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TOPICAL REVIEW

First-principles electronic-band calculations on organic conductors

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Abstract
Predicting electronic-band structures is a key issue in understanding the properties of materials or in materials design. In this review article, application examples of first-principles calculations, which are not based on adjustable empirical parameters, to study electronic structures of organic conductors are described.

Keywords: first-principles calculation, electronic structure, organic conductor

(Some figures in this article are in colour only in the electronic version)

1. Introduction

In this article, the word ‘organic conductors’ is used with the exclusion of doped polymers, graphite intercalation compounds and fullerene systems.

1.1. Brief overview of materials

1.1.1 Conducting salts. Organic conductors usually consist of two kinds of molecules. One acts as a donor and the other acts as an acceptor. Owing to the (partial) charge transfer between them, conductivity is induced. The following are several examples. They are materials whose electronic structures are described below.

TTF-TCNQ (TTF, tetrathiofulvalene; TCNQ, tetracyanoquinodimethane) is the first organic conductor reported [1, 2]. There is a charge transfer of 0.55 electrons/molecule from TTF to TCNQ at room temperature [3]. TTF-TCNQ is a typical 1 : 1 salt, where the numbers of donors and acceptors are equal to each other. Figure 1 shows the crystal structure of TTF-TCNQ [4]. There are homologous stacks of TTF or TCNQ along the b-axis, along which quasi-one-dimensional conductivity is induced.

The next examples are 2 : 1 salts. An isomorphous series of compounds of the form (TMTSF)$_2$X are called Bechgaard salts, where TMTSF is tetramethyl-tetrathiofulvalene and X is a monovalent anion such as PF$_6^-$, As$_6^-$, Sb$_6^-$ or ClO$_4^-$ [5]. There is a charge transfer of one electron from two TMTSF molecules to one X. Owing to the
Figure 2. Crystal structure of (TMTSF)₂ClO₄. Structural data are cited from [9].

Figure 3. Crystal structure of β-(BEDT-TTF)₂I₃. Structural data are cited from [10].

Figure 4. Crystal structure of Ni(tmdt)₂. Purple, yellow, white and gray balls represent Ni, S, C and H atoms, respectively. Structural data are cited from [25].

stacks of planar TMTSF molecules in columns, quasi-one-dimensional conductivity is induced. At low temperatures, this quasi-one-dimensionality results in an exotic ground state such as a spin-density-wave state or a superconducting state, depending on X [6]. (TMTSF)₂ClO₄ is the first ambient-pressure organic superconductor with transition temperatures of 1.2–1.5 K [7, 8]. Figure 2 represents the crystal structure of (TMTSF)₂ClO₄ [9].

Another series of 2 : 1 salts are (BEDT-TTF)₂X compounds, where BEDT-TTF is bis(ethylenedithio)-tetrathiafulvalene. There are many polytypes (e.g. α, β, κ and θ) among them. Figure 3 represents the crystal structure of β-(BEDT-TTF)₂I₃ [10]. The β phase has the smallest unit cell containing one chemical formula. Among the (BEDT-TTF)₂X compounds, particularly, α-(BEDT-TTF)₂I₃ has been attracting much attention [11]. This material exhibits a metal–insulator transition at 135 K [12]. There are many unique properties reported for this material such as charge ordering and disproportionation [13, 14], anomalous thermal behavior of Hall conductivity under high pressure [15], electronic-structure variation under uniaxial compression [16] and superconductivity [17]. Among organic superconductors, at ambient pressure, κ-(BEDT-TTF)₂Cu(NCS)₂ and κ-(BEDT-TTF)₂Cu[N(CN)₂]Br have the highest transition temperatures of 10.4 K [18] and 11.6 K [19], respectively. It has recently been discovered that the Mott insulator β′-(BEDT-TTF)₂ICl₂ becomes a superconductor under a high applied pressure (> 7 GPa) and its transition temperature is 14.2 K at 8.2 GPa [20], which is the highest transition temperature among the organic superconductors. In contrast to this, the isostructural material β′-(BEDT-TTF)₂AuCl₂ shows neither superconductivity nor metallic behavior under a high pressure of up to 9.9 GPa [21].

In the above two series of materials, donor molecules are responsible for the conductivity since 0.5 electrons/(donor molecule) are transferred to acceptor molecules. In contrast, M(dmit)₂ (M = Ni, Pd, Pt, dmit = 4,5-dimercapto-1,3-dithiole-2-thione) form various conducting 2 : 1 salts with organic or inorganic cations and act as acceptors [22, 23]. DCNQI systems (DCNQI = N,N′-dicyanoquinonediimine) also form 2 : 1 salts as acceptors with metallic cations [24].

1.1.2 Single-component conductors. In contrast to inorganic materials, metallic organic solids have long been thought to consist of more than two kinds of molecules. Examples are shown above. The discovery of the first single-component molecular metal Ni(tmdt)₂ (tmdt = trimethylenetetrathiafulvalenedithiolate) [25] has opened a new paradigm. Its crystal structure is shown in figure 4. Since this discovery, various related compounds such as Au(tmdt)₂ [26], Cu(dmdt)₂ (dmdt = dimethylenetetrathiafulvalenedithiolate) [27] and Zn(tmdt)₂ [28] have been synthesized and they form a new class of materials.

