Quantum chemical studies of the physics around the metal-insulator transition in (EDOTTF)2PF6
Linker, Gerrit-Jan

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
2016

Link to publication in University of Groningen/UMCG research database

Citation for published version (APA):
Linker, G-J. (2016). Quantum chemical studies of the physics around the metal-insulator transition in (EDOTTF)2PF6. [Groningen]: Rijksuniversiteit Groningen.

Copyright
Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

Take-down policy
If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): http://www.rug.nl/research/portal. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.
SUPPLEMENT A. The band structure of TTF-TCNQ

In this section, I discuss the band structure of TTF-TCNQ, a charge transfer salt with tetrathiafulvalene (TTF) electron donor and tetracyanoquinodimethane (TCNQ) electron acceptor molecules. Single-particle crystal orbitals and electronic band structures were calculated for the periodic TTF-TCNQ system using DFT and HF theory. Similar to (EDO-TTF)$_2$PF$_6$, the band structure of TTF-TCNQ shows a pseudo-gap indicating Q1D character of the electric conduction in the high temperature phase. The nature of the electronic bands of TTF-TCNQ is very different however. The band structure are discussed in the light of the material physics.

![Figure 57: Ball-stick diagram of (left) tetrathiafulvalene (TTF) and (right) tetracyano-quinodimethane (TCNQ).](image)

An introduction into TTF-TCNQ can be found in section 3.1.1, and for a ball-stick diagram of the molecules I refer to Figure 57. In the following section, I give an account of the known physics of TTF-TCNQ before discussing the calculated electronic band structure of it.

A.1. Physics of TTF-TCNQ

Observation of the change of conductivity and lattice structure with temperature reveals the phase transitions in this system: one at 54 K in the TCNQ stacks, and one at 38 K in the TTF stacks. This suggests that TTF and TCNQ chains behave as decoupled 1D electronic systems.

Around room temperature, the temperature dependence of the conductivity of TTF-TCNQ is like that of a metal: the conductivity increases with decreasing temperature. At very low temperatures, the system undergoes two phase transitions. The room temperature conductivity is $\sigma_{RT} = 0.5 \text{ kS/cm}$ and it increases dramatically to a maximum of $10 \text{ kS/cm}$ at 60 K [31]. A metal-semiconductor transition occurs at 54 K. At this temperature, geometrical distortions cause a $2\vec{a} \times 3.4\vec{b} \times \vec{c}$ super-lattice which is incommensurate with the underlying lattice of the high temperature crystal structure in the $\vec{b}$ stacking direction. Cooling further to below 49 K, the modulation continuously changes to become incommensurate in the $\vec{a}$ direction also, and ends with a discontinuous step at 38 K, to a modulation $4\vec{a} \times 3.4\vec{b} \times \vec{c}$ [28]. Below 38 K, the material is an electrical insulator.

The M-I transition at 54 K is due to Peierls disorder (section 3.2.3) of which the associated lattice deformation is linked to the amount of charge transfer from donor to acceptor molecules. At high temperatures, in the metallic phase, an anomalous dispersion of phonon energies is observed, a so-called Kohn anomaly [34, 33]. The energy of a phonon, a quasi-particle representing a normal mode of lattice vibration, is dependent on the crystal momentum $k$. In TTF-TCNQ, the temperature dependence of the dispersion of the phonon energy $E(k)$ shows an anomalous decrease at $k = 2k_F$, where $k_F$ is the crystal momentum at the Fermi level. The decrease in energy becomes stronger at lower temperatures. It is the onset of the Peierls transition to a CO state in the TCNQ stacks that

---

12 For the conductivity of other TCNQ salts we refer to Metzger [63]
occurs at 54 K. In this CO state, both charged and neutral TCNQ molecules co-exist which changes the band filling (section 3.2.2). The deformation of the lattice in the \( b \) stacking direction relates to \( k_F \) in reciprocal space: 
\[
2k_F = k_b / 3.4 = 0.295k_b \]
[31], where \( (\vec{k}_a, \vec{k}_b, \vec{k}_c) \) are the unit vectors in reciprocal space (section 2.8). This directly links the deformations in the stacking direction to the phase transition. Because \( k_F \) depends on the filling of the conduction band, the partial transfer of 0.59 electrons per molecule [28] is also directly linked to the mechanism of the phase transition.

