Quantum chemical studies of the physics around the metal-insulator transition in (EDO-TTF)2PF6
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The thermal metal-insulator phase transition in (EDO-TTF)$_2$PF$_6$ is attributed to an interplay of instabilities. The effect of structural instabilities on the electronic band structure and on the charge ordering are explored in this chapter. The instability of the system to other electronic states is also explored by studying the triplet instability. It is shown that dimerisation of EDO-TTF$_2$ dimers opens a band gap and that it alters the equal distribution of the holes over EDO-TTF molecules towards a 0110 charge ordering pattern. At high temperatures the charge order does not become manifest in the material, however below $T_{M-I}$ there is a barrier between de 0110 and 1001 charge ordered and dimerised states. It is also shown that the system is not unstable to a transition to other electronic states.
8.1 Introduction
The thermal metal-insulator (M-I) phase transition in (EDO-TTF)$_2$PF$_6$ is attributed to an interplay of instabilities: molecular flexibility of EDO-TTF (chapter 4), geometrical ordering of EDO-TTF molecules and an associated charge ordering (chapter 5), and an ordering of the PF$_6$ anions. It is interesting to explore the effect of these instabilities on the electronic band structure and on the charge ordering (CO). The structural instability of the isolated EDO-TTF molecule is explained in detail in chapter 4. In this chapter, the effects of PF$_6$ ordering and of EDO-TTF$_2$ ordering are investigated. The possibility of a triplet or open shell singlet ground state is also investigated because our tetramer and periodic calculations (chapter 6) show triplet instability [5, 17, 37]. Spin-unrestricted calculations yield lower total energies than spin-restricted calculations. To this end, spin-unrestricted calculations were performed in which artificially the exchange energy is increased.

In the physics of Bechgaard and Fabre salts, which are isostructural to (EDO-TTF)$_2$PF$_6$, the anions seem to play an important role [160]. These materials show an M-I transition due to anion ordering (AO) in the case the salts include a non-centro-symmetric anion. The anions are disordered at high temperatures (HT), and when they become ordered at lower temperatures an M-I transition occurs. Bechgaard or Fabre salts with centro-symmetric anions do not show an AO. They remain metallic or semiconducting up to very low temperatures (paragraph 3.1.2). Although we speak of AO, there may not be true long range ordering [160]. In Bechgaard salts with non-centro-symmetric anions, it was found that the rate of cooling affects the AO, and that even with slow cooling no perfect AO was achieved. In these Bechgaard salts, inter-chain coupling may be influenced by the anions and they may stabilise the charge ordered and spin ordered (SO) ground states [160].

According to Peierls’ theorem, one-dimensional conductors are unstable with respect to deformations that double the periodicity of the system (3.2.3). In chapter 7, we identified the phase transition in (EDO-TTF)$_2$PF$_6$ as a Peierls transition in which the interactions between (EDO-TTF)$_2$ dimers increase in the low temperature (LT) phase. In this phase, the dimerisation is visible from the difference in (EDO-TTF)$_2$ distances. Compared to the HT crystal structure, the height of the tetramer stack is larger at LT by 0.12 Å. The centre of mass distance between (EDO-TTF)$_2$ dimers is smaller at LT (7.21 Å) than at HT (7.34 Å). Alternatively, the negatively charged PF$_6$ molecules that reside in between EDO-TTF stacks are expected to be relatively mobile, especially in the PF$_6$ stacking direction. Nearest neighbour PF$_6$ anions are located at a distance of approximately 7 Å. Could a dimerisation of these anions bring about the phase transition by creating a double periodic potential that acts on the EDO-TTF columns? In the LT crystal, the AO of the centro-symmetric PF$_6$ anions constitutes a translation of each ion by 0.26 Å from the inversion points they occupy in the HT crystal. With that, the anions form a superstructure that creates a periodic potential, lowering the symmetry of electrons and nuclei in the EDO-TTF columns. Due to the lowered symmetry, the BPPB geometrical ordering could form along with a 0110 CO (0110 and BPPB denote a tetramer stack of EDO-TTF molecules where the numbers indicate the molecular charge and the letters denote the molecular geometry: B for bent and P for planar). It is interesting to explore what role these deformations play in the phase transition, and which deformation is the dominant factor. This effect is explored in section 8.3 of this chapter.

