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# Direct Observation of Molecular Orbitals Using Synchrotron X-ray Diffraction

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**Abstract:** The physical properties of molecular crystals are governed by the frontier orbitals of molecules. A molecular orbital, which is formed by superposing the atomic orbitals of constituent elements, has complicated degrees of freedom in the crystal because of the influence of electron correlation and crystal field. Therefore, in general, it is difficult to experimentally observe the whole picture of a frontier orbital. Here, we introduce a new method called "core differential Fourier synthesis" (CDFS) using synchrotron X-ray diffraction to observe the valence electron density in materials. By observing the valence electrons occupied in molecular orbitals, the orbital state can be directly determined in a real space. In this study, we applied the CDFS method to molecular materials such as diamond,  $C_{60}$  fullerene, (MV)I<sub>2</sub>, and (TMTTF)<sub>2</sub>X. Our results not only demonstrate the typical orbital states in some materials, but also provide a new method for studying intramolecular degrees of freedom.

Keywords: X-ray diffraction; single crystal; electron density; molecular orbital

# 1. Introduction

The degree of freedom of electron orbitals in materials is closely related to physical properties, such as electrical conductivity, magnetic, dielectric, and optical properties, and crystal structure [1–3]. An electron orbital corresponds to the existence probability of electrons in a real space. In other words, the orbital state can be correctly understood by observing the spatial distribution of electrons in materials. Among the three degrees of freedom in electrons (i.e., charge, spin, and orbital), because the charge and spin can readily respond to external electric and/or magnetic fields, their properties are relatively easy to measure. On the other hand, several experimental methods, such as electron spin resonance (ESR), nuclear magnetic resonance (NMR), high harmonics generated from femtosecond laser pulses [4], ultraviolet angle-resolved photoelectron spectroscopy [5], polarized neutron diffraction [6], resonant X-ray scattering [7], and multipole analysis [8] using X-ray diffraction (XRD), are known to extract orbital information that control the anisotropy of the physical properties. However, in these methods, the measurable substances are limited, and the results may depend on the applied model. Furthermore, as the molecular substance formed by the bonding of multiple atoms has several independent parameters that describe the crystal structure, it is very difficult to estimate the frontier orbital state of the entire system from quantum chemical or first-principles calculations.

The spatial distribution of electrons observed experimentally will be useful for understanding the orbital states in materials. In this sense, XRD is one of the most powerful experimental probes to observe electrons around atoms in a solid. XRD is based on the scattering phenomenon of electrons in a crystal, where the periodic structure of electrons and diffraction intensities are linked by a Fourier transform. In principle, a complete electron density (ED) distribution can be reproduced by performing the inverse Fourier transform on the 'infinite' number of diffraction intensities corresponding to the Fourier series. However, in reality, because the number of diffraction reflections obtained by the XRD experiment is 'finite', it is impossible to reproduce the complete ED distribution owing to the mathematical truncation effects of the Fourier synthesis. Moreover, of all the electrons around an atom, only valence electrons, which are very small in number compared to the total number of electrons in the crystal, are responsible for their physical properties. Therefore, to extract the frontier orbital information from the ED, only the valence electrons need to be extracted. Due to these difficulties, instead of observing the ED, the crystal structure is usually determined from XRD experiments by refining the internal parameters (e.g., atomic positions, atomic displacement parameters, and site occupancies) of the assumed crystal structural model through the least squares method to match the diffraction intensities. This method is called a crystal structural analysis. To access the orbital state (i.e., the distribution of electrons) with high accuracy in materials from the XRD, a new method of analysis is required.

In this paper, we introduce the core differential Fourier synthesis (CDFS) method [9,10] for directly observing the valence electron density (VED) in a crystal from XRD data. The details of the method are also explained in [10]. CDFS can efficiently extract only the valence electron information, which corresponds to the physical properties. By using this method, the orbital state that governs the anisotropy of the physical properties can be directly observed in a real space. Here, we show the results of applying the CDFS method to diamond,  $C_{60}$  fullerene, (MV)I<sub>2</sub> (MV = methyl viologen), and (TMTTF)<sub>2</sub>X (TMTTF = tetramethyl tetrathiafulvalene;  $X = PF_6$ , and AsF<sub>6</sub>).