The Peierls transition at 38 K is thought to involve CO in the TTF stacks while the transition at 54 K, as described above, is thought to involve CO only in the TCNQ stacks. It is suggested that a sliding CO in the TCNQ stacks occurs above 54 K but that it becomes pinned to the lattice at 54 K, causing the phase transition. The \( 2\vec{a} \) periodicity in the direction of alternation of donor and electron acceptor stacks implies that the two TCNQ stacks within the unit cell have anti-phase ordering. At 49 K, also ordering in the TTF stacks sets in and the ordering in the \( \vec{a} \) direction becomes incommensurate.

In the temperature regime between 49 K and 38 K, the COs in the stacks continuously order with respect to each other, locking at 38 K. The observed deformations in the \( \vec{a} \) direction, the direction of donor/acceptor stack alternation, will depend on inter-chain coupling mechanisms [35]. When the CO in both electron donor and acceptor stacks becomes pinned at 38 K, the periodicity \( 4\vec{a} \) resumes commensurability with the lattice. The locking of the CO involves a weak bonding of the charge ordered electron density in both stacks to the lattice. The bonding is overcome at temperatures slightly above 38 K where the charges are free to translate to new positions [31] and hence contribute to total conductivity.

A.2. Band structure calculations and discussion

Using density functional theory (DFT) with the PBE0 functional [82] and using Hartree-Fock (HF), single-particle crystal orbitals and band structures were calculated for the periodic system. Both spin-restricted and spin-unrestricted formalisms were used. I refer to these approaches respectively as DFT, U-DFT, RHF and UHF. The used X-ray crystal structure was obtained for the metallic state by Kistenmacher et al. [27]. For the calculations, the 6-21G basis set [56] and the Crystal [115] software were used. Qualitative atomic charges were calculated using Mulliken population analysis [11]. The Fermi surface was calculated using the DL Visualise software [93].

The band dispersion in the DFT band structure (Figure 58a) is qualitatively in good agreement with angle resolved photo emission spectroscopy [108]. However, the width of the calculated bands is too large by a factor of two approximately. The main characteristics of our band structure also match those obtained with periodic B3LYP [151], plane wave pseudo-potential DFT methods [88, 108], full-potential plane wave DFT method [104], and extended Hückel theory [29]. The calculated frontier bands are shown in Figure 58a. They originate from the TTF HOMO and the TCNQ LUMO. Due to the charge transfer (CT) from TTF electron donors to TCNQ acceptor molecules [24], the HOMO of the molecules become singly occupied. There are four symmetry unique molecules (two of each kind) in the unit cell and each molecule is part of a separate stack of molecules (Figure 4 in section 3.1.1). In the crystal, the four frontier bands originate from these highest four singly occupied molecular orbitals. These electronic bands overlap in energy and form a continuous density of states (DOS). The band conduction originates from the partial occupancy of these bands.
The small band dispersion, and also the character of the electronic bands, demonstrate that the TTF and TCNQ molecular stacks have little interaction. The relatively flat bands\textsuperscript{13} in Figure 58 indicate small intermolecular interactions. The density of states projections show that the two practically degenerate bands have TTF character and that the other two near degenerate bands have TCNQ character. These two sets of bands overlap and, despite of this, the interaction between the different stacks of molecules is not sufficient to significantly shift the bands in energy. The bands show some small avoided crossing.

![Figure 58: Energy dispersion of the frontier electronic bands, and (projected) density of states for TTF-TCNQ obtained from spin-restricted (a) and spin-unrestricted (b) $M_z=0$ BS PBE0 DFT periodic calculations. Symbols X, Γ, Y, Z refer to k-points in the BZ. $E_F$ denotes the Fermi energy.](image)

The one-dimensional (1D) character of the conduction is confirmed: most dispersion stems from interactions in the stacking direction $b$ (from $Γ$ to $Y$). The bands in the $c$ direction (from $Γ$ to $Z$) show little dispersion. No dispersion is visible in direction $a$ (from $Γ$ to $X$). This is very similar to the band structure of (EDO-TTF)$_2$PF$_6$, (Figure 45, section 7.5) which also shows relatively flat bands with dispersion mainly in the stacking direction. Just like (EDO-TTF)$_2$PF$_6$, the band structure of TTF-TCNQ shows a pseudo gap. Only in the stacking direction there is no gap between the electronic bands. The 1D character is also confirmed from the Fermi surface of the two crystal orbitals that intersect the Fermi level (Figure 59).