The archetypal TTF-TCNQ material is often classified as a radical cation salt because, due to the charge transfer, all molecules in the high temperature phase of the system can be considered open shell. Whether the TTF-TCNQ crystal can be best described by a wavefunction with a closed shell electronic configuration, or by one with a triplet or open shell singlet electronic configuration would be an interesting question. From our periodic calculations (supplement A) on the high temperature
phase, it is shown that both a band structure calculated from a closed shell wavefunction, and one from a broken spin-symmetry wavefunction, have partially occupied bands. From these calculations, it is not possible to say which description of the ground state is better. For (EDO-TTF)$_2$PF$_6$, the closed shell vs. open shell issue was researched in depth in chapter 6. We concluded that a closed shell ansatz for the wavefunction is best for (EDO-TTF)$_2$PF$_6$, but we have also concluded that there is triplet instability. The source for this instability is the difference in energy between singlet and triplet spin couplings, which is governed by the exchange energy. By artificially changing the exchange interactions we have explored the effect of triplet instability in (EDO-TTF)$_2$PF$_6$ in section 8.4.

8.2 Computational details

For the study of structural deformations, spin-restricted calculations using the HT X-ray crystal geometry [99] were performed. This unit cell was transformed and doubled in order that it contains a single stack of four EDO-TTF molecules and two PF$_6$ molecules (Figure 15 in section 3.3.3.1). We used RHF and spin-restricted DFT with the PBE0 DFT functional [82]. The 6-21G basis set [56] and the Crystal software [115] were used to perform the calculations in which the point group symmetry was not imposed on the orbitals. We note that at this level of the theory it is not expected that energy profiles for intermolecular interactions can be calculated accurately, so we discuss our results qualitatively. For the study of triplet instability, spin-unrestricted DFT with the PBE-X functional was used. The amount of Fock exchange was varied from 0% to 50% (25% corresponds to PBE0).

8.3 Exploring structural deformations

In this section, we explore the roles of PF$_6$ and EDO-TTF dimerisation in the phase transition of (EDO-TTF)$_2$PF$_6$ by applying these deformations on the crystal in the high temperature phase. A good starting point for such a study is a vibrational analysis, however a minimum energy conformation could unfortunately not be obtained for the crystal. In optimisations with spin-restricted HF and DFT, the molecules are too repulsive. Optimising the intermolecular distances in the stacking direction leads to an elongation of the stacking height from 14.616 to 15.3 Angstrom when RHF is used. An unconstrained optimisation causes molecules to slide out of the stack. Instead, we base our current study on the experimentally observed X-ray crystal structure, and take displacement patterns of the molecules based on simple models.

![Figure 48: Unique displacement patterns of a periodic linear chain of four identical particles.](image)

We assume that PF$_6$ molecules and EDO-TTF molecules form more or less separate entities in the (EDO-TTF)$_4$(PF$_6$)$_2$ crystal. Only displacements of initially equidistant, rigid EDO-TTF molecules are considered in the tetramer unit cell. There are various displacement patterns along the stacking direction (Figure 48). In the ‘dimer exchange’ displacement $Q_1$, neighbour EDO-TTF molecules move pairwise toward or away from each other. The intermolecular distances change from all $a$ to $a-2q$, $a+2q$, etc. Displacement $Q_2$ gives a dimerised pattern, with intermolecular distances $a-2q$, $a$, $a+2q$, etc. In the periodic calculations, displacement $Q_3$ is equivalent to $Q_2$ after a translation over $\frac{1}{4}$ of the unit cell length. The PF$_6$···PF$_6$ displacements can be considered separately because there is no visible contribution of PF$_6$ molecular orbitals to the frontier crystal orbitals and because they are at relatively larger distances from the EDO-TTF stack.
The effect of EDO-TTF displacements Q₁, Q₂ and Q₃ are summarised in Figure 49. Periodic RHF calculations on the crystal are performed in which the EDO-TTF molecules are displaced according to the displacements in Figure 48, while the PF₆ molecules are fixed at their crystallographic positions. Crossing states are found only following the Q₂ dimerising (EDO-TTF)₂ displacement. No crossing states were observed when performing these calculations with DFT. Also, calculations were performed on unit cell clusters in vacuum with the RHF, ROHF and CASSCF methods, for similar displacements without observing states that cross in energy.

