Theoretical Study of correlated systems using hybrid functionals

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Mainz, Dezember 2010

1 List of Publications

- Charge-Transfer Complex in UHV Co-Deposited Tetramethoxypyrene and Tetracyanoquinodimethane
 K. Medjanik, S. Perkert, S. Naghavi, M. Rudloff, V. Solovyeva, D. Chercka,
 M. Huth, S. A. Nepijko, T. Methfessel, C. Felser, M. Baumgarten, K. Müllen,
 H.J. Elmers, and G. Schönhense
 Phys. Rev. B, 81, 075208 (2010)
- Evaporation Temperature-Tuned Physical Vapor Deposition Growth Engineering of One Dimensional Non-Fermi Liquid TTF-TCNQ Thin Films
 I. Sarkar, M. Laux, J. Demokritova, A. Ruffing, S. Mathias, J. Wei, V. Solovyeva, M. Rudloffc, S.S. Naghavi, C. Felser, M. Huth, and M. Aeschlimann Appl. Phys. Lett. 97, 111906 (2010)
- Electronic Structure of Large Disc-Type Donors and Acceptors
 K. Medjanik, D. Kutnyakhov, S. A. Nepijko, G. Schönhense, S. Naghavi, V. Alijani, C. Felser, R. Rieger, M. Baumgarten, and K. Müllen
 Phys. Chem. Chem. Phys. 12, 7184 (2010)
- I-II-V Half-Heusler Compounds for Optoelectronics: Ab initio Calculations David Kieven, Reiner Klenk, Shahab Naghavi, C. Felser, and Thomas Gruhn Phys. Rev. B, 81, 075208 (2010)
- Electronic and Magnetic Phase Diagram of β-Fe_{1.01}Se with Superconductivity at 36.7 K Under Pressure
 S. Medvedev, T. M. McQueen, A. Troyan, T. Palasyuk, M. I. Eremets, R. J. Cava, S. Naghavi, F. Casper, V. Ksenofontov, G. Wortmann, and C. Felser Nature Materials, 8, 630 (2009)
- Thermoelectric Properties of CoTiSb Based Compounds Joachim Barth, Benjamin Balke, Gerhard H Fecher, Hryhoriy Stryhanyuk, Andrei Gloskovskii, Shahab Naghavi, and C. Felser Journal of Physics D: Applied Physics, 42, 185401 (2009)
- Noninnocent Effect of Axial Ligand on the Heme Degradation Process: a Theoretical Approach to Hydrolysis Pathway of Verdoheme to Biliverdin

Parisa R. Jamaat, Nasser Safari, Mina Ghiasi, S. Shahab al-din Naghavi, and Mansour Zahedi

J. Biol. Inorg. Chem. 13, 121 (2008)

- Homogeneous m-cpba-oxidation of Anthracene by Electron-Withdrawing Metalloporphyrins in Different Reaction Conditions
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- Theoretical Study of Acceptors and Donors Based on Polycyclic Aromatic Molecules Shahab Naghavi, Thomas Gruhn, Vajiheh Alijani, Gerhard H. Fecher, C. Felser, Katerina Medjanik, Dmytro Kutnyakhov, Sergej A. Nepijko, Gerd Schönhense, Ralph Rieger, Martin Baumgarten, and Klaus Müllen J. Mol. Spec. accepted (2010), arXiv:1012.3028
- The Role of Correlations in the High-Pressure Phase of FeSe Shahab Naghavi, Stanislav Chadov, and C. Felser Phys. Rev. B Submitted (2010), arXiv:1011.0848v1
- Prediction of Insulator to Metal Transition in Rubidium Sesquioxide (Rb₄O₆) Under High Pressure
 Shahab Naghavi, Stanislav Chadov, C. Felser, G. H. Fecher, J. Kübler, K. Doll, and M. Jansen (in preparation)
- Theoretical Study of Charge-Transfer Complexes Based on Polycyclic Aromatic Hydrocarbons

Shahab Naghavi, Thomas Gruhn, Claudia Felser, Katerina Medjanik, and Gerd Schönhense (*in preparation*)

2 Zusammenfassung

Diese Arbeit unterstreicht das Potential von Hybridfunktionalen (B3LYP) für die Untersuchung einer groen Bandbreite von Systemen. Durch die Einbeziehung der exakten Hartree-Fock Austauschenergie kann B3LYP für molekulare und kristalline Systeme eingesetzt werden. Zum Beispiel können stark korrelierte Systeme mit B3LYP erfolgreich erforscht werden. Die elektronische Struktur von PAHs wurde mit B3LYP Hybriddichtefunktionalen untersucht. Mit der Δ SCF-Methode wurden Elektronenbindungsenergien bestimmt, welche die mit UPS gewonnenen experimentellen Resultate bestätigen und ergänzen. Symmetrieeigenschaften der molekularen Orbitale wurden analysiert, um eine Zuordnung und Einschätzung der zugehörigen Signalstärke zu ermöglichen. Während σ -artige Orbitale nur schwer durch UPS-Messungen an dünnen Filmen detektiert werden können, bieten Rechnungen eine detaillierte Einsicht in die verborgenen Teile der Spektren. Weiterhin wurden $\pi - \pi$ -Komplexe untersucht, welche von verschiedenen Donor- und Akzeptor-Molekülen gebildet werden. Die Moleküle basieren auf polyzyklischen, aromatischen Kohlenwasserstoffen. Die Einbeziehung von van der Waals-Korrekturen verbessert den intermolekularen Abstand und die Bindungsenergie gegenüber B3LYP-Rechnungen. Eine Verkleinerung der intermolekularen Abstände führt zu einer groen Verschiebung der HOMO- und LUMO-Energie. Aus der Klasse der kristallinen korrelierten Systeme wurden Rb_4O_6 und FeSe untersucht. Im Falle von Rb₄O₆ führen Ladungsordnung und Korrelationen zu einem isolierenden Grundzustand. Das hypothetische druckabhängige Phasendiagramm wurde untersucht. Eine Erhöhung des Drucks führt zu einer vergröerten Bandlücke. Bei etwa 75 GPa wird die Bandbreite W gröer als der Bandabstand U und das System nimmt einen homogen gemischt valenten Zustand mit teilweise besetzten p-Orbitalen an. Für Drücke ab 160 GPa wird W sehr viel gröer als U und das System wird metallisch. Im Fall von FeSe finden wir eine korrelierte und isolierende Phase bei hohen Drücken, während das System bei niedrigen Drücken supraleitendes Verhalten zeigt. Die Berechnungen der Elektronenstruktur mit dem Hybridfunktional B3LYP führt zum korrekten halbleitenden Grundzustand in der NiAs- und MnP-Struktur von FeSe. Die Rolle der Korrelationen, der Stöchiometrie und der Nähe zum Magnetismus wird besprochen. Im Speziellen wird gezeigt, dass die Phase mit NiAs-Struktur starke lokale Korrelationen aufweist, was zu einem halbleitenden Zustand in einem weiten Druckbereich führt.

3 Abstract

This work emphasizes the potential of hybrid functionals (B3LYP) in the study of a wide range systems. This functional by take advantage of the exact Hartree-Fock exchange, can be used for both molecular and crystalline systems. For example, strongly correlated systems are studied by B3LYP, successfully.

The electronic structure of the PAHs has been studied with the help of B3LYP hybrid density functionals. Using the Δ SCF method, electron binding energies have been determined which affirm, specify and complement the experiment results measured by UPS. Symmetry properties of molecular orbitals are analyzed for a categorization and an estimate of the related signal strength. While σ -like orbitals are difficult to detect by UPS measurements of condensed films, calculations provide a detailed insight into the hidden parts of the spectra. Afterward, the $\pi - \pi$ complexes formed by several donor and acceptor molecules based on polycyclic aromatic hydrocarbons have been studied. For the charge transfer complexes, the DFT calculation provide minimum one the potential energy surface. This attraction is caused by Coulomb interactions. However, the attraction based on Coulomb interaction is not the strongest interaction in CTCs. The vdW corrections improve the intermolecular distances as well as the binding energy. Decreasing the intermolecular distances leads to large shifts in the HOMO and LUMO energies. For the crystalline systems Rb_4O_6 and FeSe have been studied as a correlated systems. In the case of Rb_4O_6 charge ordering and correlations leads to an insulating ground state in this system. The hypothetical pressure dependent phase diagram was studied. Applying pressure leads to increasing band-width. At about 75 GPa, W exceeds U the system becomes homogeneous mixed valent with a fractional occupation of the p-orbitals and finally for at 160 GPa W>> U the system becomes metallic. In the case of FeSe there is a correlated and insulating phases at high pressures, while at low pressure the system is superconducting. The electronic structure calculation with the hybrid functional B3LYP leads to the correct semiconducting ground state for NiAs- and MnP-type structure of FeSe. The role of correlation, stoichiometry and the borderline to magnetism are discussed. In particular, it is shown that the NiAs-phase structure exhibits strong local correlations which lead to a semiconducting state within the broad pressure range.

