CHAPTER 7. PERIODIC HARTREE-FOCK AND HYBRID DENSITY FUNCTIONAL CALCULATIONS ON THE METALLIC AND THE INSULATING PHASE OF (EDO-TTF)$_2$PF$_6$.\textsuperscript{11}

All-electron, periodic Hartree-Fock and hybrid density functional calculations were performed on the insulating and the conducting phase of (EDO-TTF)$_2$PF$_6$. Electronic properties, such as the electronic band structure, the density of states, and the Fermi surface are discussed in relation to the metal-insulator transition in this material. The nature of conduction is confirmed in both phases from their band structures and density of states. The hybrid DFT band gaps are in good agreement with experiment. Interactions are discussed on the basis of band dispersion in the inter-stack, intra-stack and inter-sheet directions. We discuss the phase transition in terms of the Peierls mechanism and our results fully support this view.

![Figure 42: Schematic representation of the unit cell at high temperature (left) and the calculated band structure and Fermi surface (right).](image)

\textsuperscript{11} The research in this chapter was published in 2015 in Physical Chemistry Chemical Physics: “Periodic H–F and hybrid density functional calculations on the metallic and the insulating phase of (EDO-TTF)$_2$PF$_6$”, G.J. Linker, P.H.M. van Loosdrecht, P.Th van Duijnen, R. Broer, Phys. Chem. Chem. Phys. 17 (2015), 30371-30377
7.1 Introduction

The highly conductive (EDO-TTF)$_2$PF$_6$ system becomes an insulator when cooled below room temperature. This metal-insulator (M-I) transition is thought to be the result of several phenomena arising from instabilities in the system: dimerisation, charge ordering (CO) with an associated geometrical ordering (chapter 5) and molecular flexibility (chapter 4). There is ample experimental evidence on these instabilities [109, 119, 146, 150] however, as of yet the mechanism of the M-I transition remains unclear.

It is reasonable to expect that many of the electronic properties of (EDO-TTF)$_2$PF$_6$ are determined by the π-electrons at the Fermi level. Therefore, the determination of the π-electron bands and of the Fermi surface is essential to clarify their origin. The small overlap of the π-orbitals of adjacent EDO-TTF molecules in the stack confines the conduction to a narrow conduction channel. The flexibility of the EDO-TTF molecules (chapter 4 and 5) causes softness of the lattice which, in turn, causes electrons to couple strongly to lattice vibrations [162]. This makes the properties of the material susceptible to external stimuli such as temperature, pressure [120] and light [114]. One of the most intriguing properties of (EDO-TTF)$_2$PF$_6$ is the ultra-fast and highly efficient photo induced phase transition from the insulating to a metallic state [114].

Tight-binding calculations by Ota et al. [107] on the metallic phase of the (EDO-TTF)$_2$AsF$_6$ salt show relatively flat bands and show a Fermi surface which features two separate sheets, a characteristic of a quasi-one-dimensional (Q1D) conductor (section 3.2.2). Sharihata et al. [161] found a metal-metal phase transition at around 230 K in a related system, dimethyl substituted EDO-TTF, (DMEDO-TTF)$_2$PF$_6$, in which the stacking between 2D sheets changes from skew to nearly perpendicular. In that system, there are interactions between anions and the methyl groups in addition to anion-EDO group interactions. The system can be viewed as being halfway between the Fabre salts in which there are no anion-EDO interactions, and (EDO-TTF)$_2$PF$_6$ in which there are no anion-methyl interactions. The tight-binding band structure of (DMEDO-TTF)$_2$PF$_6$ at high temperature resembles that of (EDO-TTF)$_2$AsF$_6$.

The aim of the work in this chapter is to understand the connection between differences in physical properties of the LT and the HT phase, and the differences in the electronic structure. Analysis of the band dispersion can provide confirmation of the Q1D nature, and can provide insight into the intermolecular interactions in the crystal. We first analyse the band dispersion in the X-ray crystal structures. Next, we analyse the band dispersion along the three main vectors of translational symmetry. Intermolecular interactions are studied by making scans in the three main molecular directions in the crystals. We provide a basis for the work in chapter 8 about the mechanism of the M-I transition. To this end, the results of all-electron periodic calculations are presented. We used Hartree-Fock (HF) theory as well as hybrid density functional theory (DFT) in which some electron correlation is taken into account. The functionals B3LYP and PBE0 [82] were used. We used spin-restricted theory, which we found to be the best ansatz for the ground state in chapter 6.