![Figure 59: Fermi surface of two frontier crystal orbitals of TTF-TCNQ at the upper and lower edge of the Brillouin zone.](image)

Analysis of the electronic bands and the DOS around the Fermi level (Figure 58a) confirm band-conductivity. There is a clear non-zero DOS at and around $E_F$. DOS projections show that the DOS originates both from TTF and TCNQ. Around $E_F$, there is some avoided crossing. An RHF band structure (not shown) has no crossing of the bands. The shape of the RHF valence band corresponds to the DFT band in Figure 58a, however the RHF band structure is gapped. As expected, the TCNQ bands form the RHF conduction bands and they are separated by 2.3 eV from the RHF valence bands that originate from TTF.

\textsuperscript{13} The band dispersion of 1.6 eV (0.06 hartree) of TTF-TCNQ compares to other materials in the following way. The approximate dispersion of the valence band of Ge or GaAs is 3 eV and the dispersion of the conduction band of Al is more than 10 eV (section 3.2.2).
The frontier electronic bands are very different to those in (EDO-TTF)$_2$PF$_6$ (Figure 44 and Figure 45 in chapter 7). In (EDO-TTF)$_2$PF$_6$, the four frontier electronic bands are due to EDO-TTF molecules from the same molecular stack. In (EDO-TTF)$_2$PF$_6$, interactions within the single molecular stack determine the physics of the material. In chapter 7, we interpret the physics in terms of shifts in the dispersion of the bands due to molecular deformations. In TTF-TCNQ, the interpretation of the physics from the band structure is different. When a gap would open due to Peierls disorder in one type of the molecular stacks, the DOS may still be gap-less due to the continuous DOS of the other type of molecular stacks. I see the processes of the CO formation at 54 K and 38 K (3.1.1) in this light. Both are due to Peierls disorder in respectively the TCNQ stacks and in the TTF stacks and above 54 K a Kohn anomaly is observed, which is indicative of a Peierls gap opening.

The band structure (Figure 58b), calculated with spin-unrestricted density functional theory, shows a gap in the β-bands. It has partially occupied α-bands. Using U-DFT, an $M_s=0$ broken spin-symmetry (BS) solution was found at 5 kcal/mol below the spin-restricted DFT solution. Its band structure shows that the degeneracy of α and β-bands is lifted. From the spin projected DOS it can be seen that the β-spin bands shift to above and below $E_F$ for TCNQ and TTF respectively. Only the α-spin bands of both molecules cross $E_F$. The total DOS has a small but non-zero value at $E_F$.

The level of CT appears to be related to the overlap in energy of the highest occupied TTF and TCNQ crystal orbitals. In the absence of band overlap, as in our RHF and BS $M_s=0$ UHF solutions, the molecular CT was calculated as 0.09 electrons. Compared to experiments [41], an incorrect direction of the CT was obtained in these calculations, namely from TCNQ to TTF. The only HF solution in which the direction of CT is correct is in the $M_s=1$ UHF calculation, which shows a CT of 0.34. Its band structure shows overlapping (in energy) TTF and TCNQ bands that are approximately half filled. In all solutions found with DFT and U-DFT, the electronic bands overlap and the direction of the charge transfer is correct: from TTF to TCNQ. In the spin-restricted DFT and U-DFT calculations presented above, a CT of respectively 0.34 and 0.31 from TTF to TCNQ was calculated. Compared to the CT of 0.59, as deduced from diffuse X-ray scattering experiments [41], our calculated values are low.

<table>
<thead>
<tr>
<th>Hartree-Fock</th>
<th>TTF</th>
<th>TCNQ</th>
<th>DFT</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E$ Solution</td>
<td>C/I</td>
<td>CO</td>
<td>SO</td>
</tr>
<tr>
<td>+40 UHF $M_s=1$</td>
<td>C</td>
<td>0.34</td>
<td>0.5</td>
</tr>
<tr>
<td>0 RHF</td>
<td>I</td>
<td>-0.09</td>
<td>0.09</td>
</tr>
<tr>
<td>-4 UHF $M_s=0$ BS</td>
<td>I</td>
<td>-0.09</td>
<td>0.09</td>
</tr>
<tr>
<td>-40 UHF $M_s=1$</td>
<td>I</td>
<td>-0.10</td>
<td>0.10</td>
</tr>
<tr>
<td>-75 UHF $M_s=0$ BS</td>
<td>I</td>
<td>-0.09</td>
<td>0.09</td>
</tr>
</tbody>
</table>

Table 15: Spin-restricted and spin-unrestricted Hartree-Fock (left) and DFT (right) solutions for TTF-TCNQ. For each solution the total energy $E$ in kcal/mol, the conduction nature (C/I = Conductor/Insulator) and the charge ordering (CO) and spin ordering (SO) in the TTF and TCNQ stacks is given.