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4 Introduction

Talking about correlations in condensed matter systems, everybody associates immediately 3d and 4f systems such as the high temperature superconductors or heavy Fermions. However recently in the context of electron or hole doped insulators such as graphene and MgO:N magnetism and correlation were considered. Although electron correlations and correlated systems have been studied in detail in d and f-electron systems, correlation in p- and s-shell systems are new and unexpected. This is not surprising due to the fact that the large family of stable organic compounds are closed shell systems based on the "octet rule (same electronic configuration as a noble gas) and therefore insulators. By adding or removing partial charge or a complete electron from the closed shell molecule, the electronic properties of the system will change. This effect can be observed in the charge transfer (CT) complexes where electron donor and electron acceptor molecules interact. As a result of the charge transfer and amount of the charge transfer, CT-salts show Mott-insulating behavior, conductivity, superconductivity, and magnetic properties [1, 2]. Mott-insulating behaviour and magnetism are signatures for strong correlations. In the case of complete charge transfer (1 electron per molecule) such as Alkali-7,7,8,8-tetracyanoquinodimethane (TCNQ) [3, 4, 5] the system is a Mott-Hubbard insulator in which the charges are localized on the anion radical site $(TCNQ^{\bullet-})$ as a result of electron correlations. Partial charge transfer can lead to a metallic state like Bechgaard salt [6, 7], TTF-TCNQ [8] and can render superconductivity. Charge transfer insulator, Mott-insulator, antiferromagnetism and superconductivity are often competing ground states in 3d systems as well as in charge transfer salts. In this context the potential of new acceptors and donors for charge transfer supercondutors, based on the coronene family were studied theoretically and compared with recent experimental results. A metal-insulator transition can result from charge ordering and is determined by the balance between Coulomb correlation U and the band width W (sometimes also described by the hopping matrix element t). Another prominent example of an open 2s-system are the $[BiO_3]^{2-}$ which will not be discussed in this thesis. However the optimal systems to study correlations in 2psystems are radicals, which are mostly not stable under ambient conditions. As the most exciting correlated 2p-shell system, Rb_4O_6 a member of the Rb_xO_y family has been studied in detail in this thesis. This system was predicted to be a half metallic ferromagnet based on local density calculations. Charge ordering and correlations

leads to an insulating ground state in this system. The hypothetical pressure dependent phase diagram was studied. Applying pressure leads to increasing band-width. If W exceeds U the system becomes homogeneous mixed valent with a fractional occupation of the p-orbitals and finally for W>> U the system becomes metallic and maybe also superconducting like oxygen or Y_4C_6 under pressure.

5 Electronic structure calculation

5.1 Hartree-Fock approximation

Finding an approximate solution to the Schrödinger equation is a crucial task, since except for very simple cases like H_2^+ , an exact solution can not be found. One of the methods to solve the problem is the Hartree-Fock approximation. Hartree-Fock plays an important role in elucidating modern chemistry and is a first step towards more accurate approximations. In order to approximate the wave function of an N electron system, one can assume that electrons are non-interacting particles. If this is true, the Hamiltonian for electrons will be written as:

$$H = \sum_{i=1}^{N} h(i)$$
 (5.1)

where h(i) describes the kinetic energy and the potential energy of electron *i*. This form is obtained if we neglect the electron-electron interaction. In the mentioned equation h(i) is an effective one-electron Hamiltonian that includes the effect of electron-electron repulsion in some average way. Operator h(i) has a set of eigenfunctions that one can call spin orbitals χ_j ,

$$h(i)\chi_j(x_i) = \varepsilon_j\chi_j(x_i) \tag{5.2}$$

When the total Hamiltonian (H) is simply a sum of one-electron operators, h(i), it follows that the eigenfunctions ψ of H are a product of the one-electron wave functions χ_j ,

$$\psi^{HP}(x_1, x_2, ..., x_N) = \chi_i(x_1)\chi_j(x_2)...\chi_k(x_N)$$
(5.3)

then the eigenvalue E of H,

$$H\psi^{HP} = E\psi^{HP} \tag{5.4}$$

is just the sum of the one-electron energies:

$$E = \varepsilon_i + \varepsilon_j + \ldots + \varepsilon_k \tag{5.5}$$

Such an expression is known as the Hartree product.

Unfortunately, the Hartree product does not satisfy the antisymmetry principle, which means exchanging two electrons does not change the sign of the Hartree product. An antisymmetrized product can be obtained by using a *Slater determinant*. For an N-electron system the *Slater determinant* is:

$$\psi(x_1, x_2, ..., x_N) = (N!)^{-1/2} \begin{vmatrix} \chi_i(x_1) & \chi_j(x_1) & ... & \chi_k(x_1) \\ \chi_i(x_2) & \chi_j(x_2) & ... & \chi_k(x_2) \\ . & . & . \\ . & . & . \\ \chi_i(x_N) & \chi_j(x_N) & ... & \chi_k(x_N) \end{vmatrix}$$
(5.6)

The Slater determinant has N electrons occupying N spin orbitals $(\chi_i, \chi_j, ..., \chi_k)$ without specifying which electron is in which orbital. Interchanging the coordinates of two electrons corresponds to an interchange of two rows of the Slater determinant changes the sign of the determinant. Thus, the Slater determinant meets the requirement of the antisymmetry principle. In the Hartree-Fock approximation the N-electron wave function is approximated by the antisymmetrized product of N one-electron wave functions $\chi_i(\mathbf{x}_i)$. Within the single Slater determinant, the motion of two electrons with parallel spins (Fermi-correlation) is correlated but the motion of electrons with opposite spins remains uncorrelated. Hartree-Fock method provides an exact description of the electron exchange (electrons with parallel spins), while correlation effects can not be considered in the Hartree-Fock approximation. Therefore, the lowest energy that would be obtained by the Hartree-Fock method is an upper bound to the true ground state energy of a given molecule which is called Hartree-Fock limit. This energy is not the same as the energy for the true electron wave function because the Hartree-Fock method does not describe correctly how electrons influence each other. Although the post-Hartree-Fock methods can solve the correlation problem, they are applicable to the small molecules and require a lot of computational time for large molecules. They have the important merit that the accuracy can be systematically improved by enlarging the size of calculation.

5.2 Density functional theory

Parallel to the Hartree-Fock approach, described in the previous part, a different idea was proposed by L.H. Thomas and E. Fermi, at about the same time as Hartree (1927-1928), that the full electronic density was the fundamental variable of the many-body problem. From this idea they derived a differential equation for density without resorting to one-electron orbitals (Thomas, 1927; Fermi, 1928). The original Thomas-Fermi approximation was actually too crude, mainly because the approximation used for the kinetic energy of electrons ($\int \rho^{5/3}(\bar{\mathbf{r}}) d\mathbf{r}$) was unable to sustain the bound states. It means within the Thomas-Fermi model no molecular system is stable with respect to its fragment! However, it sets up the basis for the later development of *density functional theory* (DFT). Conceptually, the focus changes in DFT from a many-body Schrödinger equation, which involves a many-body wavefunction $\Psi(x)$ where x indicates both space and spin coordinate. The single particle density is related to Ψ by the following equation:

$$\rho(r_1) = N \int \cdots \int |\Psi(x_1, x_2, x_3, \dots x_N)|^2 \, ds_1 dx_2 dx_3 \dots dx_N \tag{5.7}$$

 $\rho(\bar{\mathbf{r}})$ determines the probability of finding any of the N electrons within the volume element $d^3(\mathbf{r})$ but with arbitrary spin while the other N-1 electrons have arbitrary positions and spin in the state represented by Ψ . The density ρ in this case is a much simpler quantity than Ψ because it depends on three spatial coordinates (x, y, z). Therefore, density is a function of only 3 spatial variables, $\mathbf{r}(x, y, z)$, so it is a much easier function to work with, in practice.