The discussion of the band structure of (EDO-TTF)$_2$PF$_6$ in this chapter is placed in context of other important materials in the materials class in the supplements of this thesis. In supplement A and B, I respectively discuss the band structures that I obtained for TTF-TCNQ and for the Bechgaard salt (TMTSF)$_2$PF$_6$. The electronic bands of TTF-TCNQ are different from that in (EDO-TTF)$_2$PF$_6$ and I relate that to the overlap of bands that originate from the two different kinds molecular stacks in TTF-TCNQ. The band structure of (TMTSF)$_2$PF$_6$ is similar to that of (EDO-TTF)$_2$PF$_6$ and we ascribe the different physics of (TMTSF)$_2$PF$_6$ to the more 2D nature of the interactions.
7.2 Computational details

Periodic, spin-restricted *ab initio* calculations were performed, in which the single-particle periodic wavefunctions are built from Bloch functions that are defined in terms of atomic basis functions. RHF calculations were used to connect the crystal calculations to the cluster calculations on the unit cell. Hybrid DFT was employed to account for some electron correlation. We chose B3LYP, which contains 20% Fock exchange, because our experience with its description of single EDO-TTF molecules is good (chapter 5). Calculated band gaps are expected to be influenced by the percentage of Fock exchange used. We therefore chose to also perform calculations with the PBE0 hybrid functional [82], which contains 25% Fock exchange.

In the calculations the X-ray crystal structures of Ota, *et al.* [99] were used. For the crystallographic parameters we refer to appendix E. Hydrogen positions were obtained from single molecule cluster RHF calculations. The centro-symmetric lattices are triclinic and have the $P1_1$ space group. The structure of the insulating and the metallic phases was determined at 260 K and at 293 K respectively. The LT unit cell contains four EDO-TTF molecules whereas the HT unit cell contains two (HT2). For easier comparison with the tetramer LT crystal the HT unit cell was doubled in the 1D-columnar direction to make the HT unit cell also contain four EDO-TTF molecules. We refer to the doubled unit cell as HT or HT4 (appendix E).

The basis set used is 6-21G [56]. Linear dependencies are experienced when using basis sets with more diffuse functions, such as 6-31G. Mulliken charge analysis [11] in a molecule in the crystalline environment gives similar results to calculations on the monomer in vacuum with larger basis sets (chapter 5): the positive charges in EDO-TTF$^+$ molecules are located predominantly on the sulphur atoms. Also a geometry optimisation of the unit cell contents, in which the lattice parameters remain static, shows that the bent and planar molecular geometries are reproduced. In chapter 4, we established that the polarisability of the sulphur atoms must be adequately described in order to reproduce the molecular geometry. We conclude that the 6-21G basis set gives a well enough representation of the system.

The Crystal computer code [115] was used. The level of accuracy in evaluating the Coulomb and Hartree–Fock exchange series is controlled by five parameters in Crystal: ITOL1-5 [139] for which the values 9, 9, 9, 9 and 18 are used. Pack-Monkhorst and Gilat net grids were used with a shrinking factor of 8 to sample k-space. Molecular charges were obtained from Mulliken population analysis. Fermi surfaces and Bloch orbitals were created using DL Visualise [93].

The HF cluster calculations on a single HT4 unit cell were performed using the MOLCAS code [105], using the 6-31G** basis set.