1.2. Background of electronic-band calculations

1.2.1 Empirical method. In calculating electronic-band structures on molecular conductors, the tight-binding Hückel approximation has been frequently applied. In accordance
with [29], this calculation scheme is briefly described below. Firstly, the molecular orbitals of a single molecule are calculated by the extended Hückel method [31, 32]. A molecular orbital $\psi_i$ is expressed by a linear combination of atomic orbitals $\phi_j$ as

$$\psi_i = \sum_{j=1}^{n} c_{ij} \phi_j,$$

where $n$ is the number of atomic orbitals. The coefficients $c_{ij}$ are obtained by solving the set of Hückel equations

$$\sum_{j=1}^{n} [H_{ij} - \epsilon S_{ij}] c_{ij} = 0, \quad j = 1, 2, \ldots, n,$$

where $H_{ij}$ and $S_{ij}$ represent an element of the Hamiltonian matrix and the overlap matrix, $\epsilon$ is the orbital energy. The diagonal elements of the Hamiltonian matrix $H_{ii}$ are given by empirical valence state ionization energies, and the off-diagonal elements are described as

$$H_{ij} = C(S_{ij}/2)[(1 + \Delta) H_{ii} + (1 - \Delta) H_{jj}],$$

$$C = k - (k - 1)\Delta^2,$$

$$\Delta = \frac{H_{ii} - H_{jj}}{H_{ii} + H_{jj}},$$

where $k$ is empirically given as 1.75. Secondly, in the case of donor molecules, the intermolecular overlap $S$ of the highest occupied molecular orbital (HOMO) is calculated. Thirdly, the transfer integrals $t$’s are estimated using the relation $t = ES$, where $E$ is a constant of the order of the ionization potential of the HOMO. $E$ is empirically determined and has a typical value of $-10$ eV. Finally, using the obtained $t$ values, a tight-binding model is constructed and solved to obtain the dispersions of conduction bands and the shape of the Fermi surface.

The above-mentioned constant $E$ does not affect the shape of the Fermi surface but affects band width directly. Depending on the physical property, band width becomes crucial. Tajima et al [33] measured the optical conductivity spectra of $\beta$-(BEDT-TTF)$_2$I$_3$ and compared them with results calculated by the tight-binding Hückel approach. They found that transfer integrals should be modified to reproduce the experimental spectra well. The uncertainty of the band width is a drawback of the tight-binding Hückel approximation.

For the validity of the tight-binding Hückel approximation, it is required that constituent molecules in the solid state should preserve characters of isolated forms. It holds true for various molecular conductors, where the intermolecular interaction is much weaker than the intramolecular interaction. For example, in (TMTSF)$_2$X, the HOMO of TMTSF forms bands without hybridizing other states. The Fermi surface can be obtained only from information on the HOMO and molecular arrangements. For small molecules such as TMTSF and BEDT-TTF, the energy level of the HOMO is well separated from those of the lowest unoccupied molecular orbital (LUMO) and the HOMO-1 (the second-highest occupied molecular orbital). The energy separations are large enough compared with the intermolecular interaction. When a constituent molecule becomes larger, energy separations among MOs become smaller, thus the above condition holds no more. For some M(dmit)$_2$ salts, it was found that both HOMO and LUMO have significant contributions to the conduction band [34]. Ni(tmdt)$_2$ is another typical example, as shown below. Thus, it is sometimes difficult to study new materials only by an empirical method. Even in such cases, tight-binding modeling itself is possible utilizing information from experiments or first-principles calculations to adjust several parameters. Tajima et al demonstrated the determination of the tight-binding parameters for M(dmit)$_2$ salts utilizing their optical conductivity measurement results [35]. Recently, a computational scheme has been established to obtain tight-binding parameters as well as effective onsite Coulomb interactions in a first-principles manner [36, 37] based on the maximally localized Wannier function technique [38, 39].

1.2.2 First-principles calculation. First-principle calculations have a great advantage in that they require no empirical parameter. To compensate for this, much more computational resources are required than those for empirical methods. It was not until 1987 that the first application appeared in $\beta$-(BEDT-TTF)$_2$I$_3$ by Kübler et al [40]. However, it was not successful. A two-dimensional Fermi surface with a hole-like character was experimentally confirmed, and the tight-binding Hückel method successfully reproduced it [10]. The result by Kübler et al was a three-dimensional Fermi surface with an electron-like character [40]. Later, they reported a hole-like Fermi surface obtained using improved calculations, although it was rather three-dimensional [41]. Note, however, that these failures were not due to the first-principles density functional theory itself but due to their methodologies of dealing with insufficient computational resources. The first successful first-principles calculations for organic conductors were conducted by Miyazaki et al on DCNQI-(Cu,Ag) systems [42]. They utilized two major progress in the computational techniques: (i) the Car-Parrinello method [43] and its derivatives and (ii) the ultrasoft-pseudopotential (USPP) method [44]. Subsequently, several applications of first-principles calculations appeared, examples of which are given as follows. Particular attention has been paid to results obtained in recently discovered single-component conductors.