5.2.1 The Hohenberg-Kohn theorems

Today's density functional theory was born in 1964 when a landmark paper by Hohenberg and Kohn appeared in the Physical Review [9]. The first Hohenberg-Kohn theorem provides the proof about the validity of the arguments given at the beginning of the previous part. Quoting directly from the Hohenberg/Kohn paper [9], this first theorem states that:

the external potential $V_{ext}(\bar{\mathbf{r}})$ is (to within a constant) a unique functional of $\rho(\bar{\mathbf{r}})$; since, in turn, $V_{ext}(\bar{\mathbf{r}})$ fixes H we see that the full many particle ground state is a unique functional of $\rho(\bar{\mathbf{r}})$.

The authors conclude that each ground state electron density belongs to exactly one external potential. Since ρ determines the number of electrons, it follows that $\rho(\bar{\mathbf{r}})$ also determines the ground state wave function Ψ and all other electronic properties of the system as summarized below:

$$\rho(0) \Rightarrow \{N, Z_A, R_A\} \Rightarrow H \Rightarrow \Psi_0 \Rightarrow E_0 (and all properties)$$
(5.8)

 N, R_A , and Z_A are the number of electrons, the position of the nuclei in space, and the charges of the nuclei, respectively. The ground state energy of the system as a functional of the ground state density can be written as:

$$E_0[\rho_0] = T[\rho_0] + E_{ee}[\rho_0] + E_{Ne}[\rho_0]$$
(5.9)

since $E_{Ne} = \int \rho_0(\bar{\mathbf{r}}) V_{Ne} dr$ and has :

$$E_0[\rho_0] = \int \rho_0(\bar{\mathbf{r}}) V_{Ne} dr + T[\rho_0] + E_{ee}[\rho_0].$$
(5.10)

 E_{Ne} is an external potential which is fully defined by the attraction between the nuclei and electrons. In Equation 5.9 and 5.10 only the external potential which describe the nuclei-electron interaction is system dependent and the remaining parts of the kinetic energy T and electron-electron interaction E_{ee} are universal. By collecting the universal part as a system-independent Hohenberg-Kohn functional $F_{HK}[\rho_0]$, the Equation 5.10 gives:

$$E_0[\rho_0] = \int \rho_0(\bar{\mathbf{r}}) V_{Ne} dr + F_{HK}[\rho_0].$$
 (5.11)

The Hohenberg-Kohn functional is important in DFT. If it was known exactly we would have solved the Schrödinger equation exactly, and since it is an universal functional, it is not dependent to the system on hand. This functional F_{HK} contains the kinetic energy $T[\rho]$ and electron-electron interaction $E_{ee}[\rho]$. Concerning the E_{ee} part we can separate it into two parts as shown in Equation 5.12:

$$E_{ee}[\rho] = \frac{1}{2} \iint \frac{\rho(\bar{\mathbf{r}}_1)\rho(r_2)}{\rho(\bar{\mathbf{r}}_{12})} dr_1 dr_2 + E_{ncl}[\rho] = J[\rho] + E_{ncl}[\rho].$$
(5.12)

The first part in Equation 5.12 is the classical repulsion $J[\rho]$ which is already wellknown, and the second part is a *non-classical* contribution to the electron-electron interaction. The second part $E_{ncl}[\rho]$ is a very elusive and important quantity, which has contributions of self-interaction corrections, exchange and Coulomb correlations.

The second Hohenberg-Kohn theorem provides the energy variational principle. This theorem states that

 $F_{HK}[\rho]$ the functional that is used to calculate the ground-state energy of the system will generate the lowest energy if and only if the input density is the true ground-state density, ρ_0 .

The concept of the second theorem is that the density which minimizes the total energy is the exact ground-state density. In the present context, this theorem can be expressed as :

$$E_0 \leqslant E[\tilde{\rho}] = T[\tilde{\rho}] + E_{Ne}[\tilde{\rho}] + E_{ee}[\tilde{\rho}]$$
(5.13)

this means that for any trial density $\tilde{\rho}(\bar{\mathbf{r}})$ the energy obtained from the functional given in Equation 5.11 represent an upper bound to the true ground-state energy E_0 . This is analogous to the variational principle for wave functions.

5.2.2 The Kohn-Sham approach

Unfortunately, the universal functional $F_{HK}[\rho(\bar{\mathbf{r}})]$ already discussed in 5.1 is not known. To solve this problem, Kohn and Sham [10] introduced the concept of a non-interacting reference system built from a set of orbital (one electron function) such that the major part of the kinetic energy can be computed to good accuracy. This leads to independentparticle equations for the non-interacting system that can be considered soluble. They suggested to use the expression similar to the non-interacting Hartree-Fock in order to obtain the exact kinetic energy of the non-interacting reference system with the same density as the real interacting one. The kinetic energy (in Hartree units) can be written as:

$$T_s = -\frac{1}{2} \sum_{i}^{N} \langle \phi_i | \bigtriangledown^2 | \phi_i \rangle \tag{5.14}$$

Of course, T_s is not equal to the true kinetic energy of the interacting system, even if the systems have the same density. Kohn-Sham (KS) considered this problem by introducing the following separation of the functional $F[\rho]$.

$$F[\rho] = T_s[\rho] + J[\rho] + E_{xc}[\rho]$$
(5.15)

where E_{xc} is the exchange-correlation energy and can be defined as

$$E_{xc} = (T[\rho] - T_s[\rho]) + (E_{ee}[\rho] - J[\rho]) = T_c[\rho] + E_{ncl}[\rho]$$
(5.16)

Therefore, the remaining part of the true kinetic energy T_c which is not covered by the non-interacting kinetic energy T_s is hidden in E_{xc} . In other words, the exchangecorrelation energy E_{xc} is the functional which contains every thing that is unknown. It should be noted that no approximation is used in the KS approach and if E_{xc} was known exactly, the total energy would be calculated exactly.

5.2.3 Functionals for exchange and correlation

The crucial quantity in the KS approach is the exchange-correlation energy, which is expressed as a functional of the density, $E_{xc}[\rho]$. In order to estimate the exchangecorrelation functional we need to make a model. The idea of a hypothetical uniform electron gas is at the center of the local density approximation (LDA). This is the system in which electrons move on a positive background charge distribution such that the total ensemble is electrically neutral. The local density approximation (LDA) is a simple expression for $E_{xc}[\rho(\bar{\mathbf{r}})]$ and it is based on the assumption that the real $E_{xc}[\rho(\bar{\mathbf{r}})]$ is equal to the exchange-correlation energy per electron of the homogeneous electron gas of the same density $\rho(\bar{\mathbf{r}})$

$$E_{xc}^{LDA}[\rho(\bar{\mathbf{r}})] = \int \rho(\bar{\mathbf{r}}) \varepsilon_{xc}(\rho(\bar{\mathbf{r}})) \, dr$$
(5.17)

where $\varepsilon(\rho(\bar{\mathbf{r}}))$ is the exchange-correlation energy. This energy per particle is weighted with the probability $\rho(r)$ that there is in fact an electron in the position in space. Writing E_{xc} in this way defines the local density approximation (LDA). If we extend the LDA to the unrestricted case, we arrive at the *local spin-density approximation* (LSDA). For the LSDA the Eq. 5.17 replaced by:

$$E_{xc}^{LSDA}[\rho_{\alpha},\rho_{\beta}] = \int \rho(\bar{\mathbf{r}})\varepsilon_{xc}(\rho_{\alpha}(\bar{\mathbf{r}}),\rho_{\beta}(\bar{\mathbf{r}})) dr$$
(5.18)

The LDA works fine as long as $\rho(\bar{\mathbf{r}})$ is varying slowly. Hence, for the many years in which the LDA was the only approximation available for E_{xc} , density functional theory was mostly employed by solid-state physicists and hardly had any impact on the computational chemistry. LDA causes a dramatic overbinding and a substantial error in the atomization energy of molecules. The overbinding tendency of the local density approximation can be rationalized in terms of exchange hole properties. The LDA hole is spherically symmetric around the reference system which is more suitable for the binding state. To extend density approximation to systems with a more significant non-homogeneous distribution, several technics have been proposed. The most successful one is the generalized gradient approximation (GGA), where the real $E_{xc}(\rho(\bar{\mathbf{r}}))$ is expressed as a functional of density $\rho(\bar{\mathbf{r}})$ and its gradient. It can be generically written as

$$E_{xc}^{GGA}[\rho_{\alpha},\rho_{\beta}] = \int f(\rho_{\alpha},\rho_{\beta},\nabla\rho_{\alpha},\nabla\rho_{\beta}) dr$$
(5.19)

The GGA formalism gives a better description of inhomogeneous systems, like transition metal, and significantly improves the binding energy. However, although GGA shows an improvement over LDA, its accuracy must be improved for very localized systems such as biological molecules and crystalline systems with f and d states in which on-site Coulomb correlations are important.