7.3 Cluster calculations on one unit cell in vacuum

The electronic structure of the HT unit cell cluster in isolation is used as a reference for discussing the properties of the crystal. First, the neutral tetramer is considered: (EDO-TTF)₄. The highest four occupied HF orbitals of the ground state are simply linear combinations of the HOMOs of the constituent closed shell EDO-TTF molecules (Figure 43). The HOMO-3 is the fully bonding combination in which there are no nodal planes between the molecular HOMOs. Each subsequent tetramer orbital has more nodal planes and is more anti-bonding. The HOMO of the tetramer is the fully anti-bonding combination of the molecular HOMOs.
Next, charge transfer is allowed by adding two electron accepting PF₆ molecules to the EDO-TTF tetramer stack, i.e. the (EDO-TTF)₄(PF₆)₂ unit cell is created. The PF₆ molecules essentially remove two electrons from the fully anti-bonding HOMO of the EDO-TTF tetramer, now becoming the LUMO of the unit cell. The PF₆ molecular orbitals are lower in energy and they hardly mix with the frontier orbitals of the EDO-TTF stack. In the crystal, it is expected that the lowest conduction band and highest three valence bands are similar in nature to the MOs shown here. A detailed discussion on the electronic structure of the unit cell cluster is presented in chapter 6.

7.4 Band structure and density of states

Band structures and density of states (DOS) were computed. Three different scans through the Brillouin zone (BZ) were made for the LT and HT crystals. The main purpose of the first scan is to make the connection of the bands to the cluster HF MOs. We examine the band dispersion in the main directions in the crystal structures (Figure 44). These band dispersion plots are expected to be different because the cell parameters are different for the two crystals. A second scan was performed to study the band dispersion in the main directions of translational symmetry (Figure 45). The orientation of the molecules is not identical in the two crystals. To enable a better analysis of the intermolecular interactions a third scan was performed in the main molecular directions.

The band structure and DOS calculated for the experimental X-ray crystal structures is shown in Figure 44. Our B3LYP band structures are nearly identical to the PBE0 results, which shows that our results are not affected by our choice of using 20% or 25% of Fock exchange in the functional. Therefore, only the HF and PBE0 results are presented. In the band structures, the lowest conduction band is labelled $\phi_1$, the highest valence bands $\phi_2-\phi_4$. From atom projected DOS it was
concluded, as predicted from our cluster calculations, that these four band only have EDO-TTF character and have negligible contributions from PF6. The conducting nature of the crystals is confirmed. The LT crystal exhibits a valence-conduction band gap. Also the 0110 CO was reproduced. The charge distribution in the HT crystal is confirmed to be $\frac{1}{3} \frac{1}{3} \frac{1}{3}$ and with a partially filled valence it is a band conductor. Using RHF we also found for the HT crystal an insulating state 5 kcal/mol lower in energy with a 0110 CO. This result highlights the CO instability. The well-known overestimation of the HF band gap is apparent in the band structure of the insulating LT crystal. The bands are relatively flat (section 3.2.2). The smaller band widths in the LT crystal indicate smaller interactions between unit cells than in the HT crystal. For example, in Figure 44, the band width of the RHF valence band is 40 kcal/mol (6.6 kcal/mol) in the RT (LT) crystal. The band structures obtained with HF and PBE0 are in qualitative agreement. The HF bands show more dispersion. The amount of dispersion in the PBE0 bands compares well to that in the tight-binding band structures of (EDO-TTF)$_2$AsF$_6$ and also to those of (DMEDO-TTF)$_2$PF$_6$ as mentioned in the introduction. PBE0 is our functional of choice for the remainder of this chapter. The band gap compares well to experiment (fide infra). For a better comparison of the band dispersion we use, in the next sections, transformed unit cells for our analysis in which the cell parameters are comparable.

7.5 Dispersion along the main translational directions

The distinctions in the band dispersion of the four frontier crystal orbitals were analysed by scanning along the main three directions of translational symmetry (Figure 45). To enable this analysis, the original lattice was transformed to a basis $(a, b, c)$ in which $b$ is the 1D stacking vector, $(a, b)$ defines the 2D sheet and $c$ is the intra-sheet translational vector. In the LT crystal, the transformation is: $(a, b, c) = (c' - a', b' - a', -a')$ and for the HT crystal it is: $(a, b, c) = (a' + c', b', a')$, where the original basis vectors are accentuated.