2. Examples of first-principles studies

2.1. TTF-TCNQ

Ishibashi and Kohyama reported first-principles electronic-structure calculations in TTF-TCNQ [45, 46]. They utilized the norm-conserving pseudopotential (NCPP) method [47] with the plane-wave basis set and, as for the electronic exchange-correlation energy, the local density approximation (LDA) [48, 49] or the generalized gradient approximation.
(GGA) [50]. Figure 5 shows the calculated band dispersions with GGA on the experimental structure at 100 K [51]. The difference between the results obtained by LDA and GGA is small. The band dispersions for the 100 K structure [51] are slightly larger than those for the room-temperature structure [4] reflecting the changes in the lattice parameters. As shown in figure 5, there are four bands in the vicinity of the Fermi level. Except for the complicated behavior near the Fermi wave number, it looks as if two bands go up and the other two go down with increasing \( k_b \), which corresponds to the quasi-one-dimensional conducting direction. Later, similar first-principles calculation results were reported by two different groups [52, 53].

By fitting a tight-binding model to the first-principles calculation results, the amount of charge transfer from TTF to TCNQ can be estimated. The obtained values are 0.721 (LDA) and 0.707 (GGA) for the room-temperature structure and 0.718 (LDA) and 0.704 (GGA) for the 100 K structure [46]. They are significantly overestimated compared with the experimental values of 0.55 at room temperature and 0.59 below 150 K [3]. If atomic positions are optimized computationally, the estimated values are much worse such as 0.813 (LDA) and 0.768 (GGA) [54]. The lack of a description of the electronic exchange-correlation energy would be the origin of the discrepancy. In spite of this, the overall electronic structure seems reliable. The resultant \( k \)-dependent wavefunctions were utilized to simulate Compton scattering profiles [55] and positron ACAR (angular correlation of annihilation radiation) spectra [56], and the simulated results were in good agreement with the experimental results. In addition, the calculated Fermi surface morphology was in good agreement with that obtained by angle-resolved photoemission spectroscopy at 200 K [57], although the position in the \( k \) space was slightly deviated, reflecting the overestimation of the charge transfer.

The electronic structure of TCNQ was also investigated under uniaxial compression [54]. The application of uniaxial compression is a novel technique [58] and has an advantage over conventional uniaxial stress techniques. Uniaxial stress brings not only the reduction in unit cell size along the desired direction but also the expansion of the unit cell in the plane perpendicular to the stress direction due to the Poisson effect. The uniaxial compression technique is free of this and enables us to make well-screened changes in the intermolecular distance and electronic properties of the organic conductors. Figure 6 represents the Fermi surface morphology of TTF-TCNQ with the experimental 100 K crystal structure [51] as well as with the 10% compressed ones along the \( a \)-, \( b \)- and \( c^* \)-axes [54]. Views from the \( \Gamma \) point toward the \( Y \) point are shown in an area of \( 3a^* \times 3c^* \) (vertical). The four corners of each figure correspond to \((k_x, k_y) = (-1.5a^*, -1.5c^*), (1.5a^*, -1.5c^*), (-1.5a^*, 1.5c^*) \) and \((1.5a^*, 1.5c^*)\). Dark (red for online) ones represent electron surfaces, while bright (yellow) ones represent hole surfaces.

![Figure 5. Electronic-band structure of TTF-TCNQ [46].](image)

![Figure 6. Calculated Fermi surfaces of TTF-TCNQ for the experimental unit cell and compressed cells along the \( a \)-, \( b \)- and \( c^* \)-axes [54]. Views from the \( \Gamma \) point toward the \( Y \) point are shown in an area of \( 3a^* \times 3c^* \) (vertical). The four corners of each figure correspond to \((k_x, k_y) = (-1.5a^*, -1.5c^*), (1.5a^*, -1.5c^*), (-1.5a^*, 1.5c^*) \) and \((1.5a^*, 1.5c^*)\). Dark (red for online) ones represent electron surfaces, while bright (yellow) ones represent hole surfaces.](image)
represents dispersions of the two ionization potential and exponent were not well established or for Se 4d, the atomic orbital parameters such as the on the approximations and parameters chosen. In particular, with each other, there are some discrepancies depending the results of these studies are in qualitative agreement and Fermi surface morphology are shown in figures 2.2. (TMTSF)$_2$X

There are several studies of the electronic structure of (TMTSF)$_2$X obtained by the tight-binding approximation based on the extended Hückel method [30, 59–61]. Although the results of these studies are in qualitative agreement with each other, there are some discrepancies depending on the approximations and parameters chosen. In particular, for Se 4d, the atomic orbital parameters such as the ionization potential and exponent were not well established or empirically determined. That is, there was some uncertainty.

First-principles calculation was performed and reported for (TMTSF)$_2$ClO$_4$ [62]. The electronic-band dispersions and Fermi surface morphology are shown in figures 7 and 8, respectively. Qualitatively, they are in good agreement with the previous empirical results [30, 59–61]. Quantitative analysis by fitting using the tight-binding model [60] showed that the band parameters proposed by Ducasse et al. [61] are the closest to those obtained from the first-principles calculations [62]. The first-principles $k$-dependent wavefunctions were successfully utilized to simulate positron 2D-ACAR spectra [63].