5.2.4 Hybrid functionals

Exchange contributions are larger in absolute value than correlation effects; therefore, an accurate expression for the exchange functional is essential for obtaining the accurate result in molecular systems. The exchange energy of the Slater determinant (similar to Hartree-Fock) can be computed exactly and can be considered as a delocalized exchange. Therefore the first idea is mixing of E_x^{exact} with the E_c^{KS} . The exchange-

correlation energy is

$$E_{xc} = E_x^{exact} + E_c^{KS} \tag{5.20}$$

This idea has a serious problem in this formalism. Here we combine the exact delocalized exchange hole with a localized model for correlation. Because the cancellation between two individual holes can not happen, the resulting total hole has a wrong characteristic. Therefore, there is no special improvement in the obtained results.

Another approach to include the exact exchange has been made by Becke in 1993, which is known as a hybrid density functional [11, 12]. Hybrid functional in this formalism can be understood by looking at an equivalent expression for exchange-correlation energy of the KS scheme as shown in Equation 5.21. Becke [12] showed that the proper starting point for hybrid theory is the adiabatic connection formula [13, 14, 15]

$$E_{xc} = \int_0^1 U_{ncl}^\lambda \ d\lambda \tag{5.21}$$

with

$$U_{ncl}^{\lambda} = \langle \Psi_{\lambda} | V_{ee} | \Psi_{\lambda} \rangle - \frac{e^2}{2} \iint \frac{\rho(\bar{\mathbf{r}}) \, \rho'(\bar{\mathbf{r}})}{|r - r'|} \, dr dr' \tag{5.22}$$

At $\lambda = 0$ we are dealing with the non-interacting system and $E_{ncl}^{\lambda=0}$ corresponds to the exchange only (no correlation) and can be computed exactly. At $\lambda = 1$, the nonclassical contribution are for the fully interacting system, containing the exchange and correlation contributions. The simplest approximation to solve the Equation 5.21 is to assume that E_{ncl}^{λ} is a linear function of λ which leads to

$$E_{xc}^{HH} = \frac{1}{2} E_{xc}^{\lambda=0} + \frac{1}{2} E_{xc}^{\lambda=1}$$
(5.23)

Using the LDA exchange-correlation functional for $E_{ncl}^{\lambda=1}$ in Equation 5.23 represents the *half-and-half* combination of the exact exchange and the density functional exchange correlation by Becke [12]. The next step taken by Becke, was to introduce semi empirical coefficients to determine the weights of various components of the exchange-correlation energy expression as shown in the following equation

$$E_{xc}^{B3} = E_{xc}^{LSDA} + a(E_{xc}^{\lambda=0} - E_x^{LSDA}) + bE_x^B + cE_c^{PW91}$$
(5.24)

The three empirical parameters (a,b and c) were chosen to reproduce the atomization and ionization energies as well as proton affinities included in the G2 data base. This leads to a=0.20, b=0.72 and c=0.81. Here, *a* specified the amount of exact exchange, while b and c control the contribution of exchange and correlation.

The most popular hybrid functional is B3LYP [16]. The formalism is similar to the original form of Becke shown in Equation 5.24. In B3LYP the PW91 correlation functional is replaced by the empirical LYP functional. The same parameter (a,b and c) as in the original work of Becke are used. The B3LYP formalism can be written as :

$$E_{xc}^{B3LYP} = (1-a)E_x^{LSDA} + aE_{xc}^{\lambda=0} + bE_x^{B88} + cE_c^{LYP} + (1-c)E_c^{LSD}$$
(5.25)

For the B3LYP functional the average error with respect to the G2 data base is around 2 kcal/mol. Many different hybrid functionals based on the Becke's origin idea have been proposed. It should be clear that in general the parameters (a,b,c) are certainly not universal. Therefore, applying the hybrid functional on the new systems like transition metals should be done with care since the parameters are not fitted for them. Although the B3LYP and other hybrid functionals are common in chemistry and molecular calculations, they are new and not very popular in solid state studies. The application of hybrid functionals on crystalline compounds (described under the periodic boundary conditions (PBC)) has not been possible until the late 1990s, when they have been coded in CRYSTAL98. It is shown that in many cases they can show the right band gap where the local density approximation (LDA) and other standard functionals fail [17, 18, 19, 20, 21, 22].

5.3 Basis set

The basis set is a set of mathematical functions which construct the wave function. In general the basis sets can be categorized by three types: atomic sphere (AS) methods, plane-wave (PW) methods, and localized atomic-like orbitals methods. The first two methods are popular in solid state physics where periodic systems are mainly studied, while the later one has been common in chemistry and recently is getting popular in solid state physics. Since in this thesis Gaussian basis sets are implemented for the both molecular and periodic systems, in the following this basis set will be described extensively.

Gaussian type orbitals (GTOs) can be written in terms of Cartesian coordinates as shown in Equation 5.26 :

$$\chi^{GTO} = N x^{l_x} y^{l_y} z^{l_z} e^{-\alpha r^2} \tag{5.26}$$

N is a normalization factor. The sum of l_x , l_y and l_z determines the type of orbitals (for example $l_x + l_y + l_z = 1$ is a *p*-orbital). α represents the orbital exponent that shows how compact (large α) or diffuse (small α) is the resulting function. The r^2 dependence in the exponential is a deficiency of the GTOs with respect to the *Slater-type orbitals* STOs. The STO function is defined as

$$\chi^{STO} = Nr^{n-1}e^{-\xi r}Y_{lm}(\theta,\varphi) \tag{5.27}$$

Here n, is a principal quantum number and ξ is a constant related to the effective charge of the nucleus i.e. the nuclear charge being partly shielded by electrons. Y_{lm} is a spherical harmonic which describes the angular part of the wave function.

GTOs have two main problems. First an improper behavior near the nuclei at $r \to 0$, while Slater type functions show a correct behavior at $r \to 0$ with a discontinuous behavior. GTO which is a bell shaped function has a slope of zero at $r \to 0$. Another problem is that GTO falls off too rapidly far from the nuclei compared with the STO. Therefore, the tail of the wave function in the GTO is represented poorly. A rough estimate says that three time as many GTOs as STOs are required in order to reach the same level of accuracy. One of the disadvantages of STOs is that many-center integrals such as Coulomb and HF-exchange terms are difficult to compute with STOs. Therefore it does not play a role in modern wave function based quantum chemistry codes. One of the advantages of the Gaussian basis set is that the product of two Gaussian functions is another Gaussian function. As a result, for the calculations of Coulomb and HFexchange terms the analytical solution is available for the Gaussian functions. Therefore the GTO basis function in HF and related methods is popular because very efficient algorithms exist for analytically calculating the many-center integrals.

In order to improve the GTO basis sets, one usually employs a contracted GTO basis set, in which several primitive Gaussian functions are mixed to give an *contracted Gaussian function* (CGF) as shown in Equation 5.28

$$\chi_j^{CGF} = \sum_i^M c_{ij} \chi_a^{GTO} \tag{5.28}$$

Here, M is the number of Gaussian primitives used in a linear combination. As discussed before at least M=3 is required to reach the accuracy of STOs, which is named the minimal basis set and a typical representation is STO-3G in which 3 *primitive* GTO functions are combined to one CGF. The next step for improvement of GTO basis sets is a doubling of all basis functions known as *Double Zeta* (DZ) basis sets. It can also be improved by using a *Triple Zeta* (TZ) which contains three times as many functions as the minimum basis. Higher orders of Zeta can be used either. Valence electrons are responsible for the chemical bonding, and they are much more important than the core electrons. One kind of DZ basis only doubles the number of valence orbitals known as *split valence* basis set.

Pople basis sets are a kind of split valence basis sets. Pople basis sets with the X-Y1G notation like 6-31G are one of the popular basis sets in the field of computational chemistry. X shows the number of primitives for representing the core electrons. Y1 shows the double split valence and Y11 the triple split valence. Y is the number of primitives contracted for the inner part of valence orbitals and 1 is the number of primi-

itives for describing the outermost valence orbitals. Polarizations are denoted after the "G" such as G (d, p, f, etc.) and the grade of diffuse before (++) like 6-31++G(d, p). In the shown notations, p is polarization for hydrogen and d polarization for heavier elements like carbon.