#### 2. Methods

The XRD experiments using single crystals were performed on the BL02B1 beamline at the synchrotron radiation facility SPring-8 in Japan [11]. A helium-gas-blowing device (Japan Thermal Engineering Co., Ltd., Japan) was employed to cool the sample. A two-dimensional (2D) imaging plate (FUJIFILM Co., Japan) and a CdTe PILATUS (DECTRIS Ltd., Switzerland) detectors, which had a dynamic range of ~10<sup>6</sup>, were installed in the diffractometer (Rigaku Co., Japan). Diffraction intensity averaging and a structural analysis were performed using SORTAV [12] and Jana2006 [13], respectively. The crystal structure and ED distribution figures were visualized using VESTA [14].

The diffraction intensity  $I(\mathbf{K})$  obtained from the XRD experiment can be described as a Fourier transform of the ED  $\rho(\mathbf{r})$  using the scattering vector  $\mathbf{K}$  (Equation (1)).

$$I(\mathbf{K}) = S \left| \int_{\text{all}} \rho(\mathbf{r}) \mathrm{e}^{-i\mathbf{K}\mathbf{r}} d\mathbf{r} \right|^2 \tag{1}$$

Here, *S* is a scaling factor. The integration range ( $\int_{\text{all}}$  in Equation (1)) corresponds to the range in which X-rays interfere in the crystal. In the case of a crystal,  $I(\mathbf{K})$  can be described as Equation (2) using Laue functions L(s), L(t), and L(u), where  $\mathbf{K} = s\mathbf{a}^* + t\mathbf{b}^* + u\mathbf{c}^*$ .

$$I(\mathbf{K}) = S L(s)L(t)L(u) \left| \int_{\text{unit cell}} \rho(\mathbf{r}) e^{-i\mathbf{K}\mathbf{r}} d\mathbf{r} \right|^2$$

$$\propto \left| F_{\text{obs}}(\mathbf{K}) \right|^2$$
(2)

Here,  $|F_{obs}(K)|$  is the absolute value of the experimentally observed crystal structure factor. Generally, if the number of unit cells *N* in a crystal is sufficiently large, then the Laue function becomes

 $N^2$  only when all of the *s*, *t*, *u* are integers; otherwise,  $I(\mathbf{K}) = 0$ . In principle, the ED distribution can be reproduced by the inverse Fourier transform of the diffraction intensity according to

$$\rho(\mathbf{r}) = \frac{1}{V} \sum_{\mathbf{K}}^{\infty} F_{\text{obs}}(\mathbf{K}) e^{i\mathbf{K}\mathbf{r}},$$
(3)

if the infinite diffraction data were observed. However, the calculation of the ED generally has three problems. (i) To extract the VED with anisotropic information, a sufficiently wide dynamic range of intensity is required. (ii)  $|F_{obs}(K)|$  is obtained from the experimentally diffraction intensity because of the relationship of  $I(K) \propto |F_{obs}(K)|^2$ . In this case,  $|F_{obs}(K)|$  does not include information of the phase term  $P = e^{i\phi(K)}$  as  $F_{obs}(K) = |F_{obs}(K)|P = |F_{obs}(K)|e^{i\phi(K)}$ , which is necessary for the calculation of  $\rho(r)$ . (iii) Because the number of the  $F_{obs}(K)$  data is finite, the mathematical truncation effect seriously affects the ED distribution.

With regard to (i), the relationship between the number of focused electrons and the number of electrons in the unit cell is important. In the case of a quasi-one-dimensional (1D) molecular conductor  $(TMTTF)_2X$ , a 3/4-filled system, because  $X^-$  is a monovalent anion, such as  $PF_6^-$ ,  $AsF_6^-$ ,  $SbF_6^-$ ,  $Br^-$ , or  $ClO_4^-$ , there is one hole for two TMTTF molecules forming a dimer. The number of electrons in the (TMTTF)<sub>2</sub>X unit is approximately 350. To estimate the amount of charge transfer of less than 1*e* in the TMTTF dimer in the charge ordering state, a dynamic range that can accurately extract  $1^2/350^2 = 1/122500 \sim 10^{-5}$  of the measured maximum intensity is necessary. Here, the  $10^{-5}$  signal information should be observed with a sufficient signal-to-noise (*S/N*) ratio. This requirement is sufficiently fulfilled using the current synchrotron radiation facility, in which the dynamic range of  $10^6$  is guaranteed.