Geometrical distortions of the lattice that reduce the symmetry have been experimentally associated to phase transitions to charge ordered states in this material (previous section). In the above mentioned calculations, the symmetry constraints of the $P2_1/c$ space group prevent charge...
ordering (CO). All molecules of the same kind are symmetry related and adopt an equal charge and total spin. When removing the symmetry constraints, further solutions were found (all solutions found are listed in Table 15).

Our results show triplet instability: some spin-unrestricted solutions are lower in energy than the spin-restricted solution. Our results in Table 15 show there are a number of solutions close in energy, especially those obtained with DFT. It is not useful to analyse our UHF results further. Apart from the high $M_s=1$ solution, all other obtained UHF solutions show charge transfer from TCNQ to TTF.

Our U-DFT results show that various charge and spin ordered solutions are very close in energy. Just like in the UHF case, the U-DFT solutions with high spin moments are lowest in energy given a particular $M_s$ value. I obtained two $M_s=1$ solutions, one of which is conducting. It very similar in character to the highest $M_s=1$ UHF solution. The second $M_s=1$ solution is an insulator, at a relative energy of 7 kcal/mol above the spin-restricted DFT solution. It shows stacks of each molecular type with unequal charged molecules. The molecular spin moments are anti-ferromagnetically coupled in the TCNQ stacks while TTF stacks show ferromagnetic alignment. I also found two $M_s=0$ BS solutions in which the TTF and TCNQ stacks couple to a singlet. The highest $M_s=0$ solution, at 2 kcal/mol below the spin-restricted solution, shows spin ordering in both stacks. Half of the TTF and TCNQ molecular stacks have a zero total molecular spin moment. In contrast to this, in the lowest $M_s=0$ solution, at 5 kcal/mol below the spin-restricted solution, all TTF and TCNQ molecules adopt the same total molecular spin moment of 0.5 and they are anti-ferromagnetically aligned. The molecular spin moments of both stacks couple singlet. These calculations show that solutions with molecular stacks with various spin and charge distributions are very close in energy. It underlines the experimental observations [31, 35] of a complex interplay of these degrees of freedom. In order to obtain information about intra-stack CO states, a doubling of the unit cell in the stacking direction would be necessary.

Spin susceptibility has been determined experimentally from the Knight shift of NMR of $^{13}$C of TTF-TCNQ($^{13}$C) [32]. The spin susceptibility could be determined for each type of molecules separately. It was determined at 60 K as approximately $10^{-5}$ emu/mol for TCNQ and roughly three times as high for TTF. The susceptibility falls to zero below 54 K and 49 K for TCNQ and TTF respectively. These temperatures coincide with the temperature at which the charge densities become ordered. Our calculations show that spin polarised states are close in energy to states without spin polarisation. At high temperatures, these spin-polarised states may be created upon application of an external magnetic field. No indications were found that spin polarisation occurs more easily in the TTF stacks. The vanishing spin susceptibility at low temperatures, at which both stack types exhibit a charge ordering, seems to hint towards a closed shell electronic representation for that phase. However, I was unable to find such charge ordered solutions with spin-restricted formalisms.

An interesting observation was published in 2008 [129] that illustrates the nature of TTF-TCNQ. A TTF crystal and a TCNQ crystal, both insulators, were brought in mechanical contact. Metal-like conduction occurred at the interface of the two crystals. This shows that conduction originates from the direct contact of TTF and TCNQ sheets.
SUPPLEMENT B. The band structure of the Bechgaard salt (TMTSF)$_2$PF$_6$

In this section, I discuss the band structure of the Bechgaard salt (TMTSF)$_2$PF$_6$, a charge transfer salt with tetramethyl-tetraselenafulvalene (TMTSF) electron donor and phosphorhexafluoride (PF$_6$) electron acceptor molecules. Single-particle crystal orbitals and electronic band structures were calculated for the periodic system by using DFT and HF theory. The band structure of (TMTSF)$_2$PF$_6$ is similar to that of (EDO-TTF)$_2$PF$_6$. However, it shows more 2D conduction and it can be classed as a quasi-1D/2D conducting material. I found proof of the 2D character of the conduction from the shape of the Fermi surface, calculated for the material under high pressure. I discuss the band structure in the light of the material physics.