![Figure 49: Total RHF energy vs. displacement for the dimer exchange displacement and the dimerising displacement (top) and the associated change in charge distribution (below) in the EDO-TTF tetramer stack. The ball-stick diagrams denote the (EDO-TTF)_4 geometry that corresponds to the displacement. The CO patterns are indicated as 0110, 1001, 1100, or 0011.](image)

For the highest energetic displacement, the dimer exchange displacement (Q₁), the total energy changes harmonically with a minimum at the equilibrium position. During the displacement, the charge ordering changes between 1100 and 0110 at -0.22 Å. Positive charge localises in one of the two dimers. For the (EDO-TTF)₂⋅⋅⋅(EDO-TTF)₂ dimerising displacement (Q₂), three charge ordered solutions could be found using periodic RHF calculations. The 0110 and 1001 charge ordered states could be followed separately. Despite the equivalent displacement pattern in Q₃, here the charge ordering changes gradually from 0011 through 0110 to 1100 and vice versa over 0.1 Å. During these transitions the total energy changes within 1 kcal/mol. The lack of smoothness of the energy curve is likely due to choices of cut-off values in the Crystal software. At a point without geometrical distortion, the 0110 and 1001 states have the same relative energy of 1.7 kcal/mol. Moving the (EDO-TTF)₂ dimers close or separating them is equivalent due to the periodic boundary conditions. A double well energy curve is obtained with a minimum at an (EDO-TTF)₂ displacement of 0.065 Å. The distance between the dimers at the minima is 0.13 Å less on one side and 0.13 Å more on the other side, compared to the situation at zero displacement, where the EDO-TTF molecules are equidistant (at 3.67 Å). The minimum for Q₃ is found for a displacement of ±0.05 Å. The energy of the 1100 and 0011 states are intermediate between 1001 and 0110.
The periodic calculations were checked in several ways. Qualitatively the same results were obtained when integrals were calculated at higher precision (no expansions for the Coulomb integrals were used). The energy at the crossing point of the state becomes 1.4 kcal/mol while the minimum remains at a displacement of 0.065 Å. By using the 6-21G** basis set, qualitatively the same results were obtained as shown in Figure 49, thus ruling out basis set effects. Now, the crossing point of the states is at 1.9 kcal/mol and the minimum is at a displacement of 0.08 Å. An alternative calculation was performed by using spin-restricted DFT using the PBE0 functional [82]. In this calculation no bistable state was found and a harmonic, single minimum, potential was obtained. The charge distribution changes a little from $\frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2}$ (undisplaced) in the direction of 0110/1001. At small displacements the system is a band-conductor while at displacements greater than 0.28 Å the band structure exhibits a valence-conduction band gap. While our RHF results fit well to the physics of the system, clearly with DFT charge localisation is not achieved by applying the $Q_2$ displacement.

In Figure 50, the state interaction is shown. The parabola represent the total energy curves of the interacting RHF states that are also shown in Figure 49. At the X-ray geometry (at zero displacement) the 0110 and 1001 state have the same energy. We construct linear combinations of the wavefunctions:

$$\psi_{+/-} = (\psi_a \pm \psi_b) / \sqrt{(2 \pm 2S_{ab})}$$

where a and b denote the 0110 and 1001 wavefunctions respectively. Whether the bistability of the system becomes manifest depends on the temperature and on the height of the barrier. The splitting $\Delta$ between the diabatic states, at zero displacement, can be calculated as follows [62]:

$$\Delta = |2H_{ab} - S_{ab}(H_{aa} + H_{bb})|/(1 - S_{ab}^2) = 2|H_{ab} - S_{ab}E_x|/(1 - S_{ab}^2)$$
In equation 76, \( H_{ab} = \langle \psi_a | \hat{H} | \psi_b \rangle \), \( S_{ab} = \langle \psi_a | \psi_b \rangle \), and we used \( H_{aa} = H_{bb} = E_x \). Here, \( H_{ab} \) is small due to the Slater-Condon rules: \( H_{ab} = \langle \cdots 0110 0110 | \hat{H} | \cdots 1001 1001 \rangle \approx 0 \), in which a 1 (0) in the determinants indicate an (un)occupied localised EDO-TTF HOMO orbital. We assumed that the orbitals in both determinants are orthogonal. Due to a small overlap between the 0110 and 1001 states, \( S_{ab} \neq 0 \), we obtain two separated adiabatic states. The coupling of the states is indicated in Figure 50 by sketching the adiabatic potentials and dashing the diabatic potentials around the crossing point.