With regard to (ii), because the phase term can be assigned from the calculated crystal structure factor

$$F_{\rm cal}(\mathbf{K}) = \sum_{j} f_j T_j e^{-i\mathbf{K}\mathbf{r}_j}$$
(4)

as  $P = F_{cal}(\mathbf{K}) / |F_{cal}(\mathbf{K})|$ , Equation (3) can be rewritten as

$$\rho(\mathbf{r}) = \frac{1}{V} \sum_{\mathbf{K}}^{\infty} \left| F_{\text{obs}}(\mathbf{K}) \right| P e^{i\mathbf{K}\mathbf{r}}.$$
(5)

Here,  $r_j$  is the *j*th atomic position,  $T_j$  is the *j*th atomic displacement parameter, and  $f_j$  is the *j*th atomic scattering factor, which is described as

$$f_j(\mathbf{K}) = \int_{\text{atom}} \rho_j(\mathbf{r}) e^{-i\mathbf{K}\mathbf{r}} d\mathbf{r}.$$
 (6)

Figure 1 shows the atomic scattering factor of carbon as a function of  $\sin \theta / \lambda$  [15]. Here,  $\lambda$  is the wavelength of the incident X-ray, and  $\theta$  is the XRD angle. While the contribution of the core electrons extends to the high-angle region, the contribution of the valence electrons exists only in the low-angle region ( $\sin \theta / \lambda \le 0.5 \text{ Å}^{-1}$ ). When calculating the ED, it is necessary to determine  $F_{\text{cal}}(\mathbf{K})$  with high accuracy to obtain the correct phase term *P*. For this purpose, the structural refinement is performed using only the high-angle  $I(\mathbf{K})$  (i.e., high-angle analysis), where the contribution of the spatially spread valence electron is very small.



**Figure 1.** Atomic scattering factor of carbon [15]. Black, blue, and orange lines indicate the contribution of the total, core, and valence electrons, respectively.

With regard to (iii), the truncation effect of the Fourier synthesis can be suppressed using the CDFS method. The equation of the inverse Fourier transform by the CDFS method is described as

$$\rho_{v}(\mathbf{r}) = \frac{1}{V} \sum_{\mathbf{K}} \left[ \left| F_{\text{obs}}(\mathbf{K}) \right| P - \left| \sum_{j} f_{j}^{\text{core}} T_{j} e^{-i\mathbf{K}\mathbf{r}_{j}} \right| P^{\text{core}} \right] e^{i\mathbf{K}\mathbf{r}} \right] + \frac{n_{v}}{V}.$$
(7)

Here,  $f_j^{\text{core}}$  is the *j*th atomic scattering factor with only the core electron contribution, which corresponds to the blue line in Figure 1.  $P^{\text{core}}$  is the phase term with only the core electron contribution calculated as  $P = F_{\text{cal}}^{\text{core}}(\mathbf{K})/|F_{\text{cal}}^{\text{core}}(\mathbf{K})|$ .  $n_v$  is the total number of valence electrons contained in the unit cell. The 0 0 0 Bragg reflection intensity cannot be observed experimentally. When ignoring the second term  $n_v/V$  in Equation (7), the total number of electrons in the unit cell becomes zero. Therefore, the VED distribution data are corrected by adding the  $n_v/V$  term. In general,  $(\sin \theta/\lambda)_{\text{max}}$  measured experimentally is ~ 2.5Å<sup>-1</sup> ( $d_{\min} \sim 0.2$ Å) even when using the short-wavelength X-ray obtained at the synchrotron radiation facility. In Figure 1, a nonzero value remains in  $f_{\text{carbon}}(= f_{\text{carbon}}^{\text{core}})$  at  $\sin \theta/\lambda = 2.5$ Å<sup>-1</sup>. Therefore, even if a short-wavelength X-ray is used, the mathematical truncation effect cannot be avoided from the calculation using Equation (5). Meanwhile, in Equation (7), the inverse Fourier transform is performed on the term obtained by subtracting the core electron contribution from  $|F_{\text{obs}}(\mathbf{K})|$ , which contains the contribution of all electrons. Because most of the contribution of the remaining  $f_{\text{valence}}$  exists only in  $\sin \theta/\lambda \leq 0.5$ Å<sup>-1</sup>, the VED can be extracted with a little truncation effect of the Fourier synthesis by the CDFS analysis.