Figure 60: Ball-stick diagram of (left) tetramethyl-tetraselenafulvalene (TMTSF) and (right) phosphorhexafluoride (PF$_6$).

Apart from the ethylenedioxy (EDO) group, structurally the difference between the TMTSF and EDO-TTF molecule are the four methyl substituents. The four chalcogen atoms are sulphur atoms in the case of EDO-TTF and selenium atoms in the case of TMTSF. For ball-stick diagrams of TMTSF and PF$_6$ I refer to Figure 60. An introduction into Bechgaard and Fabre salts can be found in section 3.1.2.

In the next section, an account is given of the known physics of both salts before discussing the calculated band structures of (TMTSF)$_2$PF$_6$.

B.1. The physics of Bechgaard and Fabre salts

A unified phase diagram for the Fabre and Bechgaard salts with small centro-symmetric anions has been created [112, 168]. A phase transition occurs at low temperatures, which can be suppressed by external pressure towards a CO state, an anti-ferromagnetic state or a superconducting state. The CO state can change into a spin-Peierls state at even lower temperature and at relatively low pressures. Upon increasing the pressure, phase transitions can cascade from the CO or spin-Peierls state to an anti-ferromagnetic state, to an incommensurate spin ordered state from which a superconducting state can emerge at sufficient pressure [98]. With increasing pressure the dimensionality of the system becomes less 1D. The insulating phases seem to form on the basis of the symmetry of the anions. In salts with centro-symmetric anions, such as PF$_6$, AsF$_6$, etc., a metal-insulator (M-I) transition occurs towards an anti-ferromagnetic phase. Salts with non-centro-symmetric anions, such as ReO$_4$ and ClO$_4$, exhibit an order-disorder M-I transition [49]. Besides these states, there are also states induced by magnetic fields [133] in some Bechgaard salts: e.g. in (TMTSF)$_2$PF$_6$, (TMTSF)$_2$ClO$_4$ and (TMTSF)$_2$ReO$_4$. These salts show many different spin ordered phases upon increasing external magnetic fields.

The electronic, magnetic, and superconducting properties of the Bechgaard and Fabre salts are strongly influenced by structural degrees of freedom such as the effect of pressure and the interactions of the anions in the methyl-group cavity. Under high pressure, the metallic state in e.g. (TMTSF)$_2$PF$_6$ is stabilised down to temperatures (0.5–2 K) at which the transition to a superconducting state appears. The critical temperature of the metal-superconductor transition in (TMTSF)$_2$PF$_6$ depends on the applied pressure. At a pressure of 6 kbar (12 kbar), the onset of superconductivity
occurs at \(T_c=1.3\) K (0.9 K). (TMTSF)\(_2\)ClO\(_4\), which is superconducting (\(\sigma>10^5\) S/cm) at ambient pressure at \(T_c=1.4\) K [44], shows that pressure is not a necessary condition for superconductivity. The unit cell volume is reduced by 3% by using the smaller ClO\(_4\) anion compared to PF\(_6\) and this has the same effect as applying 3 kbar of pressure in the PF\(_6\) salt. It can be argued that, due to the smaller size, the anion fits better in the methyl-group cavities so there is less wedging of the TMTSF molecules, allowing them to come closer together, which is just the effect that pressure has on the system. In this view, the anions are regarded as spacers, separating the electron donor stacks. In a more subtle view, the anions can be seen as having direct attractive interaction through the Se atoms, with the \(\pi\)-holes cloud on the electron donor stack, and indirectly through weak interactions with the methyl groups. The packing and the slight dimerisation of the cation molecules are determined by these interactions. Any change of the shape of the cavity should influence the positions of the anions and vice versa. For example, non-centro-symmetric anions may display orientational disorder. It is also known that rotations of the centro-symmetric PF\(_6\) anion become restricted at lower temperatures [160]. In the band structure, the dimerisation, which is larger in (TMTSF)\(_2\)X than in (TMTTF)\(_2\)X salts [160], leads to a valence-conduction band gap that is controlled by the shape and volume of the anion.