The transformed unit cells contain one EDO-TTF tetramer stack (Figure 45c,g). The resulting band structures are shown in Figure 45a,d. Please note that $\varphi_1$ ($\varphi_2$) is partially occupied (unoccupied) in the HT phase. The Bloch orbitals of $\varphi_1$ and $\varphi_2$ are similar to the MOs in the unit cell clusters (Figure 43). At the gamma point, the amplitudes on each monomer are equal. However at the edge of the BZ in the $b^*$ direction, $\varphi_1$ is more localised on the inner EDO-TTF molecules and $\varphi_2$ more on the outer molecules. This is the case in both the LT and HT crystals. This leads to the view that dimers in the HT phase are more anti-bonding compared to dimers in the LT phase. In going from HT to LT, the bands $\varphi_1$ and $\varphi_2$ become separated, a band gap forms, and the dimers become more bonding. The transformation of the unit cells makes the comparison of the band dispersion in the directions of translational symmetry possible in both crystals. The similarities between the band structures are apparent. In both crystals, there is no visible dispersion in the k-domains $\Gamma$-X and $Z$-$U$: there negligible dispersion in the $a^*$ direction. The dispersion in $c^*$ direction is opposite for $\varphi_2$ and $\varphi_3$. From $\Gamma$ to $Z$ the dispersion in the LT (HT) crystal is towards higher (lower) energy. The strongest band dispersion is found in the $b^*$ direction, as shown in the k-domains $X$-$V$, $V$-$\Gamma$, $U$-$R$ and $R$-$\Gamma$. The LT band structure shows that the dispersion in the $b^*$ direction of $\varphi_1$ is toward lower energy and that of $\varphi_2$ toward higher energy. In the HT crystal, the dispersion is larger and both bands become degenerate at $V$ and $R$. At $V$ ($R$), the $\varphi_2$ ($\varphi_1$) band is located above (below) the Fermi level. The valence (conduction) band becomes partly unoccupied (occupied) and both bands are overlapping in energy. This is reflected in the DOS. Similarly, at lower energy the $\varphi_3$ and $\varphi_4$ bands become degenerate at $V$ and $R$. The three separate energy ranges in the DOS at LT merge into one range at HT. The large peaks in the DOS occur at energies where the bands show a maximum or minimum; they are van Hove singularities.
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7.6 Dispersion in molecular directions

The orientation of the EDO-TTF molecules with respect to the \( \mathbf{b} \) axis is different in the two crystals. For a better study of the intermolecular interactions a third band dispersion diagram was made based on the interesting molecular directions, \( \text{i.e.} \) along the three principal axes of inertia of the (planar) EDO-TTF molecules. We denoted these directions \( \{\mathbf{u}, \mathbf{v}, \mathbf{w}\} \) (Figure 46 and Table 21 in appendix E). Direction \( \mathbf{u} \) corresponds to the 1D EDO-TTF stacking direction, \( \mathbf{v} \) is the long molecular axis. Vectors \( \mathbf{u} \) and \( \mathbf{v} \) define the 2D sheet. The third principal axis, vector \( \mathbf{w} \), points in the inter-sheet direction. In these directions, we scan from the \( \Gamma \) point to the BZ edge, essentially scanning through low energy levels towards the energies around the Fermi level. Please note that these molecular directions \( \{\mathbf{u}, \mathbf{v}, \mathbf{w}\} \) are not coinciding precisely with the translational vectors \( \{\mathbf{b}, \mathbf{a}, \mathbf{c}\} \). We used the crystallographic unit cells in this study.

Figure 47 clearly shows that most interaction, and therefore most band dispersion, occurs in the EDO-TTF stacking direction \( \mathbf{u} \). The extremes in the band structure toward the BZ boundary is an indication that vectors \( \mathbf{u} \) and \( \mathbf{b}^* \) are not precisely in the same direction. Intermolecular interactions can be quantified by means of the hopping integral \( t \) from the tight-binding model for a one-dimensional chain. In this model, the width of the band dispersion \( \Delta \) is related to \( t \) as \( \Delta = 4|t| \). For example,
from width $\Delta_2=0.71$ eV of the valence band $\varphi_2$, we obtain $t_2=0.18$ eV. Because $\Delta u > \Delta v > \Delta w$ for the bands shown, it follows that $|t_u| > |t_v| > |t_w|$. Therefore, the conductivity is expected to be predominant in the $u$ direction. The Q1D conduction nature is also visible from the HT band dispersion diagram in Figure 47. The highest two valence bands, $\varphi_2$ and $\varphi_2$ are partially overlapping approximately at the Fermi energy. These bands span the energy domain [-3.02, -4.04 eV], the domain of overlap is [-3.54, -3.32 eV], and $E_F=-3.44$ eV. The intersection, however, is only visible in the stacking direction $u$. In the other two directions, these bands are not intersecting with the Fermi level. Therefore, strictly reasoning within band theory, the crystal is an insulator in these directions.