#### 3. Results and Discussion

#### 3.1. Diamond

First, we describe the VED of diamond, which is a typical compound that forms  $sp^3$  hybridized orbitals. Diamond forms a crystal structure in which C atoms are arranged in three dimensional space (space group:  $Fd\overline{3}m$ ) (Figure 2a). Each C atom has six electrons, where the inner 1*s* orbital is occupied by two electrons, and the outer 2*s* and 2*p* orbitals are occupied by two electrons. In general, the valence electrons occupying the outer shell orbitals contribute to the physical properties. In the case of diamond, the four valence electrons of each C atom occupy the  $sp^3$  hybridized orbitals, forming a very strong bond state called a covalent bond.



**Figure 2.** (**a**) Crystal structure of diamond; (**b**) Synchrotron X-ray diffraction (XRD) data of a diamond crystal at 30 K. (**c**,**d**) Total electron density (ED) distribution of diamond calculated by the general inverse Fourier transform of diffraction intensity using Equation (5); (**c**) Surface plot; (**d**) Sectional view of the (4 4 0) plane.

Because the d-glide  $(h + k + l \neq 4n$  reflections disappear) exists in the space group  $Fd\overline{3}m$ , the diffraction intensity of a  $\overline{2} \, \overline{2} \, \overline{2}$  reflection is originally zero. However, the  $\overline{2} \, \overline{2} \, \overline{2}$  (and its equivalent reflections) intensity appears in the data obtained by the synchrotron XRD experiment at 30 K (Figure 2b). This finding corresponds to the fact that the extinction rule of *d*-glide is violated by the bonding electrons existing between C atoms. Using the high-resolution diffraction data obtained by the short-wavelength X-rays of synchrotron radiation, an ED analysis based on the usual inverse Fourier transform equation (Equation (5)) is performed, where reflections that satisfy the *d*-glide extinction rule are also included. Because the obtained total ED distribution of diamond is greatly disturbed (Figure 2c,d), the VED distribution corresponding to the covalent bonds cannot be confirmed. This is the mathematical truncation effect of the Fourier synthesis mentioned above.

Figure 3 shows the VED distribution of diamond obtained by the CDFS analysis using Equation (7). A very smooth ED distribution is observed, and the VED corresponding to the C–C covalent bonds is clearly visible. The density at the center point of the C–C covalent bonds is ~  $1.3e/Å^3$ . Compared with the VED distribution obtained by the first-principles calculation [16], this result not only qualitatively reproduces its shape, but also quantitatively reproduces its density well. As shown here, the VED distribution can be extracted with high accuracy through the CDFS analysis. In diamond, valence electrons contributed only to covalent bonds. In the following, we will introduce some systems in which the valence electrons play more roles. In particular, beginning with a small, simple molecule with a rather localized electronic system, we will progressively go into the details of more complicated molecular systems with delocalized electrons, concluding with discussion of those capable of phase transitions.



**Figure 3.** Valence electron density (VED) distribution of diamond calculated by the CDFS method using Equation (7): (**a**) Surface plot, and (**b**) Sectional view of the (4 4 0) plane.