Generally, in the case of significant interactions between stacks, the Peierls transition can be eliminated. The conduction of e.g. (TMTSF)\(_2\)AsF\(_6\) has significant 2D character, originating from a 2D network of Se···Se interactions. In this material, the Se···Se distances are all similar (<4 Å). The conduction is largest in the stacking direction of the TMTSF molecules due to overlap of Se orbitals of \(\pi\)-character. In (TMTSF)\(_2\)PF\(_6\), a dimensional crossover from a 2D to a 3D conductor was experimentally observed by Jacobsen, Tanner and Bechgaard [45] at low temperatures. At higher temperature, a transition to a Q1D conductor was observed. Besides the interactions along the TMTSF stacking direction, there is also significant interaction along the short molecular axis of TMTSF in these materials. The inter-stack chalcogen···chalcogen interactions along this axis play a key role in eliminating the Peierls transition. I show, from the shape of the Fermi surface that I calculated, that under pressure the material is a 2D conductor.

Despite being structurally similar, Bechgaard and Fabre salts have different electrical properties\(^{14}\). This can be explained from differences in dimensionality. As exemplified in the previous paragraph, for (TMTSF)\(_2\)AsF\(_6\), inter-chain interactions in Bechgaard salts lead to 2D character of the conduction. In Fabre salts, these interactions are smaller and hence the conduction in these materials is more 1D. The room temperature metallic conductivity of Bechgaard salts is \(\sigma_{RT}=300\) S/cm. For Fabre salts this is \(\sigma_{RT} \approx 0.1-20\) S/cm with a temperature dependence of that of a semiconductor. For example, the maximum conductivity of (TMTTF)\(_2\)PF\(_6\) is around room temperature and is \(\sigma_{max,RT} \approx 1\) S/cm. In contrast, the conductivity of (TMTSF)\(_2\)PF\(_6\) at room temperature is 100 times larger, which increases with lower temperatures to a maximum\(^{15}\) at 15 K of \(\sigma_{max} \approx 3\) kS/cm. The magnetic susceptibilities of Bechgaard and Fabre salts are similar. (TMTSF)\(_2\)PF\(_6\) has a rather temperature independent susceptibility of \(\chi=4.2.10^{-6}\) emu/mol [42]. For (TMTTF)\(_2\)PF\(_6\) the magnetic susceptibility is \(\chi=5.6.10^{-4}\) emu/mol at 300 K and it decreases to \(\chi=4.10^{-4}\) emu/mol at low temperatures [47].

B.2. Band structure calculations on (TMTSF)\(_2\)PF\(_6\) and discussion

Single-particle crystal orbitals were calculated for the periodic system using RHF, UHF, spin-restricted DFT and spin-unrestricted DFT (U-DFT). The 6-21G basis set [56] was used. For the Se

\(^{14}\) For the temperature dependence of the conductivity of several Bechgaard and Fabre salts, we refer M. Dressel [127].

\(^{15}\) In older publications [42,49,53], often higher conductivities are reported: of the order of 50-300 S/cm for Fabre salts and 500 S/cm for Bechgaard salts.
atoms a Hey and Wadt large core effective core potential [51] was used. The PBE0 functional [82] was used in DFT calculations. For all calculations the Crystal [115] software was used. The X-ray crystal structure was used obtained by Thorup et al. [46] at ambient temperature and pressure. In the calculations, the unit cell was doubled in the stacking direction and symmetry constraints were removed to allow several possible charge and spin orderings. Experimentally it is observed by X-ray diffraction that, after applying 5.5 GPa pressure, the unit cell doubles in (TMTSF)$_2$PF$_6$ in a transition from a triclinic to a monoclinic phase [145]. Qualitative atomic charges were calculated using Mulliken population analysis [11]. The Fermi surface was calculated using the DL Visualise software [93], and for graphing purposes the original not-doubled unit cell was used.

A general introduction into the (TMTSF)$_2$PF$_6$ material can be found in section 3.1.2.