The zero-point energy for the 0110 (left) and 1001 (right) states is calculated at \( \frac{1}{2} \hbar \nu = 0.25 \) kcal/mol, and it is shown as a horizontal line in the potential in Figure 50. In fact, below the crossing, which we calculated at \( E_x = 1.7 \) kcal/mol, the nuclear wavefunctions of the system are superpositions:

\[
\phi(q)_{+/-} = \left[ \phi(q)_{\text{left}} \pm \phi(q)_{\text{right}} \right] / \sqrt{2(1 \pm S_{\text{left}/\text{right}})}
\]

(q denotes the displacement coordinate). The splitting of the energy levels depends on the overlap \( S_{\text{left/right}} \) of the nuclear wavefunctions. The dashed lines under the barrier indicate the overlapping nuclear wavefunctions. The overlap lowers the gerade combination but it raises the ungerade combination in energy more. In Figure 50 the unperturbed levels are dashed while the split levels are solid. For \( \nu_0 \), \( S = 0 \), and there is a very small splitting in energy between \( \phi_{0g} \) and \( \phi_{0u} \) (not shown). For \( \nu_2 \), \( S > 0 \), and the energy of \( \phi_{2g} \) is shifted to above \( E_x \). The wavefunctions penetrate the potential curve into the classically forbidden region. When the amplitude is non-zero where the decaying wavefunction reaches the potential curve for the other state, tunnelling is possible. The tunnelling probability between the states left and right depends on this amplitude. For example, for \( \nu_2 \) there is a significant tunnelling probability. Above \( E_x \), the nuclear wavefunction is determined by the walls of the potential on either side. For this wider potential, the quanta are smaller than it is the case below \( E_x \) for the two potentials. Above \( E_x \), there is less probability for the system to be found close to the barrier and we indicated that with a damped function. The effect of which is decreased for higher vibrational levels. At high enough energies the system can go to the excited adiabatic state.

With this, the phase transition can be summarised as follows. Using a halved unit cell, with two EDO-TTF molecules, we found, in section 6.6 and in chapter 7, an RHF state at \( E = 4.7 \) kcal/mol. We regard this system as highly symmetric: all EDO-TTF molecules are equidistant and the charge ordering is \( \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \). This system is unstable to forming a 0110/1001 charge ordering, comparable to how Paldus and coworkers describe a similar instability of RHF solutions in cyclic polyenes [136]. They described that the existence of a broken symmetry solution implies the tendency towards a distorted geometry. We observed a similar instability. Using a dimerised geometry we always find a charge ordered RHF electronic wavefunction. Only for a geometry with equidistant molecules we also find a higher symmetric solution with delocalised holes. The lowering may be due to the gain in induction energy. Induction energy increases quadratically with the electric field and therefore it is also quadratic with charge. The equidistant periodic system with a \( \frac{1}{2} \frac{1}{2} \frac{1}{2} \) charge distribution has a smaller induction energy than the same system with a 0110 charge ordering. In Figure 50, we obtain a better representation of the system with a delocalised hole, compared to the highly symmetric RHF state.

At high temperatures, the vibrational levels above \( E_x \) are populated. The system has an average geometry with equidistant molecules. Above \( E_x \), the nuclear wavefunctions in between the two minima are damped due to the barrier. At these energies, the effect of the barrier is that the probability to find the system in one of the two dimerised geometries is increased but the system vibrates rapidly with a frequency of a few THz. Below the barrier, the nuclear wavefunctions become
superpositions of the 0110 and 1001 states and there is a high probability that the system can tunnel between them. At these temperatures, the electronic wavefunction fluctuates between 0110 and 1001. Thereby it can be considered as symmetry broken. At lower temperatures and hence at lower energies, the tunnelling probability is diminished. The phase transition occurs when the tunnelling probability is significantly reduced, e.g. at $\nu_1$. We calculate energies of 0.25 and 0.75 kcal/mol for $\nu_0$ and $\nu_1$, respectively, the difference of which is of the order of $k_B T_{M-I}$ (0.55 kcal/mol). At very low temperatures the system freezes into the 0110 or 1001 charge ordered states with a dimerised geometry. In chapter 7, we found these states to be band insulators.