Figure 47: PBE0 band structure from $\Gamma$ to the directions {u,v,w} and DOS diagrams in the LT, HT4 and the HT2 crystal. Fermi surface in the HT4 and HT2 crystals (see text). The arrow indicates the nesting vector.

In the insulating LT crystal, in Figure 47 it is observed that a band gap formed: a Peierls gap. The dispersion of the LT bands $\varphi_1$ and $\varphi_2$ in the $u$ direction is less than that in the HT crystal. Where these bands overlap in the HT crystal, in the LT crystal they are separated by 0.40 eV. From the band structure obtained with the HT2 unit cell we see clearly that one needs to consider a unit cell doubling for a band gap to form. The Fermi level in the HT2 crystal intersects roughly midway through the highest valence band. The bands fold when doubling the number of molecules creating the HT4 (HT) unit cell. The Fermi level is at the intersection of these bands. The deformations present in the LT lattice, the slight dimerisation of dimers, and perhaps also the geometrical deformation of half of the near planar EDO-TTF molecules to a bent geometry are the cause for the Peierls gap to form.

Analysis of Fermi surfaces shows also that it is necessary to consider the HT4 crystal to study the phase change. We note that the shape of the Fermi surface (HT2 surface in Figure 47) confirms the Q1D nature of the conduction. It consists of two separated sheets that are slightly warped. A Fermi surface consisting of separated sheets is an indication of one-dimensionality (3.2.2) and the slight warping indicates small 2D conductivity. The nesting vector $\mathbf{n}=2\mathbf{k}_F$, indicated by the arrow, is connecting the two sheets: $\varepsilon(k)=\varepsilon(k-n)$. In this crystal, the Fermi surface has contributions from $\varphi_1$ and $\varphi_2$. The Fermi surface is located at the edge of the BZ. To indicate the overlapping bands extend further into the BZ, the energy surfaces are also plotted at the extremes of the overlapping domain.
This region in k-space where both bands overlap is rather large. Because crystal orbital $\varphi_2$ is more bonding than $\varphi_1$, the band overlap may provide the conditions for a lowering in total energy when the lattice distorts toward a more bonding dimer at LT. The surface of $\varphi_1$ may be pushed out of the first BZ, $\varphi_2$ may be lowered in energy and become fully occupied. Or, reasoned the other way around, the deformation of the lattice may be due to interactions of the electrons. In the region of overlap, the bands mix to form a bonding and anti-bonding combination. The energy gap between them would be reflecting the strength of the interaction. In summary, the phase transition can best be analysed using the HT4 unit cell containing four molecules.

Although we provide no direct proof for the Peierls effect, it is reasonable to assume with these results that these deformations of the lattice can stabilise the electrons in the stacking direction, with the consequence that the valence band is lowered in energy. The Peierls gap has formed.

### 7.7 Band gap and the Fermi level

Different computational methods lead to different band gaps $E_g$ of the LT crystal and Fermi energies $E_F$ of the HT crystal. The HF band gap of the LT crystal is 3.38 eV and the hybrid DFT band gap is 0.40 eV (0.30 eV) using the PBE0 (B3LYP) functional (Table 13). Experimentally the band gap was determined at 0.35 eV [150]. It is generally known that the HF band gap is overestimated and that the band gap obtained with traditional DFT underestimates it. HF (DFT) gives rise to too localised (delocalised) wavefunctions generally. The success of hybrid-DFT functionals is sometimes attributed to the mixing in of the HF exchange which drives the conduction band to higher energies. Our hybrid DFT band gaps compare well to the experiment. The Fermi energy $E_F$ was calculated at -3.52, -3.16 and -3.44 eV using HF, B3LYP and PBE0 respectively.