## 3.2. C<sub>60</sub> Fullerene

Next, we show the VED of  $C_{60}$  fullerene [17,18], which has two types of features of the  $sp^2$  and  $sp^3$  hybridizations. Many structural studies of  $C_{60}$  have been reported so far [19–24]. The  $C_{60}$  cluster consists of 20 hexagons and 12 pentagons. The former involves the  $sp^2$  hybridization, and the latter  $sp^3$  hybridization. There are two different types of C–C bonds; one is on the regular pentagon (single bond), and the other is shared by two hexagons (double bond). In the high-temperature phase of a  $C_{60}$  crystal, the  $C_{60}$  molecules are completely orientationally disordered and continue to randomly rotate, where the space group is  $Fm\overline{3}m$ . At 260 K,  $C_{60}$  exhibits a first-order phase transition; below that temperature, there is a discontinuous reorientation principally around the [111] direction, where the space group is  $Pa\overline{3}$ . Below 90 K, the discontinuous rotational motion is frozen, although a small amount of static disorder still exists [19,23].

In this study, we focus on the low-temperature phase at 30 K without a dynamical motion of  $C_{60}$  molecules. The lattice parameter in  $Pa\overline{3}$  is a = 14.0279(6) Å at 30 K. The detail of the structural analysis results is shown in Appendix A (Table A1). As reported in previous structural studies [22,23], there may be two types of domains in the low-temperature phase. One is the merohedral domain described in [22], in which I(hkl) and I(khl) are superimposed, and the other is the rotational domain around the [111] direction described in [23], in which two kinds of  $C_{60}$  configurations exist. Our structural analysis results show that the ratio of the merohedral domain is 0.4995(8):0.5005, and the ratio of the rotational domain is 0.818(3):0.182. When observing the VED distribution, the contributions of the former domain can be separated analytically. In the latter domain, the two components appear independently, where the VED in two directions coexist in a real space. However, in this case, because the ratio of the rotational domain was quite different, the VED was observed as almost one domain.

Figure 4a shows the crystal structure and VED of a  $C_{60}$  molecule, and Figure 4b shows a sectional view of the  $(1 \ 1 \ \overline{1})$  plane. The (i) and (iii) bonds, ~ 1.45 Å, correspond to the single bonds, and the (ii) bond, ~ 1.39 Å, corresponds to the double bond. Certainly, the double bond forms a stronger bond than the single bond. The VED distribution is clearly observed along the shape of the  $C_{60}$  molecule, which is very similar to the results of previous density functional theory calculations [25]. Furthermore, the difference in the ED is confirmed between the single (shown as (i) and (iii)) and double (shown as (ii)) bonds (Figure 4b). The ED at the double bond is higher than that at the single bond, which corresponds to the strength of the C–C covalent bond. We succeeded in quantitatively evaluating the covalent bond strength in the  $C_{60}$  molecule from the VED.



**Figure 4.** VED distribution of  $C_{60}$  fullerene: (a) Surface plot; (b) Sectional view of the  $(1 \ 1 \ 1)$  plane. The (i) and (iii) bonds correspond to the single bonds, which are on the regular pentagons. The (ii) bond corresponds to the double bond, which is shared by two hexagons.

## 3.3. $(MV)I_2$

In (MV)I<sub>2</sub> (space group:  $P2_1/c$ ) [26], the valence of an MV molecule is 2+ because of two I<sup>-</sup> ions. The crystal structure of (MV)I<sub>2</sub> and the molecular structure of MV<sup>2+</sup> are shown in Figure 5a,b, respectively. We performed the structural analysis and CDFS analysis of (MV)I<sub>2</sub> at 100 K. Figure 5d shows the VED of an  $MV^{2+}$  molecule, in which H, C, and N atoms have  $1s^1$ ,  $2s^22p^2$ , and  $2s^22p^3$  valence electrons, respectively. Although C and N<sup>+</sup> have the same number of valence electrons, the distribution states of valence electrons on the C and N atoms in the  $MV^{2+}$  molecule are quite different from each other. The ED around C is spatially spread, whereas that around N<sup>+</sup> is localized on the atom. This result corresponds to the difference in electronegativities between the C and N atoms, where the N atoms are more electronegative than the C atoms. Furthermore, there is a difference in the EDs around the two C atoms bonded to N in the six-membered ring of the MV<sup>2+</sup> molecule. The ED around the C(1) atoms close to the I<sup>-</sup> anions (surrounded by red dotted circles) on the MV<sup>2+</sup> molecular plane, which is in the direction of the hydrogen bond, is lower than that of the C(2) atoms located at the opposite side. This result suggests that the anisotropic VED distribution on the MV<sup>2+</sup> molecule is realized by the anisotropic electrostatic interactions with the surrounding the I<sup>-</sup> ions. A CDFS analysis directly visualized the distribution state of complicated molecular orbitals composed of different types of atoms.

