Quantum chemical studies of the physics around the metal-insulator transition in (EDO-TTF)$_2$PF$_6$
Linker, Gerrit-Jan

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CHAPTER 1. MOTIVATION AND AIM OF THIS RESEARCH

The research in this thesis is aimed at understanding the physics of \((\text{EDO-TTF})_2\text{PF}_6\), and related materials. Theoretical studies are undertaken to provide insight into the geometrical and electronic structure. With this insight, I intend in particular to reach a better understanding of the observed metal-insulator (M-I) transition in \((\text{EDO-TTF})_2\text{PF}_6\) and the related geometrical reorganisations and charge ordering phenomena.

Research conducted in our institute is driven by curiosity of how ‘things work’ at the molecular level. An understanding of which might give clues for the design of new molecules and materials with desirable properties for use in devices in the field of nanotechnology. Material science can be performed by empirical characterisation of devices and measurement of material properties in the laboratory. Material science research can also be performed by using theory. Nowadays ‘in silico’ sciences also make great contributions to the field, as simulations or as calculations based on theory. With that, experiments can be carried out that are impossible to do in the laboratory. While empirical experiments are limited to the study of observable quantities, using theory a wider range of properties can be investigated. Theoretical and computational chemistry is the branch of chemistry that uses computational techniques for research. The sub-field of quantum chemistry uses quantum chemical theory to study the structure and properties of molecules and solids. As a first step, known properties of materials can be studied, and with that knowledge, new properties can be designed and tested. For example, knowing the electronic structure of a material, the effect of chemical modifications on the desired properties can be tested in designed materials before they are actually synthesised in a laboratory. Studies are also possible in which certain interactions are switched off, or in which the system is simplified to its bare essentials.

Examples of such theoretical studies in this thesis include the study of the Peierls instability in the hypothetical hydrogen polymer (section 3.2.3). Another example is the unravelling of the band structure of \((\text{EDO-TTF})_2\text{PF}_6\) (section 3.3.3.6) by breaking up the three-dimensional crystal into two-dimensional slabs of molecular stacks, or further into one-dimensional chains of \(\text{EDO-TTF}\) molecules. The study of the electronic band structure of such hypothetical materials leads to a good understanding of the real system. As a last example I mention the fruitful analysis of crystal orbitals. Frontier crystal orbitals of \((\text{EDO-TTF})_2\text{PF}_6\) have similar characteristics as the orbitals of a single tetramer unit cell, or those of the neutral \((\text{EDO-TTF})_4\) tetramer cluster. The nodal structure even resembles that of the Hückel orbitals of 1,3-butadiene (Figure 17). The realisation is that the properties of \((\text{EDO-TTF})_2\text{PF}_6\) are largely due to electrons that are described by orbitals that are simply linear combinations of molecular HOMOs. This way, the complex physics of the material can be understood in terms of a simpler models.

It is not possible to solve the many body problems in chemistry exactly. To solve the equations of motion, frequently, approximate theory or semi-empirical theory is used in which empirically observed quantities are included as parameters or in which part of the complexity is treated in an approximate or average way. Examples of semi-empirical theory are the Hückel method and also density functional theory can be classed as a semi-empirical method when the parameters used in it are sourced from experiments. An example of approximate theory is the Hartree-Fock \textit{ab initio} theory in which the complexity of electron-electron interactions is treated in an average field way and in which only a single electronic configuration is considered. The results of performing such theoretical chemistry calculations and studies on \((\text{EDO-TTF})_2\text{PF}_6\) are the subject of this thesis.
The work for this PhD project was carried out in a multi-disciplinary environment, one of the strengths of the Zernike research institute. The theoretical work was carried out in the Theoretical Chemistry group and there was collaboration with the Optical Condensed Matter Physics group where I received co-supervision. Receiving feedback from both groups enabled me to better gauge the relevance of my calculations for the material physics.