Qualitatively, the spin-restricted band structures I obtained (E$_2$ in Figure 62) are in agreement to those obtained by using tight-binding calculations [69], extended Hückel calculations [128], extended Hubbard calculations [153], and periodic DFT calculations [167, 168]. The calculated band widths are larger, 30% (150%) larger in our spin-restricted DFT (RHF) calculations. Unfortunately, no spin-unrestricted band structures were found in the literature. The band structure of (TMTSF)$_2$PF$_6$ is very similar to that of (EDO-TTF)$_2$PF$_6$ (Figure 47, section 7.5). It is noted that in Figure 62, the RHF band structure of (TMTSF)$_2$PF$_6$ is not shown because it is very similar to the spin-restricted DFT band structure labelled E$_2$. It shows four electronic bands around the Fermi level. They originate from two unfolded TMTSF bands that are just separated by a small energy gap of 2 kcal/mol (0.003 hartree). This gap is probably due to a small dimerisation of the TMTSF molecules. The long (short) TMTSF distances are 3.6 Å (3.4 Å). The crystal orbitals have negligible PF$_6$ character and are mainly due to the electron donor molecules. The valence band is folded just above the Fermi level. The partially filled band confirms band-conductivity and Mulliken charge analysis [11] confirms that each molecule adopts an equal amount of positive charge. A charge transfer from TMTSF$_2$ to PF$_6$ of 0.67 e$^-$ (0.53 e$^-$) is calculated with RHF (DFT).

The dispersion of electronic bands is largest in the X direction, the direction in which the TMTSF molecules stack, while the dispersion in the Y direction is much less but not negligible. This looks comparable to (EDO-TTF)$_2$PF$_6$ (Figure 47, section 7.5). Also from the shape of the Fermi surface (Figure 61) it is concluded that the conduction anisotropy is Q1D. In comparison to the Fermi surface of (EDO-TTF)$_2$PF$_6$ in Figure 47, the Fermi surface of (TMTSF)$_2$PF$_6$ is also nearly planar and it is slightly curved towards the edge of the Brillouin zone (BZ) in only one direction (horizontal in Figure 61). In (EDO-TTF)$_2$PF$_6$, the curvature is like a half cylinder however in (TMTSF)$_2$PF$_6$ the curvature is more S-shaped.

Seven different electronic states could be obtained (Figure 62). For each state the energy relative to the spin-restricted solution is given in kcal/mol and also the M$_s$ value, the charge ordering (CO), and spin ordering (SO) pattern in the tetramer stack are shown. In these patterns, a number or arrow is indicative for a molecular charge or spin moment. The four frontier bands are well separated from the other electronic bands, therefore I only analyse these four bands in the band structures.
Figure 62: Band structures, charge ordering (CO) and spin ordering (SO) for several electronic states that were obtained, with HF and DFT, for \((\text{TMTSF})_2\text{PF}_6\). Symbols \(\Gamma, \text{X}, \text{Y}, \text{Z}\) refer to the \(k\)-points in the BZ. The energy in kcal/mol is relative to the spin-restricted HF/DFT solution. A double arrow indicates nonzero atomic spin moments that sum to a zero molecular spin moment.

The \(M_s=0\) solutions obtained from spin-unrestricted calculations show \(\alpha\) and \(\beta\)-spin bands that appear to be degenerate (Figure 62), however atomic spin moments have formed. Comparing the \(M_s=0\) band structures to that of the spin-restricted solution \(E_2\) obtained with U-DFT, it is noted that band gaps form. For example, in \(E_3\) the middle two bands are separated both from the highest and from the lowest band. Using UHF instead of U-DFT, these energy gaps become more pronounced. Also a gap opens between the central two bands in the case of the \(E_5\) solution, which shows a charge distribution of \(\frac{1}{2}\). However, this is not the case in the \(E_6\) solution, in which the charge ordering (CO) is 0101. The band dispersion in all these band structures is less than in the spin-restricted case. The spin ordering (SO) patterns of the \(M_s=0\) solutions are anti-ferromagnetic with a tetramer periodicity.

Despite being close in energy, the orbitals of the \(M_s=0\) and \(M_s=1\) solutions are clearly different. The spin flip of the highest \(\beta\) electron to obtain \(M_s=1\) solutions cause \(\alpha\) and \(\beta\)-bands to be shifted in energy. Comparing the band structures for the \(M_s=1\) solutions to that of the spin-restricted solution, un-occupying the highest \(\beta\) valence band shifts this \(\beta\)-band to above the Fermi level and the \(\alpha\) conduction band becomes occupied and shifts to below the Fermi level. The highest two bands in the \(M_s=1\) band structure are conduction \(\beta\) electron bands, the six bands below it are the four \(\alpha\)
electron and two β electron bands. The $E_4$ and $E_7$ solutions, obtained with UHF, show a much larger band gap compared to the $E_1$ U-DFT solution. Due to the dispersion in the Γ to Y direction in the $E_1$ state, the conduction and valence band touch, forming a semi-metallic band conductor. Having the same charge distribution of \( \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \), the $M_s=1$ solutions $E_1$ and $E_4$ show that broken spin-symmetry solutions are close in energy to the spin-restricted solution.