## 3.4. $(TMTTF)_2 X$

Finally, we applied the CDFS analysis to quasi-1D molecular conductors (TMTTF)<sub>2</sub>X [27], which shows various electronic properties in the pressure–temperature phase diagram [28–31]. Figure 6a,b shows the crystal structure of (TMTTF)<sub>2</sub>PF<sub>6</sub> and the molecular structure of TMTTF, respectively. For the charge ordering phase transition of (TMTTF)<sub>2</sub>PF<sub>6</sub> ( $T_{CO} \sim 67$  K) at ambient pressure, although responses associated with the charge ordering are confirmed by the dielectric constant [32,33], NMR [34,35], ESR [36], infrared, and Raman spectroscopies [37,38], no evidence of charge ordering has been observed from the crystal structure [39,40]. Thus, this transition from the dimer Mott phase to the charge ordering phase (Figure 6c), which is associated with the lack of an inversion center, has been called a mysterious 'structureless transition' [41–43]. We investigated the crystal structure and VED distribution of the charge ordering phase in (TMTTF)<sub>2</sub>PF<sub>6</sub> using synchrotron XRD [9].



**Figure 5.** (a) Crystal structure of  $(MV)I_2$ ; (b) Molecular structure of  $MV^{2+}$ ; (c) Relationship between a  $MV^{2+}$  molecule and surrounding I<sup>-</sup> ions. There is an inversion center at the central C–C bond in the  $MV^{2+}$  molecule. The least square (LS) plane, on which the central six C atoms are located, is shown in green. The I<sup>-</sup> ions surrounded by the red dotted circles exist near the green plane. (d) VED distribution of the  $MV^{2+}$  molecule. This density plane corresponds to the green plane in (c). The orientations of the  $MV^{2+}$  molecules are the same between (c,d).



**Figure 6.** (a) Crystal structure of  $(TMTTF)_2PF_6$ ; (b) Molecular structure of a TMTTF; (c) Schematic configuration of the dimer Mott and charge ordering (CO) phases; (d,e) Bond length in the (d) hole-rich and (e) hole-poor TMTTF molecules at 30 K in the charge ordering phase of  $(TMTTF)_2PF_6$ . The red (blue) values indicate that the bonds are shorter (longer) than the others at the same positions. The black values indicate that bonds at the same position are consistent within the error range.

The precise structural parameters at 30 K in the charge ordering phase are obtained by a high-angle analysis. Figure 6d, e shows the bond length in the hole-rich and hole-poor TMTTF molecules at 30 K, respectively. The C=C bonds at the center and both sides in the hole-rich molecule are longer than those in the hole-poor molecule. The central C–S bonds in the hole-rich molecule are shorter than those in the hole-poor molecule. These results correctly reflect the tendency of the charge ordering state in the TMTTF dimer. The amount of charge transfer  $\delta_{co}$  is estimated from the bond length in the TMTTF molecule. Two types of formulas, q = -15.55 + 20.42r (set 1) and q = -26.88 + 34.98r (set 2), are given for empirically calculating the valence of a TMTTF molecule in [44]. Here, q is the valence of the TMTTF, and r(=a/b) is a ratio of the central (a) C=C bond and (b) C–S bonds length. The amount of charge transfer  $\delta_{co} = (q_{hole-poor} - q_{hole-rich})/2$ . By using these formulas,  $\delta_{co} = 0.10e$  (set 1) and 0.17e (set 2) are obtained from our structural analysis results at 30 K. The difference of the highest occupied molecular orbital levels between the hole-poor and hole-rich TMTTF molecules,  $\sim 21.7$  meV, was confirmed by the extended Hückel calculation [45]. These results