\((\text{EDO-TTF})_2\text{PF}_6\) is a member of a class of compounds referred to as organic charge transfer (CT) salts. These exciting materials exhibit a wide range of interesting physical phenomena, such as electronic conductance, order-disorder transitions, and many more. As such, they provide a ‘playground’ for material scientists. Consisting of \(\pi\)-stacked, often planar, weakly interacting molecules, many of the electronic properties of members of the material class relate to the CT. By the electron transfer, holes are created in the closed shell electronic structure of electron donor and/or acceptor molecules. Intermolecular interactions cause the molecular electronic levels to broaden into bands in the crystal. The CT can lead to partial filling of these electronic bands, and this gives rise to a so-called band conduction of the crystalline system. The (de)localisation of these holes determine the physics of the material to a large extent. \((\text{EDO-TTF})_2\text{PF}_6\) is a good example of such a material. In this thesis, the physics around the metal-insulator transition in this material is studied as well as the related geometrical reorganisations and charge ordering phenomena. The research is brought in the context of the material class by studying two further materials: TTF-TCNQ and a so called Bechgaard salt. Despite being highly similar to \((\text{EDO-TTF})_2\text{PF}_6\), these materials have different properties. This shows the richness of the physics of these materials. In sections 3.1 to 3.3 of this introductory Part I of the thesis, an exposition of these materials and their physics is given. The research on \((\text{EDO-TTF})_2\text{PF}_6\) is contained in part II and III while the physics of the other materials is discussed in detail in the supplements to this thesis.

\((\text{EDO-TTF})_2\text{PF}_6\), which consists of ethylenedioxy-tetrathiafulvalene (EDO-TTF) electron donor molecules and phosphorhexafluoride (PF\(_6\)) electron acceptor molecules, is an organic crystal that is an electrical conductor at room temperature. This is an eye-catching feature because most solid organic compounds are insulators. The conduction in \((\text{EDO-TTF})_2\text{PF}_6\) occurs in a single crystal direction which coincides with the direction in which the near planar EDO-TTF molecules stack. Upon cooling, \((\text{EDO-TTF})_2\text{PF}_6\) becomes insulating due to a first order transition at \(T_{\text{M-I}} = 278\) K. Within the insulating phase, geometrical deformations apparently stabilise the system. It looks like this behaviour is a consequence of the Peierls theorem (section 3.2.3) that states that any one-dimensional (1D) conductor is unstable with respect to geometrical deformations. Many instabilities interplay in the phase transition of \((\text{EDO-TTF})_2\text{PF}_6\): flexibility of the EDO-TTF molecules, geometrical ordering (GO), charge ordering (CO), anion ordering (AO), and anion disorder. It is interesting to understand the interplay of these instabilities and to know the conditions leading to the phase transition. An intriguing feature of \((\text{EDO-TTF})_2\text{PF}_6\) is that a phase transition can also be induced by light [109, 171]. In this optically induced transition, the electronic state is forcefully altered by means of a local excitation. In the new electronic state, molecules follow the change in electronic structure by means of deformations and repositioning. This process was observed a few years ago [165, 169] with state of the art electron diffraction technology.

In Part II of this thesis I look at single molecule properties. Understanding the properties of the building blocks, the molecules, will help to understand the properties of the \((\text{EDO-TTF})_2\text{PF}_6\) molecular crystal. A salient feature of EDO-TTF is its molecular shape. The neutral molecule is boat-shaped, and it is planar when positively charged. The co-existence of these two molecular geometries in the crystal lies at the heart of the physics of the thermal M-I transition. In chapter 5
Chapter 1

it is shown that molecular charge and molecular shape are directly connected. Located at the bending axes in the molecule, the polarisability of the sulphur atoms of EDO-TTF determines the molecular shape. In positively charged EDO-TTF, most of the hole is located at the sulphur atoms, thereby reducing their polarisability. As a direct consequence, the molecular geometry of EDO-TTF is planar. The direct relationship of the atomic polarisability and the chemical bond angle is the subject of chapter 4. We created a new electrostatic model for general case of an A₂B bond angle. The strength of this classical model is that the bond angle is only dependent on the ratio of the polarisabilities of atoms A and B. This removes the difficulty that arises in similar models for obtaining absolute values for the atomic polarisability in molecules, which can never be determined without arbitrariness. Being a classical model, our model also does not rely on presumptions about hybridisation nor on orbital analysis.

In Part III, I look at properties of the condensed phase of (EDO-TTF)$_2$PF$_6$. The metallic and insulating nature is confirmed in the high and low temperature phase respectively. It is verified that the hole in the high temperature phase is delocalised and we verified that the holes localise into a 0110 charge ordering pattern in the low temperature phase. The thermal transition is found to originate from a Peierls instability. In chapter 6, it is shown that states with different charge ordering patterns are very close in energy and that the best description of the system is obtained by using spin-restricted theory.