2.2. (TMTSF)$_2$X

![Figure 7. Electronic-band structure of (TMTSF)$_2$ClO$_4$ [62].](image)

![Figure 8. Fermi surface profile of (TMTSF)$_2$ClO$_4$ [62].](image)

$a$-axis. It seems quite natural because the $a$-axis corresponds to the direction along which the TTF and TCNQ columns are aligned alternately.

2.3. (BEDT-TTF)$_2$X

2.3.1 (BEDT-TTF)$_2$I$_3$. As described above, the early first-principles calculations of this compound [40] failed to obtain a reasonable two-dimensional Fermi surface. Ishibashi and Kohyama [45] performed first-principles calculations based on the plane-wave NCPP method and obtained a two-dimensional Fermi surface successfully. The band dispersions and Fermi surface are shown in figure 9. Except for the details, they are very similar to those obtained by Mori et al. [10] and consistent with the experimental results.

2.3.2 α-(BEDT-TTF)$_2$I$_3$. The interesting properties of α-(BEDT-TTF)$_2$I$_3$ mentioned in the previous section have been stimulating theoretical studies to understand their origins. Kino and Fukuyama developed a systematic way of clarifying the nature of the metal–insulator transition by mean-field calculations treating the on-site Coulomb interaction within the Hartree–Fock approximation [64–66]. Seo investigated the charge ordering by the extended Hubbard model with both on-site and intersite Coulomb interactions [67]. Hotta proposed a new minimal model based on an anisotropic triangular lattice and obtained ground-state phase diagrams for (BEDT-TTF)$_2$X and related materials [68]. The existence of the zero-gap semiconducting state, in other words, the Dirac cone dispersion near the Fermi level was found for α-(BEDT-TTF)$_2$I$_3$ by empirical band calculations, and it is related to the unique conducting properties [69–73].

The Dirac cone dispersion near the Fermi level was also confirmed with first-principles calculations by Kino and Miyazaki [74]. Figure 10 represents dispersions of the two eigenstates near the Fermi level. They made tight-binding fittings and obtained temperature-dependent density of states (DOS) spectra and estimated effective carrier density as a function of temperature, as shown in figure 11.

Although α-(BEDT-TTF)$_2$I$_3$ has a strong two-dimensional character, there are small dispersions of electronic bands in the third direction. As a result, string-like Fermi surfaces are formed as shown in figure 12 [75].

![Figure 9. Electronic-band structure and Fermi surface profiles of β-(BEDT-TTF)$_2$I$_3$ [45].](image)

2.3.3 κ-(BEDT-TTF)$_2$X. Xu et al. [80] studied the electronic structures of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ by first-principles calculations based on the orthogonalized linear combination
Figure 10. Electronic structure of $\alpha$-(BEDT-TTF)$_2$I$_3$ at $k_z = 0$ near anisotropic Dirac cone dispersion at ambient pressure and temperature (reproduced with permission from [74]). Dispersions of the two eigenstates near the Fermi level are shown.

Figure 11. Electron density of states of $\alpha$-(BEDT-TTF)$_2$I$_3$ at room temperature (RT) (a) and 8 K (b) at ambient pressure (ap, solid lines), with uniaxial compressions of 2 kbar along the a-axis (a2, thin dashed lines) and 3 kbar along the b-axis (b3, thick dashed lines) and (c) effective carrier density (reproduced with permission from [74]).

Figure 12. Fermi surfaces of $\alpha$-(BEDT-TTF)$_2$I$_3$ for 120 K structure [75]. Hole-like surfaces are shown in blue, whereas electron-like surfaces are shown in red.

Figure 13. Electronic-band structure of $\kappa$-(BEDT-TTF)$_2$Cu(NCS)$_2$ (reproduced with permission from [80]).

Figure 14. Fermi surface of $\kappa$-(BEDT-TTF)$_2$Cu(NCS)$_2$ (reproduced with permission from [80]).

Figure 15. Calculated electronic-band structure and density of states (reproduced with permission from [81]).

Figure 16. The corresponding Fermi surface is shown in figure 16. The number of bands crossing the Fermi level and, as a result, the number of Fermi-surface sheets differ from those obtained by empirical tight-binding calculations [19].

In the empirical tight-binding calculations, only a two-dimensional network of BEDT-TTF molecules is considered. $\kappa$-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br has a crystal structure where BEDT-TTF blocks and anion blocks are alternately stacked.
Figure 15. Electronic-band structure and density of states of \(\kappa-(\text{BEDT-TTF})_2\text{Cu[N(CN)]}_2\text{Br}\) (reproduced with permission from [82]).

Figure 16. Fermi surface of \(\kappa-(\text{BEDT-TTF})_2\text{Cu[N(CN)]}_2\text{Br}\) (reproduced with permission from [82]).

In an actual three-dimensional crystal unit cell, there are two BEDT-TTF blocks [19]. The first-principles calculations by Ching et al [82] were conducted using a three-dimensional unit cell. This is the reason for the difference in the number of Fermi surfaces between the empirical and first-principles calculations.