Figure 7a,b shows the VED of the hole-rich and hole-poor TMTTF molecules in the charge ordering phase of (TMTTF)<sub>2</sub>PF<sub>6</sub> obtained from the CDFS analysis. In this case, the valence electrons of H, C, and S constituting the TMTTF molecule correspond to  $1s^1$ ,  $2s^22p^2$ , and  $3s^23p^4$ , respectively. The ED corresponding to the bonding orbital on the C=C bonds and the node of ED corresponding to the antibonding orbital on the C=S bonds are clearly shown. Moreover, the ED reflecting the isotropic *s* orbitals is observed on the S and C atoms of the methyl groups. Almost no difference is observed between the appearance in the two VED distributions (Figure 7a,b), because the amount of charge transfer ( $\delta_{co} \leq 0.5e$ ) is too small compared to the number of valence electrons of a TMTTF molecule (64*e*). Therefore, we compared the number of valence electrons between the two molecules in the dimer. By comparing the number of valence electrons in the atomic basin of the respective atoms in the TMTTF molecule calculated by Bader's topological analysis [46], the amount of charge transfer was determined as  $\delta_{co} = 0.10e$  [9], which is consistent with the estimation from the bond length ( $\delta_{co} = 0.10e$ ) (set 1), from the Raman ( $\delta_{co} = 0.055e$  [38]), from the infrared ( $\delta_{co} = 0.075e$  [31]), and from the NMR spectroscopies ( $\delta_{co} = 0.14e$  [35]).

show that our crystal structural analysis revealed the charge ordering state in (TMTTF)<sub>2</sub>PF<sub>6</sub>.

To investigate the intramolecular degrees of freedom, we focus on  $(TMTTF)_2AsF_6$ , which has the common crystal structure  $(TMTTF)_2PF_6$  and undergoes a charge ordering phase transition at  $T_{CO} \sim 100 \text{ K}$  [47]. A larger charge transfer in the dimer than that of  $(TMTTF)_2PF_6$  was confirmed in the charge ordering phase of  $(TMTTF)_2AsF_6$  by the Raman ( $\delta_{co} = 0.09e$  [38]), infrared ( $\delta_{co} = 0.105e$  [31]), and NMR spectroscopies ( $\delta_{co} = 0.25e$  [48],  $\delta_{co} = 0.17e$  [49]). We investigated whether the difference in the amount of charge transfer affects the VED distribution of the TMTTF molecule. As a result of the high-angle analysis of  $(TMTTF)_2AsF_6$  at 30 K,  $\delta_{co} = 0.34e$  (set 1), which is larger than that of  $X = PF_6$ , is determined from the bond lengths in the TMTTF molecules using the formulas in [44]. This tendency is consistent with those described in previous reports of  $X = PF_6$  and  $AsF_6$  [31,35,38,48,49].

Figure 7c,d shows the VED of the hole-rich and hole-poor TMTTF molecules in the charge ordering phase of  $(TMTTF)_2AsF_6$  obtained from the CDFS analysis, respectively. Almost no difference is observed in the appearance between the hole-rich and hole-poor TMTTF molecules in  $X = AsF_6$ , and the VED distributions of  $X = AsF_6$  are also approximately identical to those of  $X = PF_6$ . In this case, the difference in the magnitude of the absolute value of the ED between  $X = PF_6$  and  $AsF_6$  is of little significance because the CDFS analysis is based on the inverse Fourier transform of finite data (Equation (7)). However, when calculating the amount of the charge transfer in the dimer from the VED of  $X = AsF_6$ , the charge transfer  $\delta_{co} = 0.43e$  is obtained, which is larger than that of  $X = PF_6$ . This tendency is consistent with that in our structural analysis.



**Figure 7.** (**a**–**d**) VED distribution of hole-rich and hole-poor TMTTF molecules of  $(TMTTF)_2PF_6$  and  $(TMTTF)_2AsF_6$  on LS planes, respectively. The LS planes are defined by the central two C and four S atoms of the TMTTF molecules. (**e**) H–F distances of 2.7 Å or less in the hole-rich TMTTF molecule of  $(TMTTF)_2AsF_6$ . The orientations of the TMTTF molecules are the same between (**c**,**e**). (**f**) Charge ordering patterns of hole-rich and hole-poor TMTTF molecules in  $(TMTTF)_2X$  ( $X = PF_6$  and  $AsF_6$ ), which indicate a 2D Wigner crystal state. The region surrounded by the dotted square shows a TMTTF molecule dimer.