It should be noted that GTOs have some advantages in solid state calculations. Although, for the DFT in periodic systems *plane wave* methods are powerful and the natural choice for such systems, they face a difficulty in the case of hybrid density functionals like B3LYP. In these cases many-center electronic integrals for the exact exchange part (HF-exchange) are notoriously difficult to compute with the plane waves, while algorithms for analytical solution with GTOs are available. Therefore, by using the GTOs, the hybrid functionals as well as the pure Hartree-Fock methods are much faster and more accurate than with plane waves basis functions.

5.4 From molecule to solid

Electronic configuration of a molecule can be represented by molecular orbitals (MOs) provided by the molecular orbital theory. One common approximation that allows us to generate a molecular orbital diagram for some small molecules is called *Linear Combination of Atomic Orbitals* (LCAO) approach. The goal of the molecular orbital theory is to describe molecules in a similar way as describing atoms, that is terms of orbitals, orbital diagrams and electron configurations. A simple example of MO for H₂ is shown in Fig. 5.1. As it is seen in Fig. 5.1 the symmetric contribution called bonding (σ) is lower than the asymmetric contribution called anti-bonding orbital (σ^*). In general by increasing the nodal planes the energy of MOs increases. The highest occupied molecular orbital is HOMO. The lowest unoccupied molecular orbital is called LUMO.

The number of molecular orbitals (MOs) increases when the number of atomic orbitals increases. Therefore, in the solid or surface which are very large one has to deal with a very large number of states. If there are n atomic orbitals in the unit cell and the macroscopic crystal has N unit cells (N approach Avogadro), then we will have the nN MO-levels. Many of them are very close together so that we can not distinguish them. Instead of separate MOs, there is an energy band here. Within energy bands, energy levels are so numerous as to be nearly continuous as plotted in the Fig. 5.2. Therefore, instead of HOMO the Fermi energy indicates the highest level that is occupied by electrons. An instructive example is a one dimensional chain of hydrogen molecules. In this case we encounter the periodic concept instead of a molecule, but because the chain is just an overlapping of 1s orbitals, it is easy to solve. Such a one-dimensional



Figure 5.1: Construction of the MOs from the atomic orbitals is shown for the hydrogen molecule. The corresponding arrangement of the orbitals is also shown. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are shown here. In this case HOMO and LUMO are the bonding (σ) and the anti-bonding (σ^*) respectively.

periodic system can be represented as follow:

$$- \stackrel{\chi_0}{\bullet} - \stackrel{\chi_1}{\bullet} - \stackrel{\chi_2}{\bullet} - \stackrel{\chi_3}{\bullet} - \stackrel{\chi_4}{\bullet} -$$

$$\psi_k = \sum_n e^{ikna} \chi_n$$
(5.29)

In Equation 5.29, k is the wave vector and a and χ_n are unit cell and basis function, respectively. Now one can evaluate the form of the crystal wave function as it varies with the reciprocal-space vector k. For k=0 (center of BZ) Equation 5.29 gives:

$$\psi^{k=0} = H = \sum_{n} \chi_n = \chi_0 + \chi_1 + \chi_2 + \chi_3 + \chi_4 + \dots$$
 (5.30)

Another situation is when $k = \frac{\pi}{a}$ (edge of first BZ). The e^{ikx} can be written as $\cos(x) + i\sin(x)$. When $k = \frac{\pi}{a}$, the sin term is zero, leaving only the $\cos(n\pi)$, which can be expressed as $(-1)^n$. Therefore, Equation 5.29 gives:

$$\psi^{\frac{\pi}{a}} = H = \sum_{n} (-1)^{n} \chi_{n} = \chi_{0} - \chi_{1} + \chi_{2} - \chi_{3} + \chi_{4} - \dots$$
(5.31)

When the atomic orbital is symmetric to the C_2 rotation (perpendicular to the overlap direction), then at k = 0 we have the bonding state, otherwise it is located at $k = \frac{\pi}{a}$.



The band dispersion for the s orbital is shown in Fig. 5.2. The dispersion E(k) as

Figure 5.2: Variation of the energy with respect to the k for a 1D lattice of the s orbitals and the density of state (DOS) are plotted. The corresponding arrangements of the orbitals are also shown. The band width (W) or dispersion is shown as a difference between the highest and the lowest levels in the bands.

drawn in Fig. 5.2 is named the band structure. The band width (W) is the difference in energy between the highest and the lowest levels in the band. The overlap between the interacting orbitals affects the band width; the greater the overlap the larger the band width. For example, pressure can increase the band width by decreasing the bond length and thus increasing the overlap. As seen in Fig. 5.2, DOS(E) is proportional to the inverse of slope of E(k) vs k; hence, the flatter the band, the greater the density of state. Aforementioned button up approach (from molecule to solid) is useful to show that in the solid the important concept is periodicity. Such an approach that the electronic structure of the solid constructs from the wave function of isolated atoms located at each atomic sites called *tight binding approximation* (TBA). The method is closely related to the LCAO method used for molecules.

Another common approach is the nearly free electron model (NFE) where the electrons move freely under the rather weak influence of the nuclei. This method starts from exactly the opposite premise of the LCAO approach, where the nuclei and the orbitals are starting points of the electronic structure.

5.5 HOMO and LUMO calculations

The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are the two most important molecular orbitals. At the Hartree-Fock (HF) level, Koopmans theorem suggests that the energy of the HOMO is a good approximation to the negative experimental ionization potential (-IP) [23]. Similarly, it

suggests that the electron affinity (EA) for an N-electron system is equal to the negative of the LUMO energy, assuming that the orbitals do not relax. In general, the prediction of the EA using Koopmans theorem is unreliable due to the generally large effect of orbital relaxation on the LUMO eigenvalue. In addition to the question of the effect of relaxation on the validity of Koopmans theorem, there has been a substantial uncertainty as to the degree of physical significance of the Kohn Sham (KS) orbitals of density functional theory (DFT) applied within the KS framework [10].

A standard view expressed in the literature for the KS orbital energies of the occupied molecular orbitals lower than HOMO, is that they are merely auxiliary quantities. However, several authors have pointed to the interpretative power of KS orbitals in traditional qualitative molecular orbital schemes [24, 25, 26, 27], and KS orbitals also show uniform shift with respect to ionization energies [25, 28]. In this sense, B3LYP with its exact Hartree-Fock exchange contribution leads to a better description of ionization energies by reducing the related shift [27]. However, there is a difference between a calculated HOMO eigenvalue and the experimental one [29].

Electron binding energies or ionization potentials of molecules can be calculated by the delta self consistent field (Δ SCF) method. In this method effects of the final state can be included in the calculation. For comparison with UPS measurements, the ground and final states have the same geometry named the vertical ionization potential. In this way, first the vertical ionization potentials (IP_v,1) are calculated as a difference in the total energy between a molecule and its radical cation at the former geometry. For the higher ionization energies (IP_v,1+n), the energy difference (Δ E) between IP_v,1 and the HOMO energy is added to the energy of next higher orbitals ε_{HOMO-n} (with "higher" referring to higher electron binding energy not higher total energy) as a uniform shift [30, 31, 25].

$$IP_{v,1} - |\varepsilon_{HOMO}| = \Delta E$$

$$|\varepsilon_{HOMO-n}| + \Delta E = IP_{v,1+n}$$
(5.32)

According to Equation 5.32 the eigenvalue of the HOMO-n orbital should be used in order to calculate the electron binding energy (BE) of HOMO-n.

HOMO-LUMO gaps calculated with B3LYP are also close to the first electronic excitation energies [29]. Such a behavior is also observed after applying the B3LYP to crystalline systems [32]. In these cases calculated band gaps show a better agreement than pure DFT calculations with respect to the experimental results.

5.6 Quantum chemistry codes

5.6.1 Gaussian03

The Gaussian series of electronic structure programs [33], which can calculate energies, and frequencies of molecular structures, along with numerous molecular properties is used for the molecular calculations. As it is clear from the name this program uses the Gaussian basis set for the electronic structure calculation of molecules. This program can provide molecular mechanics, semi empirical methods and *ab initio* calculations containing the HF, post HF and DFT methods. Moreover, excited state calculations can be done by different methods in this program.