2.3.4 \(\beta'-(\text{BEDT-TTF})_2X\). Miyazaki and Kino [76] investigated the crystal and electronic structures of \(\beta'-(\text{BEDT-TTF})_2\text{ICl}_2\) at several pressures up to 12 GPa by first-principles calculations within GGA. They reported that the width of the band crossing the Fermi level becomes almost twice at 8 GPa, and that the character of the Fermi surface changes from quasi-one-dimensional to almost two-dimensional, as shown figure 17. Kino et al [77] constructed an effective model using the fluctuation-exchange (FLEX) approximation utilizing band parameters derived from the results of first-principles calculations [76]. In the phase diagram they reported, superconductivity is realized next to the antiferromagnetic phase as a result of the dimensional crossover mentioned above.

Subsequently, Miyazaki and Kino [78] studied the pressure effects on \(\beta'-(\text{BEDT-TTF})_2\text{AuCl}_2\), which shows no superconductivity under high pressure in contrast to \(\beta'-(\text{BEDT-TTF})_2\text{ICl}_2\). As for the AuCl\(_2\) salt, they reported that the width of the band crossing the Fermi level does not increase above 8 GPa and concluded that the electronic structure is three-dimensional rather than quasi-one- or two-dimensional owing to direct contribution of the AuCl\(_2\) part to the electronic structure near the Fermi level. The reported electronic-band structure and Fermi surface at several pressures are shown in figures 18 and 19, respectively. The effective model analysis by Kino et al [79] revealed that the Néel temperature is high under pressure and that no superconducting phase is expected for \(\beta'-(\text{BEDT-TTF})_2\text{AuCl}_2\).
Figure 18. Electronic-band structures of β′-(BEDT-TTF)$_2$AuCl$_2$ at $p =$ (a) 8, (b) 16 and (c) 24 GPa (reproduced with permission from [78]).

2.4. M(dmit)$_2$

Miyazaki and Ohno studied the electronic structures of (CH$_3$)$_4$N[Ni(dmit)$_2$]$_2$ and β-(CH$_3$)$_4$N[Pd(dmit)$_2$]$_2$ by first-principles calculations [83]. They found that the electronic states near the Fermi level show a strong one-dimensional character for the Ni salt but a two-dimensional character for the Pd salt. These characters are mainly contributed by the LUMO of Ni(dmit)$_2$ for the former and the HOMO of Pd(dmit)$_2$ for the latter, respectively. The electronic-band structures of the Ni and Pd salts are shown in figures 20 and 21, respectively, together with schematic views of their energy levels. They ascribed the origin of the difference to the degree of dimerization of M(dmit)$_2$ molecules.

Later, they investigated the pressure effects on these materials and β′-(CH$_3$)$_4$P[Pd(dmit)$_2$]$_2$ [84]. They used GGA and found that the errors of the stress tensors are large only for diagonal parts. The errors are rather isotropic with values of 5–10 kbar. They mentioned that van der Waals interactions are not important or isotropic for these materials. The obtained electronic-band structures of these materials at ambient pressure and high pressure are shown in figures 22–24. They reported the pressure effects for these materials as follows.

Figure 19. Fermi surfaces of β′-(BEDT-TTF)$_2$AuCl$_2$ at $p =$ (a) 0, (b) 8, (c) 16 and (d) 24 GPa (reproduced with permission from [78]).

Figure 20. Electronic-band structure of (CH$_3$)$_4$N[Ni(dmit)$_2$]$_2$ and schematic view of energy levels (reproduced with permission from [83]).

Figure 21. Electronic-band structure of β-(CH$_3$)$_4$N[Pd(dmit)$_2$]$_2$ and schematic view of energy levels (reproduced with permission from [83]).
For (CH$_3$)$_4$N[Ni(dmit)$_2$]$_2$, the applied pressure makes the strong one-dimensional character of LUMO bands more isotropic within the $ab$-plane. In contrast, for $\beta$-(CH$_3$)$_4$N[Pd(dmit)$_2$]$_2$, the band structure under pressure becomes more anisotropic. The pressure effects for $\beta$'-(CH$_3$)$_4$P[Pd(dmit)$_2$]$_2$ seems similar to those for $\beta$-(CH$_3$)$_4$N[Pd(dmit)$_2$]$_2$.

2.5. (R$_1$, R$_2$-DCNQI)$_2$M

Miyazaki et al. [42] performed first-principles LDA electronic-structure calculations for (DMe-DCNQI)$_2$Cu, (DMe-DCNQI)$_2$Ag (R$_1$ = R$_2$ = CH$_3$) and (DI-DCNQI)$_2$Cu (R$_1$ = R$_2$ = I). The calculated Fermi surfaces of (DMe-DCNQI)$_2$Cu (figure 25) have a three-dimensional character and are in good agreement with the experimentally observed ones [85]. The first-principles electronic-band structure near the Fermi level (figure 26) agrees well with that obtained by the empirical method [86]. The band structure of (DI-DCNQI)$_2$Cu (figure 27) is significantly different from that of (DMe-DCNQI)$_2$Cu. Miyazaki et al. summarized the following five important aspects: (i) The LUMO band width for the DI salt is about half of that for the DMe salt; (ii) the HOMO–LUMO band gaps are about 0.8 eV for the DI salt and 1.2 eV for the DMe salt; (iii) the hybridization between the neighboring one-dimensional LUMO bands is slightly stronger in the DI salt than in the DMe salt; (iv) the $p\pi$–$d$ hybridization is suppressed; (v) the Fermi-surface nesting vector deviates from the commensurate one. As for (DMe-DCNQI)$_2$Ag, the $d$ states of Ag are located fairly deep in energy from the Fermi level, and the $p\pi$–$d$ hybridization is significantly suppressed. Consequently, the small hole pocket around the $\Gamma$ point is absent and the Fermi-surface nesting vector is close to one-quarter of $c^*$ (one of the reciprocal vectors). The electronic-band structure of (DMe-DCNQI)$_2$Ag is shown in figure 28. The authors
also mentioned that the calculated specific heat and magnetic susceptibility of $\text{(DMe-DCNQI)}_2\text{Cu}$ and $(\text{DI-DCNQI})_2\text{Cu}$ were smaller than the experimental values by a factor of 2–3, implying appreciable roles of the electron–phonon and electron–electron interactions.