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<th>HF</th>
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<td>$E_g^{LT}$</td>
<td>3.38</td>
<td>0.30</td>
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<td>$E_F^{HT}$</td>
<td>-3.52</td>
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Table 13: Band gap $E_g$ and Fermi energy $E_F$ of the crystals at LT and HT determined by the methods HF, B3LYP and PBE0.

### 7.8 Conclusions and discussion

The band structure and density of states of the low and high temperature phase of (EDO-TTF)$_2$PF$_6$ have been obtained using periodic HF and hybrid density functional calculations. Our results confirm the insulating (at LT) and conducting (at HT) nature. Their respective CO is confirmed to be 0110 and $\frac{3}{4}\frac{3}{4}\frac{1}{2}\frac{1}{2}$ with the side note that an insulating 0110 ordered RHF solution was also found at almost the same energy at HT. At LT, the 0110 CO corresponds to a geometrical ordering of BPPB and at HT the $\frac{3}{4}\frac{3}{4}\frac{1}{2}\frac{1}{2}$ charge distribution corresponds to PPPP. In chapter 8 we show both phases to be connected by molecular deformations.

The electronic properties, obtained with the hybrid functionals, were found to be in good agreement with experiment, and also with theoretical/computational studies on related materials. The frontier bands originate from EDO-TTF molecules. The recognition that the lowest conduction band is the fully anti-bonding combination of the HOMOs of the neutral EDO-TTF molecules, leads to the realisation that its partial population at HT reduces the bonding between EDO-TTF$^+$ dimers. The analysis of the crystal in terms of interacting EDO-TTF$^+$ dimers is fruitful: (EDO-TTF$^+$)$_2$(PF$_6^-$)$_2$. The view in terms of EDO-TTF$^+$ dimers arises as follows. The geometrical ordering at LT is associated with the localisation of charge on the planar molecules, one in each dimer. The two cation dimers in the unit cell interact, and their interplay forms the basis for the phase transition (chapter 8). Compared to the situation at HT, the stronger bonding of the cation dimers at LT lowers the valence band and it raises the conduction band. A gap separates the fully anti-bonding conduction band.
from the more bonding valence band. The small cost for making the geometrical deformations of half of the EDO-TTF molecules is likely to be compensated by the electronic stabilisation of the cationic dimers. In this view, the transition is a Peierls transition.

The PF$_6^-$ anions are closed shell entities. Their MOs do not mix into the frontier bands and the anions are spectator molecules in this sense. The anion disorder instability of the system may be more electrostatic in nature or stem from the anion contribution in vibrational modes. The system therefore consists of stacks of cations in which the conduction takes place, and stacks of anions that separate the conduction stacks.

The dispersion of the bands shows that most interactions occur in one dimension, namely the EDO-TTF stacking direction. Interactions in the intra-sheet direction are smaller, and the inter-sheet interactions are yet smaller. Therefore, the conduction is confirmed to be quasi one-dimensional. This is also confirmed from the shape of the Fermi surface. It consists of two separate sheets, a signature of a 1D conductor, and the warping of the sheets indicate that interactions in a second direction are not negligible.

At high temperatures, the band dispersion is such that the conduction and valence band overlap. The Fermi level is positioned in the middle of this region of overlap. The Fermi surface satisfies a nesting condition: the two sheets of the Fermi surface are connected by a $2\mathbf{k}$ nesting vector. It connects points on the sheets where $\epsilon(\mathbf{k})=\epsilon(-\mathbf{k})$. It is well known that this condition causes the conducting phase to be unstable with respect to the formation of the CO [146]. Small geometrical deformations may shift the bands to remove the region of overlap. This will destroy the Fermi surface and break the nesting condition. The CO phase forms and the system becomes an insulator. In chapter 8 it is shown that this deformation is the (EDO-TTF)$_2$ dimerising displacement.