5.6.2 CRYSTAL06

The CRYSTAL 06 program [34] is known for *ab initio* Hartree-Fock calculations of periodic systems, slabs and polymers; however, it can do different kinds of calculations for molecular systems as well. Other DFT exchange-correlations are also included in this program. The program provides full and constraint structure optimizations followed by frequency calculations at the Γ point. CRYSTAL06 can calculate the band structure and density of states and different properties of periodic systems.

The advantage of CRYSTAL is that it can use Gaussian basis sets for periodic systems. It can solve the Kohn-Sham or Hartree-Fock equation on the basis of orbital, by a fully "ab initio" approach. Unlike plane waves, however, the orbitals must be chosen for the given system to be accurate and efficient. In addition, Gaussian basis sets can facilitate many-center integrals calculation as already discussed in 5.3. Doing *Hartree-Fock* calculations is a unique performance of CRYSTAL. In order to implement the localized Gaussian basis sets in a periodic system, the wave functions (crystalline orbitals) are expanded as a linear combination of Bloch functions defined in terms of local functions. The local functions are expressed as a linear combination of individually normalized Gaussian type functions.

Gaussian basis sets in crystalline systems should be used with care. Most of the databases contain only the Gaussian basis sets optimized for molecular systems. Therefore, they should be optimized for use in crystalline systems. In the crystalline systems there is a limitation for using the diffuse functions and the functions with an α exponent less than 0.1 should be removed. The easiest strategy is to optimized just the outer exponents in order to minimize the energy of the system.

5.7 Structure of the thesis

As described in the last part, main purpose of this thesis is the electronic structure calculation of correlated systems by means of hybrid functionals. This work is divided into two parts. Part one provides electronic structure calculations of polycyclic aromatic hydrocarbons (PAHs) for the charge transfer study. The second part is dedicated to calculations of correlated solids using B3LYP. The main purpose of the second part is the study of correlated systems, where local density approximation based exchange correlations (LDA, GGA, ...) fail. This thesis contains 6 chapters. The first chapter is the publication list related to this thesis and second chapter gives an introduction. The third chapter provides some overview over *ab initio* calculations and the relation between molecules and solid.

In chapter 6, the electronic structure of PAHs is studied in order to find good donor and acceptor molecules for the charge transfer study. It is shown that the results agree very well with the experimental ultraviolet photoelectron spectroscopy (UPS) on condensed PAH films. The experiments have been done in the group of Professor Schönhense. In the chapter 7 dimer molecules (Donor-Acceptor pairs) are studied by means of B3LYP followed by vdW correction. It is shown that although qualitative behavior of CT complexes can be described by simple B3LYP, vdW can improve the results by decreasing the intermolecular distances between the donor and acceptor pairs.

The remaining chapters are solid state calculations. In chapter 8, Rb_4O_6 which is a strongly correlated 2p shell system is studied with the B3LYP functional at ambient and high pressures. This compound can by considered as a molecular solid with oxygen molecules inside the solid.

In the last chapter (9), FeSe in the insulating phase is studied. The interesting aspect is that it is a superconductor in the tetragonal phase. Above a certain pressure the system has new stable phases. The electronic structure of these new systems have been studied by means of B3LYP and GGA methods. The last chapter is the summary of the thesis.

5.8 Methodology in the different chapters

• Chapter 6: Donor and acceptor molecules based on coronene are studied. The calculations are performed using the Gaussian03 code [33] and visualized by VMD [35]. Calculations are carried out with the B3LYP hybrid functional [16]. The standard 6-31G(d) basis set [36] is employed for the geometry optimization and the energy calculation. This level of theory ensures a reliable estimate of structural, energetic and spectroscopic quantities for the PAHs. The accuracy is comparable with that of the correlated MP2 [37, 38, 39] which requires an extremely high computational effort for large molecules.

Electron binding energies or ionization potentials of molecules are calculated by the delta self consistent field (Δ SCF) method applied together with the B3LYP hybrid functional. Vertical ionization potentials are calculated using Δ SCF method in order to compare with UPS data in which vertical ionization potentials (IP_v) are measured. In IP_v, final and ground states have the same geometry.

The B3LYP/6-311++G(d,2p) level of theory was implemented on both the anion and the neutral species for the electron affinity calculations. In case of an anionic final state, the use of diffuse functions is important to ensure the accuracy of the calculation since there is an extra electron in the system. The spin unrestricted B3LYP (UB3LYP) is employed when species are ionized with an open-shell doublet (one unpaired electron) electron configuration. Spin contamination is found in an accepted limit for the open shell systems, with $\langle S^2 \rangle$ values of about 0.75 – 0.78 in all cases.

The results obtained with the ΔSCF method are compared with the Hartree-Fock calculations based on the traditional Koopmans' theorem. [23]. Moreover, eigenvalues based on B3LYP/6-311++G(d,2p) are used to estimate HOMO-LUMO gaps and LUMO energies. In the former approach, inclusion of the exact Hartree-Fock exchange via the hybrid B3LYP functionals leads to HOMO-LUMO gaps in good agreement with the experimental excitation energies [22]. Time dependent density functional theory based on B3LYP hybrid functionals (TD-B3LYP/6-31G(d)) is used to estimate the band gap referring to the singlet excited state. Moreover, HOMO-LUMO gaps obtained with TD-DFT are not very sensitive to the basis set and it is shown that 6-31G(d) can show reasonable agreement for optical properties with the experimental results for the hydrocarbon molecules [29, 40, 41].

• Chapter 7: The dimer of donor and acceptors are investigated. The calculations were performed using the Gaussian03 code [33] and visualized by VMD [35]. The geometry optimization was carried out with the B3LYP hybrid functional [16]. The starting structure for the further calculation were taken from B3LYP/6-31G optimization.

Because the number of the basis functions increase rapidly with the size of the model and quality of the basis set, a compromise had to be found. Therefore, single-point energies of studied donors and acceptors were calculated using 6-31G* basis set [36] which has been shown to be adequate for calculations on weakly bound CT complexes [42, 43]. This basis set is applied to all structures in order to use the same benchmark for all the dimers. All the energies were corrected by basis set superposition error (BSSE) using counterpoise method [44]. The vdW correction is applied on the PES of few dimers by using the optimized vdW parameters in the previous studies [45, 46].

• Chapter 8: The rubidium sesquioxides (Rb_4O_6) is studied. The calculations were performed using the CRYSTAL06 code. CRYSTAL06 is used for the structural optimization and electronic structure calculation of high pressure phases. For the rubidium, we chose Sadlej-PVTZ [47], a medium-size polarized basis sets for the alkali and alkaline-earth, and 6-311G^{*} [48] for oxygen. In order to use these basis sets for the solid they are re-optimized for the studied crystalline systems [34]. The optimization of the fractional coordinates of the dioxygen anions was performed for both the ferromagnetic and the antiferromagnetic ground states. In both cases, the initial symmetry of the structure was $I \overline{4}3d$ where all dioxygen molecules are symmetrically equivalent. Relaxing this symmetry requirement by allowing peroxide and hyperoxide to have different bond-lengths, the fractional coordinate optimization results in structures with reduced symmetry. The ferromagnet acquires the space group symmetry $I \overline{4}2d$ and the antiferromagnet $I 2_1 2_1 2_1$ which is the highest possible symmetry for an antiferromagnetic phase.

• Chapter 9: In this chapter the high pressure phases of FeSe are studied. Firstprinciple electronic structure calculations were performed by CRYSTAL06 [34] using B3LYP exchange-correlation functionals. GGA implemented in WIEN2K [49] is also used.

6 Donor and Acceptor Molecules

6.1 Introduction

Charge transfer salts have become of particular interest during the past two decades. Typically, charge transfer (CT) complexes, consisting of π -electron donors (D) and acceptors (A), show one or several properties like metallic conductivity, superconductivity, and magnetism that are relevant for nanoelectronic applications [1, 2]. Many of the organic conductors and superconductors are based on the bis (ethylenedithio) tetrathiafulvalene (BEDT-TTF) donor and various acceptors [2, 50]. Furthermore, poly cyano derivatives have mainly been used as acceptors like tetracyanoquinodimethane (TCNQ) [51]. Recently, a novel type of donor and acceptor molecules based on polycyclic aromatic hydrocarbons (PAHs) has been investigated [52]. In this chapter, a detailed theoretical study of the electronic properties of new PAHs is presented, which allows to identify the experimental results and complements the picture of experimentally determined orbital states.