Miyazaki and Terakura [87] further investigated various DCNQI systems by first-principles GGA calculations. They reported that, on the same material and structure, the GGA results are almost the same as the LDA results. In addition to the three materials mentioned above, the electronic structures of $(\text{DMe-DCNQI})_2\text{Li}$, $(\text{DI-DCNQI})_2\text{Li}$ and $(\text{DBr-DCNQI})_2\text{Cu}$ are described. Their electronic-band structures are shown in figures 29–31.
of (DMe-DCNQI)$_2$Cu is qualitatively the same as that of (DMe-DCNQI)$_2$Li. The band structure of (DI-DCNQI)$_2$Li is completely different from that of (DMe-DCNQI)$_2$Li. The former is quasi-one-dimensional, whereas the latter is rather three-dimensional. The nesting vector existing for (DMe-DCNQI)$_2$Li seems lost for (DI-DCNQI)$_2$Li.

Pressure effects on the electronic structure were also studied for (DMe-DCNQI)$_2$Cu and (DI-DCNQI)$_2$Cu by the same authors [88]. They reported a marked change in the electronic structure of (DI-DCNQI)$_2$Cu with pressure application in contrast to a less prominent change in that of (DMe-DCNQI)$_2$Cu. The electronic-band structures of (DI-DCNQI)$_2$Cu under several pressures are shown in figure 32.

2.6. Single-component conductors

2.6.1 Ni(tmdt)$_2$. Rovira et al [89] studied the electronic structure of Ni(tmdt)$_2$ by first-principles NCPP calculations based on GGA. They calculated the band structure and clarified the presence of two kinds of Fermi surfaces due to two bands crossing the Fermi level. Similar results were also obtained by first-principles NCPP calculations with LDA, and the experimentally obtained anisotropic cross sections of the Fermi surfaces are reasonably explained using the calculated Fermi surfaces [90]. The electronic structure near the Fermi level of Ni(tmdt)$_2$ was calculated by the projector augmented-wave (PAW) method with GGA and compared systematically with those of other materials (i.e. Au(tmdt)$_2$, Au(tmstfdt)$_2$ (tmstfdt = trimethylenebis(dithiole)diselenolate), Cu(dmdt)$_2$ and Zn(tmdt)$_2$) [91]. The electronic DOS of Ni(tmdt)$_2$ is shown in figure 33 together with those of Au(tmdt)$_2$ and Au(tmstfdt)$_2$. Again, two bands cross the Fermi level. The DOS of the lower band overlaps with that of another band in energy space. For these three bands,
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Figure 32. Electronic-band structures of (DI-DCNQI)$_2$Cu at $p = (a) 0$ kbar, (b) 15.3 kbar and (c) 37.61 kbar (reproduced with permission from [88]).

Seo et al [92] constructed an effective Hubbard model by fitting tight-binding parameters to the first-principles calculation result. The model consists of a $\pi$ orbital for each of the two tmdt ligands and a $pd\sigma$ orbital. They found that both orbitals contribute to realizing the metallic character of Ni(tmdt)$_2$. In figure 33, it is also shown that a band with quasi-one-dimensional character, which originated from the anti-bonding $pd\sigma$ orbital, is located slightly higher than the Fermi level.

2.6.2 Au(tmdt)$_2$. Ishibashi et al [93] reported the electronic structure of Au(tmdt)$_2$ obtained by first-principles NCPP calculations with both LDA and GGA. Although Ni(tmdt)$_2$ and Au(tmdt)$_2$ are isostructural, the former has even valence-electron numbers in the unit cell, whereas the latter has odd ones. Thus, as shown in figure 33, only one band crosses the Fermi level for Au(tmdt)$_2$. The Fermi-surface cross sections are shown in figure 34. The Fermi surface appears three-dimensional, although a nesting vector of $a^*/2$ seems to exist by the noninteracting susceptibility analysis, as

Figure 33. Electron density of states for nonmagnetic Ni(tmdt)$_2$ (left), Au(tmdt)$_2$ (center) and Au(tmstfdt)$_2$ (right) solids [93]. The Fermi energy is set to be zero for each.

Figure 34. Fermi surface cross section of Au(tmdt)$_2$ [93].
Figure 35. Geometrical part of the intra-band generalized susceptibility for Au(tmdt)$_2$ [93].