It is also interesting to analyse the effects of (EDO-TTF)$_2$ and PF$_6$ displacements in the conducting state with the delocalised holes. When using DFT, a single minimum potential is obtained when making such displacements while the holes remain delocalised. In periodic DFT calculations we used the displacements (analogous to $Q_2$) shown in Figure 51. In comparison to the HT crystal structure, in which anions and cations are equidistant (left), displacements up to 0.3 Å were made to all EDO-TTF$_2$ dimers and PF$_6$ molecules.

<table>
<thead>
<tr>
<th>EDO-TTF$_2$ displacement /Å</th>
<th>Total Energy (/kcal.mol$^{-1}$)</th>
<th>Charge Transfer (/el.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.0 0.1 0.2 0.3</td>
<td>0.0 0.1 0.2 0.3</td>
</tr>
<tr>
<td>PF$_6$ displacement /Å</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.0</td>
<td>0.0 1.6 7.3 21.4</td>
<td>0.72 0.74 0.77 0.79</td>
</tr>
<tr>
<td>0.1</td>
<td>0.1 1.7 7.4 21.7</td>
<td>0.72 0.74 0.76 0.78</td>
</tr>
<tr>
<td>0.2</td>
<td>0.3 2.0 7.9 22.2</td>
<td>0.71 0.74 0.76 0.78</td>
</tr>
<tr>
<td>0.3</td>
<td>0.9 2.6 8.6 23.3</td>
<td>0.71 0.73 0.75 0.78</td>
</tr>
</tbody>
</table>

Table 14: The effect of displacements on the total energy and on the charge transfer from EDO-TTF$_2$ to PF$_6$. Horizontally the dimerisation of (EDO-TTF)$_2$ dimers and vertically the dimerisation of PF$_6$.

The effect of these displacements on the total energy is minor. In Table 14, the change in total energy of the deformations is listed. The energetic effect of EDO-TTF$_2$ displacements is larger than the displacement of PF$_6$ molecules, probably due to the larger intermolecular distance. The displacements of PF$_6$ molecules have almost no effect on the charge transfer to EDO-TTF$_2$. Displacement of EDO-TTF$_2$ dimers cause a little enhancement of the charge transfer: 0.02 electron for each 0.1 Å displacement (Table 14). The positive charge of the EDO-TTF molecules change more strongly as shown in Figure 52. The molecules are numbered sequentially top/down and indicate the molecular charge as +Q. The effect of PF$_6$ dimerisation (Figure 52b) is that a little positive charge shifts from the first two EDO-TTF molecules (1 and 2) to the last two molecules (3 and 4). EDO-TTF$_2$ displacements (Figure 52a) lead to more positive charge on the outer molecules (1 and 4) and a smaller hole on inner molecules (2 and 3). The combined displacement changes the CO, from one in which all EDO-TTF molecules are uniformly charged, in the direction of a 0110 CO pattern. The
charge disproportionation effect in the EDO-TTF₂ dimerisation is about five times larger compared to effect due the anion dimerisation. When both displacements are applied together (Figure 52c), all molecules adopt a different charge. The outer molecules adopt most positive charge.

Figure 52: Charge +Q of the four EDO-TTF molecules in the unit cell in dependence of deformation: a. EDO-TTF₂ displacement (left), b. PF₆ displacement (middle) and c. together (right).

The effect of the displacements on the electronic band structure is shown in Figure 53. The displacements cause a diminished dispersion of the energy of the electronic band and these bands also shift in energy. In the HT reference crystal, the energy of the four electronic bands, as shown, are dispersed in such a way that there is no band gap; the horizontal line indicates \( E_F \), the Fermi energy. The effect of PF₆ displacements is that a gap opens between the two bands that intersect
with $E_r$, visible in the band structures in Figure 53 at V and R, however it is not enough for a gap to open in the density of states also. Likewise, a small dimerisation of the EDO-TTF$_2$ dimers does not lead to an insulating state. The effect of such small dimerisation is that the conduction band and valence band shift to higher and to lower energy respectively. When EDO-TTF$_2$ dimers are displaced by 0.2 Å or more, the effect is sufficient for a band gap to open.