Flat aromatic molecules as polycyclic aromatic hydrocarbons (PAHs), have attracted attention because of their extended π -electron systems [53, 54]. Garito and Heeger concluded that the extension of the π system would lead to a lowering of intramolecular Coulomb repulsion in the anions of the acceptors, resulting in more stable radical anions and in highly conducting CT complexes [55]. Larger PAH molecules called nanographene have been synthesized via the bottom-up approach with desired size, structure, and symmetry [56]. The electronic structure of PAHs can be tuned via the type and number of substitutions in periphery. This way the functionalized PAHs may serve as a prototype for the creation of a new class of molecules with tailored chemical and electronic properties. However, although the electronic structure of different donor and acceptor molecules have been widely studied, little attention has been paid by theory and experiment to illustrate the electronic structure and the effect of functional groups on donors and acceptors based on PAHs.

In this thesis, the electronic structure of new acceptors and donors based on coronene and pyrene (see Fig. 6.1) are calculated. A hybrid density functional (B3LYP) method is used to calculate the ionization potentials (IPs). The results are compared with ultraviolet photoelectron spectroscopy (UPS) measurements. All the measurements have been done in the group of Prof. Dr. Gerd Schönhense by Katerina Medjanik. The comparison allows to assign the measured signals to specific molecular orbitals, providing a self consistent validation of the experimental results. Furthermore, the calculations provide the IPs of orbitals that could not be measured, experimentally.

UPS measurements had been performed on PAH multilayer on a Au surface. As the molecules are preferentially planar to the surface while measurements are made in the perpendicular direction σ -type orbitals could not be measured in practice. In the theoretical study all orbitals can be investigated so that the respective IPs become accessible. In general, the IPs of PAHs adsorbed on a metal surface are shifted by a constant energy with respect to the gas phase results. The discrepancy stems from the photo-hole screening induced by the image charge in the metal [52] and partly from the polarization energy induced by the screening action of the neighboring molecules as described in Ref. [57]. The latter effect persists in thick multilayer films, whereas the image-charge screening acts only on the first three layers. A similar effect occurs in multilayer films in which the screening is induced by the neighboring molecules. The energy shift between the theoretical results that corresponds to isolated molecules and the measurements on the condensed multilayer can be taken into account by adjusting the HOMO levels of both systems. Applying this energy shift to all IPs must provide a good correspondence between the experimentally measurable orbitals and the theoretical results, which serves as a useful consistency check of both measurement and calculation. For the given set of molecules the energy shift is very small so that the theoretical IPs for isolated molecules and those in the multilayer can be compared directly.

Coronene has a high symmetry (D_{6h}) , a small band gap and the right size for processing techniques. Therefore, coronene and its derivatives are promising for applications in molecular electronics, optoelectronics, and sensors [58, 59, 60, 61]. Kato *et al.* also predicted superconductivity of coronene in a charge transfer configuration [62]. In this chapter, properties of hexamethoxycoronene (HMC) and coronene-hexaone (CHO) are studied. The functional groups are tailored such that HMC is a donor while CHO is an acceptor molecule. Since both molecules are based on coronene and have a similar geometry they are expected to form excellent charge transfer complexes.

Calculations of tetramethoxypyrene (TMP) and pyrene-tetraone (PTO) have been performed and compared with experimental results. These poly aromatic molecules have a different structure and symmetry in comparison with coronene based molecules, which makes a comparison of these two families instructive. Calculation of tetracyanoquinodimethane (TCNQ), a well-known classical acceptor, is used as a benchmark for the calculations of the acceptor molecules. All investigated molecules are shown in Figure 6.1. Electronic structures of the donor and acceptor molecules are theoretically studied by B3LYP/6-31G(d) level of theory and compared with the ultraviolet photoemission spectroscopy (UPS) measurements [52]. Electron binding energies or ionization
potentials of molecules are calculated with the delta self consistent field (Δ SCF) method using the B3LYP hybrid functional.



Figure 6.1: Structure of the donor and acceptor molecules studied in this work.

6.2 UPS measurements

In a measurement the work function of a clean Au surface increases significantly if the acceptor TCNQ or coronene-hexaone is adsorbed. This can be understood in terms of a partial charge transfer from the metal surface to the first molecular layer thus forming the interface dipole with its negative side pointing toward the organic film. The opposite behavior for work function is observed donors (HMC, TMP and coronene). The decrease of the work function by about 0.5 eV is indicative of the Pauli push-back effect leading to a push-back of the spill-out electrons and thus to a reduction of the surface dipole of the metal. In practice, polar metal-organic interfaces due to charge



Figure 6.2: In (a) the schematic representation of molecule on the gold is shown. (b) shows how ionization potential is obtained with respect to the vacuum level.

transfer between molecules and surface, change the work function and thus the binding energies with respect to the vacuum level.

The electron binding energies in condensed films of the studied acceptors and donors (Fig. 6.1) are measured by UPS in a setup described in [52]. In the UPS spectra the signals derived from the occupied frontier orbitals of the organic over layer are referenced to the Fermi energy of the Au substrate. By adding the value for the work function of the molecular film the electron binding energies are referenced to the vacuum level. An acceptor molecule in direct contact with a metal surface may form a negatively charged species as was found for TCNQ on Ni(111) [63]. TCNQ on Au, on the other hand, was found to be almost neutral [64] because its acceptor character does not suffice to form a strong charge-transfer complex with Au, which is the metal with the highest Pauling electronegativity. For coronene in the gas phase an IP of 7.29 eV is reported [65]. For coronene on Au surface a value of IP=7.1 eV has been measured as shown in Table 6.1. As a result, the Au surface is rather neutral with respect to both donor (coronene) and acceptor (TCNQ) molecules.

Work function values have been measured for different molecular films with a thickness of several layers deposited on Au: coronene-hexaone (5.6 eV), hexamethoxycoronene (4.8 eV), coronene (4.8 eV), tetramethoxypyrene (4.9 eV) and TCNQ (5.9 eV).

Electron binding energies for the molecular orbitals (MOs) can be extracted from the UPS spectra by assigning peak positions of the spectra, but one by one assignment for all UPS signals is not possible since in some cases they result from a superposition of several occupied molecular orbitals with closely spaced binding energies. However, in most cases the HOMO signal is well separated from the deeper-lying levels and can be evaluated with high precision.

6.3 Symmetry analysis

For the analysis and comparison of the calculated ionization potentials, with the UPS measurement, the symmetry of the molecular orbitals must be extracted. σ or π symmetry is determined, followed by related degeneracy (E, A, ...). This information is shown in Figure 6.3 for the frontier orbitals and in Table 6.1 and 6.2 for the lower lying orbitals of studied molecules.

Having π symmetry is essential in order to observe the orbital in UPS. The oxygenderived σ states appear only weakly in photoelectron spectroscopy because of the lower cross section of O-2*p* in comparison with carbon π at the photon energy (21.2 eV) used in the experiment [66, 67]. Another reason for the weak σ -derived signals in the experiment might be that the molecules are predominantly oriented parallel to the surface and the UPS spectrometer probes the normal emission direction. Electronic structure calculations allow to determine the electron binding energies of the σ -type orbitals, which are not accessible in the experiment. This way a detailed picture of the electronic structures of donor and acceptor molecules is available. Orbital symmetries with σ and π character of MOs are listed in Tables 6.1, 6.2 and Figure 6.3.

Coronene and its derivatives have a degeneracy of two for the HOMO and all orbitals with E symmetry because of more than a 2-fold axis (coronene has a 6-fold and HMC and CHO have a 3-fold axis). CHO and HMC have a doubly degenerated HOMO with a π characteristic as depicted in Figure 6.3. For HMC and TMP there is no symmetry plane, so σ and π orbitals are not clearly distinguishable for the lower lying orbitals. However, they are reported according to major contributions of σ - or π -type symmetry in the orbital's notations in Tables 6.1 and 6.2.

Pyrene derivatives and TCNQ have a non-degenerate orbital because of the 2-fold axis. In Pyrene-tetraone (PTO), HOMO and HOMO-1 have the σ -type symmetry and are in-plane as shown in Figure 6.1. Therefore, they are not traceable in UPS because of the low cross section of O-2*p* since these MOs are located mainly on the oxygen atoms (see Figure 6.3). For PTO, reliable UPS binding energies could not be determined due to charging.