The importance of H–F interactions between the methyl group in the TMTTF molecule and *X* anions is pointed out in this system [50]. Thus, we investigated the distance between hydrogen in the methyl group and fluorine in the anion. Figure 7e shows the H–F distances of 2.7 Å or less in the hole-rich TMTTF molecule. In this regard, we focused on the anisotropy of the VED distribution in the TMTTF molecule in  $X = AsF_6$  (Figure 7c). The VED is concentrated around the methyl groups, but there seems to be no correlation between the distribution state and H–F distances. This tendency is the same for the hole-poor TMTTF in  $X = AsF_6$  (Figure 7d) and for the hole-rich and hole-poor TMTTF in  $X = PF_6$  (Figure 7a,b). Therefore, no clear effect of closed-shell anions was confirmed from the VED distribution of TMTTF.

From the above results, we directly revealed that the spatial charge ordering pattern formed a 2D Wigner crystal state (Figure 7f) from the molecular structure and VED distribution in the charge ordering phase in  $(TMTTF)_2X$  ( $X = PF_6$  and  $AsF_6$ ). This pattern is also consistent with previous ESR experiment [36] and theoretical expectations [51–53].

### 4. Conclusions

We succeeded in directly observing the VED distribution of several molecular materials, i.e., diamond,  $C_{60}$  fullerene, (MV)I<sub>2</sub>, and (TMTTF)<sub>2</sub>X, using synchrotron XRD and the CDFS method. When a molecule is formed by bonds between atoms, various interactions work depending on the shapes and energy levels of the hybridized orbitals. As a result, even molecules with relatively simple structures produce complex molecular orbitals. Therefore, it is difficult to observe the whole picture of molecular orbitals with existing experimental methods. On the other hand, because the CDFS method using synchrotron XRD can directly observe the distribution state of valence electrons occupying the reconstructed molecular orbitals in a real space, it is possible to take an approach which differs from the existing methods for the study of molecular substances. Furthermore, the VED distribution obtained from the CDFS analysis corresponds to the square of the wave function, which provides essential information for quantum chemical and first-principles calculations. In fact, with complementary study of the CDFS analysis and first-principles calculations in transition metal oxides, we succeeded in clarifying the whole orbital state formed by the localized 3*d* orbitals on an atom and the metal–ligand hybridized orbitals [10]. The research methods we propose may signal a breakthrough in the study of the orbital states in materials.

**Author Contributions:** S.K. and H.S. designed and coordinated this study. R.K., T.N. (Toshio Naito) and T.N. (Toshikazu Nakamura) synthesized the samples. S.K., Y.H. and H.S. performed the XRD experiment; S.K. and Y.H. analyzed the XRD data. S.K. and H.S. wrote the manuscript. All authors have read and agreed to the published version of the manuscript.

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#### Appendix A

CCDC 2036797 contains the supplemental crystallographic data of  $C_{60}$  fullerene at 30 K. The data is provided free of charge by The Cambridge Crystallographic Data Centre [54].

CCDC Deposit Number	2036797
Temperature (K)	30
Wavelength (Å)	0.35044
Space group	Pa3
a (Å)	14.0279(6)
V (Å <sup>3</sup> )	2760.4(2)
Z	24
F (000)	1440
$(\sin\theta/\lambda)_{Max}$ (Å <sup>-1</sup> )	1.11
N <sub>Total,obs</sub>	65,092
$N_{\rm Unique,obs}$	4920
Average redundancy	11.4
Completeness (%)	100
# of reflections ( $I > 1.5\sigma$ )	5424
$R (I > 1.5\sigma)$	4.36
$wR \ (I > 1.5\sigma)$	3.73
$GOF(I > 1.5\sigma)$	1.21

**Table A1.** Summary of the crystallographic data of C<sub>60</sub>.

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