### 8.4 Exploring triplet instability

In this section, the instability of the (EDO-TTF)$_2$PF$_6$ system to other electronic states is explored. We artificially alter the difference between the lowest singlet and triplet states by tuning the exchange interactions in our calculations. From Equations 23 and 24 in paragraph 2.3, the singlet-triplet splitting can be deduced in the following way:

$$\langle \psi_S | \hat{H} | \psi_S \rangle = \frac{1}{\sqrt{2}} \left( \langle |a\bar{b}| + |b\bar{a}| \rangle / \sqrt{2} \right) \langle |a\bar{b}| + |b\bar{a}| / \sqrt{2} \rangle = h_a + h_b + J_{ab} + K_{ab}$$

$$\langle \psi_T | \hat{H} | \psi_T \rangle = \frac{1}{\sqrt{2}} \left( \langle |a\bar{b}| - |b\bar{a}| \rangle / \sqrt{2} \right) \langle |a\bar{b}| - |b\bar{a}| / \sqrt{2} \rangle = h_a + h_b + J_{ab} - K_{ab}$$

$$\Rightarrow \langle \psi_S | \hat{H} | \psi_S \rangle - \langle \psi_T | \hat{H} | \psi_T \rangle = 2K_{ab}$$

Figure 54: Total UKS energy in kcal/mol relative to the RKS singlet energy at each point is shown for the $M_S = 0$ and the $M_S = 1$ solutions. X is the percentage HF exchange used in the functional PBE-X. The total RKS energy in eV relative to the RKS energy at X=0%, is shown in the insets.

We performed periodic density functional calculations with the PBE-X functional in which X is the percentage of HF exchange that is mixed into the functional. The results (Figure 54) show a gradual decrease in total energy with increasing X. As can be seen from equation 20 in section 2.3, increasing the exchange energy causes a lowering of total energy. The absence of abrupt energy change indicates that there is no change in electronic state. The spin-restricted Kohn-Sham (RKS) total energy of the singlet state, shown in the insets, decreases nearly linearly with X, about 40 eV from X=0% to X=50%. This is roughly 1.3% of the total energy. The main graphs in Figure 54 show the relative energy of the spin-unrestricted Kohn-Sham (UKS) $M_S = 0$ and $M_S = 1$ broken symmetry (BS) solutions. At each point of X, the total energy is shown relative to the RKS energy at the same point of X. In the LT phase, the $M_S = 1$ UKS solution is higher in energy solution over the whole range of X. The $M_S = 0$ UKS and the RKS solution have the same energy until X=10% and from X=15% the $M_S = 0$ UKS solution is slightly (4 kcal/mol for X=50%) lower in energy. The behaviour in the HT crystal is different. At X=0%, the $M_S = 0$ UKS solution is the lowest in energy. With increasing X, the energy with respect to the RKS energy is lowered. This decrease is stronger for the $M_S = 1$ solution. The solutions become approximately degenerate at X=30%. From the absence of any abrupt change in the properties we conclude that the M-I transition is not governed by instabilities to other electronic states.
It is not possible to say which percentage of mixing in of HF exchange is most physical. Hence a further discussion of changes of the characteristics of the wavefunction with increasing X will not provide much insight into the physics of the system. Nevertheless, it is interesting to discuss the changes from the perspective of the performance of the DFT PBE-X functionals. In that respect, we will look briefly at the dependency of the charge ordering (CO) and on the spin ordering (SO) on the percentage of HF exchange mixing (X).

![Figure 55: Charge ordering (CO) of the RKS, and the M_s=0 and M_s=1 UKS BS solutions in the LT and HT crystal as a function of the percentage HF exchange X.](image)

For the LT crystal, the CO of the RKS and M_s=0 UKS solutions involves higher charged inner (planar) molecules with increasing X (Figure 55). The CO increases from (0.1 0.4 0.4 0.1) at X=0% to (0.0 0.7 0.7 0.0) at X=50%. The numbers indicate the positive charge of the EDO-TTF molecules in the tetramer stack. The holes in the M_s=1 UKS wavefunction is slightly more localised on the inner, planar molecules. With increasing X the positive charge on the molecules become equal. At HT, the molecular charge for the RKS and UKS M_s=0 and M_s=1 wavefunctions are equal. With increasing X the charge transfer from EDO-TTF molecules to PF_6 increases but the positive charge remains fully delocalised over all four molecules in all three solutions.