No significant difference between the results by NCPP and LDA/GGA [93] or those by PAW and GGA [91] exists except for a small difference in the estimated magnetic moment. Corresponding to the nesting vector, an antiferromagnetic ground state was determined by magnetic calculations with a doubled unit cell along the $a$-direction, as shown in figure 36, although the magnetic stabilization energy is negligible. Seo et al [92] also constructed an effective Hubbard model for this material. The target bands are different from those of Ni(tmdt)$_2$. A band corresponding to the lowest one of Ni(tmdt)$_2$ is excluded and, instead, a higher band is included. As a result, the model consists of a $\pi$ orbital for each of the two tmdt ligands and a $p_d\sigma$ orbital in this case. The origin of the antiferromagnetic transition observed in Au(tmdt)$_2$ at approximately 110 K [26, 94, 95] is discussed. It should be mentioned that the magnetic moment obtained from hydrogen nuclear magnetic resonance experiments [95] is rather large, more than 0.6 $\mu_B$ per tmdt, which is inconsistent with the calculated ones, which are less than 0.2 $\mu_B$ per tmdt [91–93].

Au(tmstfdt)$_2$ is isostructural with Au(tmdt)$_2$ [96]. The four outermost S atoms are substituted by Se atoms. As a result, the lattice parameters are slightly larger than those of Au(tmdt)$_2$. Comparing the electronic DOS of Au(tmstfdt)$_2$ with that of Au(tmdt)$_2$, note that the position of the quasi-one-dimensional band for Au(tmstfdt)$_2$ is slightly higher than that for Au(tmdt)$_2$. The Fermi surface of Au(tmstfdt)$_2$ shows a quasi-one-dimensional character, which however is not strong, and the nesting vector of $a'/2$ disappears [91]. This would be the reason for the much lower Néel temperature of about 7 K [96].

2.6.3 Cu(dmdt)$_2$. Figure 37 shows the nonmagnetic electronic-band structure of Cu(dmdt)$_2$ [91]. The corresponding DOS is shown in figure 38. Two bands cross the Fermi level. Thus, the system is a semimetal, or, since the overlap of those two bands is large, it would be better to describe it as a metal. Experimentally, a magnetic moment of 0.84 $\mu_B$ per molecule was reported from the susceptibility measurement [27] though no magnetic order has been observed. Magnetic calculations using a conventional monoclinic cell, whose volume is twofold that of the base-centered monoclinic primitive cell, gives a magnetic moment of 0.61 $\mu_B$ per molecule [91]. The corresponding spin distribution is shown in figure 39. In contrast to Au(tmdt)$_2$, a significant spin density exists on the center metal. The electronic DOS is shown in figure 40 revealing that the DOS at the Fermi level is rather small.

2.6.4 Zn(tmdt)$_2$. Figure 41 shows the nonmagnetic electronic-band structure of Zn(tmdt)$_2$ [91]. The corresponding DOS is shown in figure 42. Except the position of the Fermi level, the overall features look similar to those of Cu(dmdt)$_2$. The DOS at the Fermi level is
small, and the system is a semimetal with small hole and electron pockets. Experimentally, the system seems a semiconductor although temperature-independent paramagnetism is observed [28]. This paramagnetism may be related to small Fermi pockets.

2.6.5 Isolated molecules. Ni(tmdt)\(_2\) and Au(tmdt)\(_2\) have planar molecular forms in their crystalline phases, whereas Cu(dmdt)\(_2\) and Zn(tmdt)\(_2\) have twisted molecular forms. For each isolated molecule, total energy is calculated as a function of the dihedral angle between two ligands and is shown in figure 43 [91]. The energy minima are found at 0° for Ni(tmdt)\(_2\) and Au(tmdt)\(_2\), whereas at 80° for Cu(dmdt)\(_2\) and at 90° for Zn(tmdt)\(_2\). Experimentally, the dihedral angle \(\theta\) between two ligands was reported to be 0°, 0°, 80.29° and 89.63° for Ni(tmdt)\(_2\), Au(tmdt)\(_2\), Cu(dmdt)\(_2\) and Zn(tmdt)\(_2\), respectively, when they form crystals. The calculated results are in excellent agreement with those values.

To elucidate the central metal dependence of the electronic structure of constituent molecules, first, states around HOMO and LUMO for isolated molecules with planar forms are calculated and shown in figure 44 [91]. The antibonding \(pd\sigma\) state consisting of a center-metal \(d\) orbital
Figure 43. Total energy variation with dihedral angle \( \theta \) [91]. Filled circles are for non-magnetic results, whereas open circles are for spin-polarized results. For each molecule, \( \Delta E \) is defined as the difference from the energy value at \( \theta = 0 \) in the nonmagnetic case.

Figure 44. Nonmagnetic wavefunctions and energy eigenvalues for planar Ni(tmdt)_2, Au(tmdt)_2, Cu(dmdt)_2, and Zn(tmdt)_2 molecules [91]. Four states including HOMO (SOMO) and LUMO are shown for each molecule.

and the surrounding sulfur orbitals changes its energy level systematically. In contrast, the other states with only a small metal \( d \) component show a small variation.

