vibration, distortion, tautomerism, and internal rotation, only the totally symmetric modes can couple with the electron charge density (the Jahn-Teller theorem). The conduction electron spin can interact with the external magnetic field and with local spins, if exist. The possible interplay between the conduction electrons and the local degrees of freedom is basically limited to these two mechanisms.

## Role of degenerated orbitals

If more than one orbitals in each unit cell have close or equal energies and they are partially occupied together, the situ-



Fig. 1. Two examples of a possible coupling,  $J\sigma \cdot \sigma'$ , between doubly degenerate orbitals and molecular distortion modes. Here,  $\sigma$  can be taken as position of an electron, while  $\sigma'$  describes the normal mode coordinate (A) or position of the H atom (B).

ation changes qualitatively. The conduction electrons have orbital degrees of freedom at each cell. The orbital degrees of freedom can exhibit long-range order; it is called the orbital order. A manifest effect appears in magnetism. The spin densities on different orbitals are regulated to have some specific alignment by the Hund coupling or by the spin polarization effect due to electron correlation effect. The spin alignment can propagate through the electron transfer among the cells. Thus the spin correlation, which may be ferromagnetic or ferrimagnetic, can be enhanced by the transfer interactions in contrast to the single MO cases. The spin interaction mediated by the on-site Hund coupling and inter-site transfer is called the double exchange interaction. Recently, these phenomena are studied extensively for transition metal compounds.

Let us think of other possibilities. The orbital degrees of freedom, corresponding to the type of electron distribution within the cell, can couple to any combined mode of molecular distortions, as displayed schematically in Fig. 1. This coupling can be expressed in an exchange-like formula,  $J\sigma \cdot \sigma'$ , where  $\sigma$  is an operator for the orbitals,  $\sigma'$  is a normal mode coordinate operator for distortions, and J is the coupling constant. (When J is regarded as spin-orbit coupling,  $\sigma'$  is a usual spin operator.) Similar models were used to describe proton-based ferroelectric materials (the Ising spin model  $^{10)}$  for  $\rm KH_2PO_4$ etc.), where  $\sigma$  and  $\sigma'$  are the double-minimum positions of protons on neighboring sites, or tunneling of a muon in a metal.<sup>11)</sup> The analogy to the spin-spin coupling is apparent and useful. However, if  $\sigma'$  stands for molecular distortions, it is much more sensitive to various kinds of external perturbations such as electric field or structural stress than the spin which sees only magnetic field. This scheme should open a way to realize various types of interplays among conduction, local modes, and external perturbations; it would be a candidate for designing novel phenomena like switching, crossover or phase transitions using the rich degrees of freedom of organic molecules.

### How to introduce orbital degeneracy in molecular systems

Orbital degeneracy usually appears on a transition metal ion. This is due to the highly symmetric geometry of the coordination as a result of weak bonding between the 3d and ligand orbitals. (If the bonding is strong enough, the degeneracy is removed as in a Jahn-Teller distortion, so that the system becomes a low-spin state (spin-0 or 1/2). The

role of 3d orbitals is extensively studied also in molecular conductors, by incorporating 3d complexes as counterions of  $\pi$  donor/acceptor. From this point of view, we have studied the cases of rare-earth (4f) complexes, whose bonding character is much weaker than that of the 3d orbitals. The effect of 4f orbital degeneracy can be clearly observed as strongly anisotropic magnetism depending on temperature and structure in our cases.<sup>12</sup>) We have obtained a few compounds which are metallic down to low temperature for the first time, and studied their electronic properties. However, the coupling between the 4f and  $\pi$  electrons is still so weak that no interplay between the conduction and local orbitals has been found yet in our cases.<sup>12</sup>)

The  $\pi$  orbital degeneracy due only to geometrical symmetry is not hopeful, because the Jahn-Teller effect should be dominant. Instead, an alternative scheme based on non-bonding orbitals due to connectivity is proposed here. Two examples are shown in Fig. 2. Both models have doubly degenerated flat bands. When the site energy, electron filling and intrasite Coulomb repulsion are appropriately chosen, these systems possess orbital degrees of freedom. The common key factor is the connectivity. Essential is the no connection between the sites 2, 3,  $\cdots$ , which may interact with the site 1. No geometrical symmetry is required for the degeneracy. It is easy to extend these models to the two- or three-dimensional



Fig. 2. Two models affording connectivity degeneracy: danglingsite model (A) and Lieb-ferrimagnet-lattice model (B). The site energy for the site 1 in the model (A) is taken as  $2\Delta$ , while the others are zero. One-electron hamiltonian and its eigenvalues for each model are also shown. E = 0 is the doubly degenerated flat band. cases without change in the situation, though Fig. 2 shows only one-dimensional ones. Noteworthy is that the proposed approach has close relation to the design of organic magnets.<sup>13)</sup> Although no example is known in the  $\pi$  molecular conductors by now, it is believed that the proposed structures are possible to design by the supramolecular chemistry directed toward this purpose.

#### References

- H. Akamatsu, H. Inokuchi, and Y. Matsunaga: Nature 173, 168 (1954).
- L. R. Melby, R. J. Harder, W. R. Hertler, W. Mahler, R. E. Benson, and W. E. Mochel: J. Am. Chem. Soc. 84, 3374 (1962).
- L. B. Coleman, M. J. Cohen, D. J. Sandman, F. G. Yamagishi, A. F. Garito, and A. J. Heeger: Solid State Commun. 12, 1125 (1973).
- D. Jérome, A. Mazaud, M. Ribault, and K. Bechgaard: J. Phys. Lett. 41, 195 (1980).

- Y. Nakazawa, M. Tamura, N. Shirakawa, D. Shiomi, M. Takahashi, M. Kinoshita, and M. Ishikawa: Phys. Rev. B 46, 8906 (1992).
- R. M. Fleming, A. P. Ramires, M. J. Rosseinsky, D. W. Murphy, R. C. Haddon, S. M. Zaburak, and A. V. Makhija: Nature 352, 787 (1991).
- S. Uji, H. Shinagawa, T. Terashima, T. Yakabe, Y. Terai, M. Tokumoto, A. Kobayashi, H. Tanaka, and H. Kobayashi: Nature 410, 908 (2001).
- J. H. Schön, Ch. Kloc, and B. Batlogg: Science 293, 2432 (2001).
- T. Mori: Bull. Chem. Soc. Jpn. **71**, 2509 (1998); T. Mori, H. Mori, and S. Tanaka: Bull. Chem. Soc. Jpn. **72**, 179 (1999).
- 10) R. Blinc and B. Zeks: Adv. Phys. **21**, 693 (1972).
- J. Kondo: Physica B 132, 299 (1985); J. Kondo: Physica B 132, 303 (1985).
- 12) M. Tamura et al.: Synth. Met. **102**, 1716 (1999); M. Tamura et al.: Synth. Met. **120**, 1043 (2001).
- K. Itoh and M. Kinoshita: *Molecular Magnetism* (Kodansha; Gordon and Breach, Tokyo, 2000).