![Figure 56: Spin ordering (SO) in the EDO-TTF tetramer stack as a function of X, the percentage of HF exchange in the PBE-X functional, for the UKS BS M_s=0 and M_s=1 solutions for the LT crystal and the UKS BS M_s=0 solution for the HT crystal.](image)

In the LT crystal, the M_s=0 wavefunction is not spin polarised up to X=20% after which the spin population increases on both the inner planar and the outer bent molecules (Figure 56). Beyond X=25% the spin population decreases on the bent molecules and increases on the charged planar ones. In the M_s=1 UKS wavefunction, slightly more spin population is found on the inner planar molecules. With increasing X the spin density on the molecules becomes equal. In the HT crystal, the spin population in the UKS M_s=0 wavefunction increases with X from zero at X=0% to 0.47 at X=50%. In the M_s=1 UKS wavefunction (not shown in Figure 56), the spin density on all molecules equals 0.5 and this value does not change when X is varied.
8.5 Conclusions and discussion

Using periodic calculations, it was shown that dimerisation in the EDO-TTF stack leads to a change in the electronic structure. It changes from a conducting state, with the holes equally delocalised over all EDO-TTF molecules, to an insulating state with a 0110 CO pattern. Our calculations also show that small displacements are energetically easy to achieve.

Calculations with DFT show that EDO-TTF$_2$ dimerisation leads, in the conducting state with delocalised holes, to a shift of the conduction band to higher energies. The separation with the valence band increases with larger degree of dimerisation. At the same time, also the dispersion of the electronic bands becomes less. Both effects go towards an opening of the band gap. We also conclude that, in the state with a delocalised hole, dimerisation of PF$_6$ molecules alone is not enough for a band gap to open. Therefore, these results do not support the idea that the symmetry lowering of the system due to anion dimerisation forms the conditions for the dimerisation in the EDO-TTF stacks.

Periodic RHF calculations show the path from a state with delocalised holes at temperatures above $T_{M-I}$ to a charge ordered state below it. The 0110 and 1001 states could be followed separately in the (EDO-TTF)$_2$⋯(EDO-TTF)$_2$ stretching displacement. The states are separated by a barrier. At temperatures well above $T_{M-I}$, the molecules are equidistant on average and the charge ordering averages to ½½½½. At, and also below, the crossing point of the states, the system is described as a superposition of 0110 and 1001 nuclear wavefunctions. At a geometry with equidistant molecules, this provides a better description of the high temperature state because the system is lower in energy than the RHF state in which the holes are delocalised. Directly below the barrier, the tunnelling probability between the states is high and the system can still interchange between 0110 and 1001. The phase transition occurs when the tunnelling probability becomes small. The system freezes into one the two equivalent charge ordered states with a dimerised (EDO-TTF)$_2$ geometry.

We have also been able to show that hopping of electrons costs very little energy. In a dimerising displacement, a 1100 state has been gradually changed through a 0110 charge distribution to a 0011 state within 1 kcal/mol. In a dimer exchange displacement, an abrupt shift between the charge distributions 0110 and 1100 was observed to occur without an associated change in energy. A few years ago, dithiazolyl-based materials were found to be bistable magnetic materials [172]. In these materials dimer exchange dynamics shows a double minimum potential in a paramagnetic phase. The origin for this bistability is attributed to vibrational entropic gain. In our periodic RHF calculations on the dimer exchange displacement, we found a single minimum for the electronic energy. We have not calculated the entropy however and therefore we do not know its contribution to the zero-point vibrational energy. An analysis of vibrational frequencies might be beneficial because it would also enable a thermodynamic analysis.

In this chapter we also looked at the triplet instability and the possibility for other ground states. The absence of any abrupt change in the total energy in our calculations, in which the exchange energy was increased artificially, shows that the M-I transition does not find its origin in instabilities towards another electronic state. Besides this, also no abrupt changes were found in the charge ordering and in the spin ordering of the solutions of our periodic calculations, in which the whole crystal was treated explicitly.