From the results of periodic calculations in chapter 7, in which the X-ray crystal geometry for the high temperature phase is used, and in which the whole crystal with all its electrons is treated explicitly, it is shown that (EDO-TTF)$_2$PF$_6$ is a one dimensional conductor. The holes are delocalised along the EDO-TTF molecular stacks. Electronic bands become partially occupied due to the electron transfer to PF$_6$. From the band structure and the Fermi surface we show that the material is an electrical band conductor mainly in the stacking direction while in other directions of the crystal the material exhibits a pseudo-gap. Crucial for the analysis of the thermal transition, we find that the frontier electronic bands are linear combinations of molecular EDO-TTF HOMOs. These electronic bands have negligible PF$_6$ character and from that we conclude that the only role of PF$_6$ seems to be as electron acceptor, and it appears to be a spectator molecule otherwise. Residing in cavities in between the EDO-TTF stacks, the PF$_6$ molecules form spacers. An important conclusion in chapter 7 is that the thermal phase transition is due to a symmetry lowering deformation which becomes manifest with the co-existence of planar and bent molecules in the unit cell. Our calculations confirm that the electronic band structure exhibits a band gap when using the X-ray crystal geometry of the low temperature phase. Confirming the empirically deduced charge ordering, it is shown that a 0110 tetramer charge distribution has formed in the EDO-TTF stacks. Despite the seemingly large difference between the metallic and insulating phase, in which the conductivity drops by a factor of four million, the electronic band structures of the two phases are actually very similar. The band structures in Figure 22 in the introductory text in section 3.3.3.6, illustrate that this is the case. From the band structure of a single EDO-TTF stack that I isolated from the crystal, it becomes clear that the effect of having slightly displaced bent and planar molecules in the unit cell at low temperatures is a reduced broadening of the electronic bands. The band structure of one single EDO-TTF stack having the high temperature X-ray crystal geometry, in which all molecules are equal and planar, and in which they stack regularly, shows only a small valence-conduction band gap. The effect of including more EDO-TTF stacks and PF$_6$ molecules to form a two-dimensional slab/sheet is that the gap disappears and that a contiguous density of states forms. The Fermi level, the energy of the highest filled electronic level in the system, precisely intersects the connection point of the valence and conduction band, highly resembling the Dirac points observed e.g. in the band structure of
graphene. In the band structure of the three dimensional high temperature X-ray crystal, these points shift to above and below the Fermi energy. This causes the conduction band to become somewhat populated at the expense of the depopulation of the valence band. Because the conduction band is anti-bonding between (EDO-TTF)$_2$ dimers and the valence band is bonding, the total effect is a reduced bonding between dimers in the high temperature phase. At low temperatures, the band structure is gapped, dimers bond more and a dimerisation becomes manifest. By unravelling the electronic band structure in this way we reach the conclusion that this dimerisation constitutes a symmetry lowering, hence we interpret the thermal transition as a Peierls transition.

In Peierls’ book “Quantum Theory of Solids” [12], the instability towards an ordered phase is described by applying a perturbing potential to the system of study. In chapter 8, it is explored whether a symmetry lowering potential due to dimerisation of negatively charged PF$_6$ molecules can also cause a transition of the conducting state, in which holes are delocalised along the EDO-TTF columns, to an insulating state. The PF$_6$ molecules in the crystal are relatively free to move from their average positions, with the next neighbour PF$_6$ molecules at approximately 7 Å distance along the stacking direction. An anion dimerisation creates a perturbing potential that acts on the electron density of the EDO-TTF stacks. In chapter 8, I show that anion dimerisation alone is not strong enough to remove the overlap in energy of the valence and conduction band. Both bands shift in energy but not to a sufficient extent. A band gap forms only after dimerisation in the EDO-TTF stack is applied also.

I also show in chapter 8 that an (EDO-TTF)$_2$ stretching displacement leads to the charge ordered state. By following the dimerising (EDO-TTF)$_2$ stretching displacement in the high temperature structure it is shown that a better description of the high temperature phase is obtained in terms of a superposition of the 0110 and 1001 charge ordered states. I managed to separately obtain the 1001 and 0110 charge ordered states when making use of periodic spin-restricted Hartree-Fock theory. Both states are equivalent due to the symmetry of the crystal. Without geometrical distortions, the total energy of both states is the same, and at a displacement of +0.13 Å (-0.13 Å) the 0110 (1001) state shows a minimum. We expect that the barrier between the two states is low enough to be overcome by thermal vibrational excitations at temperatures above T$_{M-I}$=278 K, whereas at lower temperatures the system will reside in either one of the dimerised, charge ordered states.