The HOMO and LUMO for Ni(tmdt)_2 are basically the bonding and antibonding states of the LUMOs of the ligand tmdt molecules, respectively, as has already been pointed out [89]. The closeness of their energy levels is a key factor in the metallic nature of Ni(tmdt)_2. The energy separation between HOMO and LUMO is controlled by a slight mixing of a Ni \( d \) state to HOMO. There is no \( d \) component in LUMO for symmetry reason. In HOMO, on the other hand, there is a weak antibonding-type \( d-\pi \) hybridization, which pushes the HOMO level upward to higher energy. For Au(tmdt)_2, the energy difference between the corresponding states (HOMO-1 and singly occupied molecular orbital (SOMO)) is even smaller because of a smaller \( d \) component in SOMO. In addition, the antibonding \( p\sigma \) state approaches these two levels. The unique properties of Au(tmdt)_2 have been ascribed to these features. For Cu(dmdt)_2, the antibonding \( p\sigma \) state is singly occupied and comes in between the ligand bonding and antibonding states. The difference between Cu and Au in the energy level of the antibonding \( p\sigma \) state comes from the difference in the extension of the \( d \) orbital. Although the 5d level of Au is even deeper than the 3d level of Cu as free atoms, the wavefunction is much more extended for 5d of Au than for 3d of Cu, and the anti-bonding \( p\sigma \) state for Au(tmdt)_2 is more strongly pushed upward in energy. For Zn(tmdt)_2, the state with a strong metal \( d \) orbital character goes to a deeper level.

Since Au(tmdt)_2 and Cu(dmdt)_2 have SOMO, they are spin polarized. The results of spin-polarized calculations for isolated planar molecules are shown in figure 45. The electronic structures of the Au(tmdt)_2 molecule are more or less the same for both spins. This is because the spin density distribution is determined by the SOMO orbital whose wave function is extended over the ligands leading to a very small exchange splitting (0.146 eV). In marked contrast to this, for the Cu(dmdt)_2 molecule, the spin polarization is quite localized with a strong Cu \( d \) character, and the exchange splitting of the antibonding \( p\sigma \) state is as large as 0.557 eV. The stable molecular structure of Cu(dmdt)_2 is not planar but twisted, and the electronic and magnetic properties of the molecule become quite different as discussed below.

The symmetry of the Cu(dmdt)_2 or Zn(tmdt)_2 molecule depends on dihedral angle: D_2h for \( \theta = 0^\circ \), D_2d for \( \theta = 90^\circ \) and D_2 for \( \theta \neq 0^\circ, 90^\circ \). Among these three symmetry groups, only D_2d has a two-dimensional representation. The electronic structures of isolated molecules of Cu(dmdt)_2 (\( \theta = 80^\circ \)) and Zn(tmdt)_2 (\( \theta = 90^\circ \)) are shown in figure 46. The dihedral angle for each molecule corresponds to the angle in figure 43, where the minimum total energy is given. In accordance with the above symmetry argument, Zn(tmdt)_2 with the D_2d symmetry has doubly degenerate states, as shown in figure 46. For Cu(dmdt)_2, the D_2d structure with \( \theta = 90^\circ \) will undergo the Jahn–Teller distortion because the doubly degenerate HOMO orbitals in the majority spin state is singly occupied. This is the reason why \( \theta \) deviates from 90°, as
observed experimentally. The twisted molecular shape has an important effect on the magnetic property of the Cu(dmdt)$_2$ molecule. For the planar Cu(dmdt)$_2$ molecule, its SOMO has a relatively strong $d$ component, and the SOMO wave function extends only over to the nearest S atoms. On the other hand, the SOMO of the twisted molecule is more delocalized and the exchange splitting is suppressed.

The metal-element dependence of a molecular structure may be explained as follows. As sulfur atoms next to the metal element are negatively charged to some extent, the electrostatic interaction may favor the configuration with $\theta = 90^\circ$. However, in the cases of Ni(tmdt)$_2$ and Au(tmdt)$_2$, the fact that the anti-bonding $p\sigma$ state is pushed up in energy to be unoccupied implies that the planar structure is stabilized by the $p\sigma$ bond. On the other hand, the stability of the planar structure is reduced by the half filling of this anti-bonding $p\sigma$ state for Cu(dmdt)$_2$. Moreover, such stabilization is absent in Zn(tmdt)$_2$.

3. Summary

A brief history and examples of first-principles calculations for molecular conductors are described. It is shown that first-principles calculations give useful information on electronic structures. Furthermore, crystal structures under high pressure can be determined and the corresponding electronic properties can be predicted.

There are several known problems in the calculations, however. For molecular solids, the van der Waals interaction is sometimes significant. Neither LDA nor GGA can treat it properly. Band gaps or HOMO-LUMO gaps are usually underestimated with LDA or GGA. Mott insulator or charge-ordered phases appear frequently for molecular conductors but they cannot be correctly described with LDA or GGA. Advanced schemes dealing with electronic exchange–correlation interaction should be introduced in the future.

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Figure 46. Wavefunctions and energy eigenvalues for twisted Cu(dmdt)$_2$ ($\theta = 80^\circ$) and Zn(tmdt)$_2$ ($\theta = 90^\circ$) molecules [91]. Spin-polarized results are shown for the former, whereas nonmagnetic ones are shown for the latter.


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