Using UHF, solutions could also be obtained that show a mixed molecular valence CO of 0101, while this was not possible by using U-DFT. Also here, the $M_s=1$ solution ($E_7$) is very close in energy to the $M_s=0$ solution ($E_6$). I conclude from this that the electron spins have little interaction. These band structures show a large conduction-valence band gap.

In all spin polarised solutions, the spin populations are predominantly located on the selenium atoms, and also on the two central carbon atoms. In the U-DFT case, these atomic spin moments are very small: typically 0.07 (0.1) in the $M_s=0$ ($M_s=1$) solution. When summing the atomic spin moments to give the molecular spin population, cancelations of atomic spin moments with opposite sign, as indicated by the double arrows, occur for two molecules in the lowest UHF states ($E_6$ and $E_7$). Finally, it must be noted that no measure for the spin contamination could be obtained from these spin-unrestricted calculations. There is a tendency to interpret the $M_s=0$ and $M_s=1$ solutions as singlet and triplet solutions, respectively. But it is likely that higher multiplet wavefunctions are mixed into the solutions I calculated, and unfortunately to an unknown amount. Despite of this, the solutions obtained show that instabilities in the system can give rise to several low-lying states.

The calculated states can be related to experiment in the following way. Our spin-restricted band structure with a charge distribution of \( \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \) is well in agreement with experiment, showing no long range ordering of molecular charges and band conductivity. The Q1D dimensionality of the conduction was confirmed from the band structures and the density of states. Experimentally, a dimensional crossover from a Q1D to a 2D/3D conductor is observed at lower temperatures [45]. Using a geometry obtained by neutron diffraction at $T=4$ K and ambient pressure [54], a Q1D conduction anisotropy was found. From an X-ray geometry obtained at 0.98 GPa pressure and at ambient temperature [54], a 2D Fermi surface was calculated (Figure 63), which confirms the dimensionality crossover. For these calculations spin-restricted DFT using the PBE0 functional [82] were used.

The M-I transition at $T = 12$ K in (TMTSF)$_2$PF$_6$ is attributed to the onset of itinerant anti-ferromagnetism with the formation of a spin ordering [112]. A CO state is not observed in (TMTSF)$_2$PF$_6$, but X-ray scattering experiments [78] show that an instability exists at high temperature. This instability towards a CO state in (TMTSF)$_2$PF$_6$ becomes weaker at lower temperature [160] while at the same time the tendency to form a spin-Peierls state increases, to eventually become dominant in a transition towards a spin ordered state. In fact, these CO and SO states co-exist below $T_m$. In contrast to this, in the sulphur equivalent Fabre salt, a transition to a 0101 CO is observed with a small charge disproportionation (difference between charge rich and charge poor TMTTF molecules) of 0.28 [159]. This transition is often termed structureless as it is not associated with geometrical deformations. Our spin-unrestricted solutions with a charge
distribution of $\frac{1}{2}\frac{1}{2}\frac{1}{2}$, that are close in energy to the spin-restricted solution, reflect the instability towards spin polarised states. Experimentally a small paramagnetic susceptibility $\chi_{295K}=6.45 \times 10^{-4}$ emu/mol was measured [38] which indicates the material has a small tendency towards broken spin-symmetry state in the presence of a magnetic field. The susceptibility is twice that of the high temperature phase of $(EDO-TTF)_2PF_6$ (3.3.3.3). In a review article from 2007, Dressel [127] summarised magnetisation data from nuclear magnetic resonance, spin resonance and anti-ferromagnetic resonance experiments, showing for $(TMTSF)_2PF_6$ and other Bechgaard salts, a magnetisation decreasing to zero from $T=0$ K to 12 K. That our CO=0101 solutions are the lowest in energy confirms an instability of the system towards a charge ordered state which, as described above, does not become manifest in $(TMTSF)_2PF_6$ but which is observed in the sulphur equivalent $(TMTTF)_2PF_6$. 