A survey of Tables 6.1 and 6.2 reveals that the presence of O atoms and cyanide groups increases the σ -type part of the occupied orbitals of acceptor molecules. Thus, acceptors have more σ -symmetry orbitals near the HOMO. The experimentally inaccessible σ -type orbitals are provided by the electron structure calculations as shown in Tables 6.1, 6.2.



Figure 6.3: HOMO and LUMO orbitals computed for the studied molecules. The symmetry of each molecule and the symmetry of the related molecular orbitals are shown in parentheses. Among all PAHs donor and acceptor molecules just PTO has a σ -type HOMO orbital. All the coronene derived molecules show a doubly degenerate HOMO.

6.4 Effect of functional groups

The electron-withdrawing carbonyl groups of CHO and PTO reduce the charge density in the π system, while in HMC and TMP, electrons are donated to the π system by the methoxy (OMe) groups. Therefore, the aromatic rings in CHO and PTO are positively charged, while the methoxy substituted molecules are negatively charged. Thus, CHO is an acceptor in comparison with coronene and HMC, and PTO is an acceptor compared to TMP.

The bond lengths of CHO along the symmetry plane are distinctly larger than those of coronene. The first C–C bond length at the edge of the double bonded oxygen atoms increases from 1.37 Å (coronene) to 1.54 Å for CHO. The other bond lengths increase by about 0.02 Å with respect to coronene. For CHO, all the bond lengths inside the

aromatic ring are larger than those in HMC and coronene. In HMC, the C–C bond lengths are of the same size as those of coronene, but the Mulliken population analysis shows that the C atoms of the aromatic rings are slightly more negatively charged compared to coronene. A similar behavior is found for TMP and PTO.

Donor and acceptor molecules are best investigated by analyzing the molecular orbitals. Any change in the functional groups of the molecules will be reflected in the binding energies and the molecular orbital energies. Therefore, the evaluation of molecular orbitals shows how the functional groups tune the electronic structure. Also, with the help of ab initio calculations one can analyze details of the electronic structure and in particular σ orbitals which are not accessible by UPS measurement. Also the underlying orbital structure of overlapping UPS signals can be analyzed by the calculation.

6.5 Electron binding energies of coronene derivatives

Theoretical and experimental binding energies of coronene and its derivatives coronenehexaone (CHO) and hexamethoxycoronene (HMC) are listed in Table 6.1 and MOs diagram of Figure 6.4. A survey of Table 6.1 reveals that electron binding energies (IPs) calculated in Δ SCF-B3LYP approximation are, on the whole, in good agreement with the corresponding experimental IPs. Calculations based on the Δ SCF method correspond to the vertical IP of the molecules in the gas phase. In general, they may differ from measurements of condensed molecular layers on a metal surface by a constant energy value. As shown in Table 6.1 the energy shift between the multilayer measurements and the calculations corresponding to the gas phase are very small. This corresponds to the fact that the IP=7.1 eV of coronene on Au is close to the reported gas phase value IP=7.29 eV [65].

For coronene and the derivatives the Koopmans' energies for the HOMO differ by less than 0.5 eV from the Δ SCF binding energies. For the deeper-lying orbitals, the Koopmans' energies are too large in comparison with Δ SCF and experimental results. This deviation is caused by correlation and relaxation effects which are neglected in Koopmans' theorem. For comparison, results from Koopmans' theorem are presented for HMC in Table 6.1. For coronene and CHO deviations of the Koopmans' energies are of the same order of magnitude. Note that the σ -like orbitals of CHO appear only very weakly in the UPS spectra. Δ SCF-B3LYP results cover a wide range of MOs and show good agreement with the UPS data. The first ionization potential (binding energy of the HOMO) of HMC is shifted up by 0.5 eV in comparison to coronene.

As displayed in Table 6.1, hexamethoxycoronene has three main signals in the experimental spectrum below 10 eV [52]. The first of them at 6.5 eV is the HOMO with π -like symmetry with the double degenerate representation E (Figure 6.3). The calculation yields a (Δ -SCF) binding energy of 6.41 eV in excellent agreement with the photo-

Table 6.1: Electron binding energies in unit of eV for coronene and its derivatives with the symmetry labels calculated by B3LYP/6-31G* and compared to vertical excitation energies from ultra violet photoelectron spectroscopy (UPS) and Koopmans' theorem (KT).

		CHO(D_{3h})			HMC	(D_3)		Co	oronen	$e(D_{6h})$	
MOs	Symmetry	/ KT	ΔSCF	UPS	Symmetry	· KT	ΔSCF	UPS	Symmetry	·KΤ	ΔSCF	UPS
HOMO	$E''(\pi)$	9.27	8.78	8.8	$E(\pi)$	6.86	6.41	6.5	$E_{2u}(\pi)$	7.00	6.84	7.1
HOMO-1	$E'(\sigma)$	10.13	8.80		$E(\pi)$	8.74	7.66		$E_{1g}(\pi)$	8.94	8.11	
HOMO-2	$A'_1(\sigma)$	11.56	8.82		$A_2(\pi)$	9.25	7.80	7.9	$B_{2g}(\pi)$	9.31	8.56	8.8
HOMO-3	$A_1^{\bar{\prime}\prime}(\pi)$	11.77	9.23		$A_1(\pi)$	9.44	8.15	J	$B_{1g}(\pi)$	9.92	8.62	J
HOMO-4	$E^{\bar{\prime}}(\sigma)$	11.81	10.05		$E(\sigma)$	11.03	8.38		$A_{2u}(\pi)$	11.35	9.84	
HOMO-5	$A_2'(\sigma)$	12.05	10.11		$A_1(\sigma)$	11.59	8.51		$E_{2g}(\sigma)$	12.08	9.94	
HOMO-6	$E^{\overline{\prime\prime}}(\pi)$	13.80	10.33	10.2	$E(\pi)$	11.65	9.11		$E_{2u}(\pi)$	12.40	10.25	
HOMO-7	$A_2^{\prime\prime}(\pi)$	14.07	10.70	10.5	$A_2(\pi)$	11.65	9.17	9.3	$B_{2u}(\sigma)$	13.83	11.09	
HOMO-8	$\mathbf{E}^{\overline{\prime\prime}}(\pi)$	14.16	11.80		$A_2(\pi)$	12.47	9.52	J	$E_{1u}(\sigma)$	13.85	11.13	
HOMO-9	$E'(\sigma)$	14.89	11.84		$E(\pi)$	12.64	9.71		$A_{2g}(\sigma)$	14.14	11.54	
HOMO-10	$A_1''(\pi)$	15.03	12.37		$E(\pi)$	12.94	9.95		$B_{1u}(\sigma)$	14.27	11.55	

electron spectra. The calculated binding energy of electrons in the HOMO of HMC is about 0.4 eV lower than that of coronene due to the six methoxy groups on the periphery which increase the charge density in the π system. The effect of the methoxy groups is weaker than that of electron-withdrawing keto groups of CHO since the methoxy groups contain the electron-donor methyl and the acceptor oxygen which partially compensate each other; therefor, HOMO of CHO distinctly decreases with respect to coronene and HMC as plotted in Figure 6.4. There are three pairs of methoxy groups in the ring system and each pair is in trans configuration (see Figure 6.1 and 6.3). The methoxy groups can easily rotate in a solvent but this rotation will be blocked on the surface. The orientation of the methoxy group configurations has a strong influence also on the interaction between the metal surface and the molecule. The trans configuration of methoxy groups may reduce the contact of the aromatic ring system with the surface so that it can effectively suppress charge transfer between the molecule and the metal surface. The second signal in the UPS spectra appears at 7.9 eV and is assigned to the group HOMO-1, HOMO-2 and HOMO-3 all having π -like symmetry. Note that there is no strict π - and σ -type symmetry in HMC, but one can identify ' π -like' and ' σ -like' symmetry by comparison with the parent molecule coronene. HOMO-4 and HOMO-5 orbitals are very weak in the experimental spectra because they have σ -like symmetry, and contain a high contribution from oxygen 2p which has a low cross section at the photon energy $(21.2 \,\mathrm{eV})$ used in the experiment [66, 67]. For perfectly parallel orientation, σ emission is forbidden by symmetry selection rules. The UPS signal at 9.3 eV corresponds to the group of HOMO-6 to HOMO-8 states with π -like symmetry.

Coronene-hexaone (CHO) constitutes a more complicated adsorption behavior than HMC. CHO is a planar molecule with high electron affinity. The first layer, being in direct contact with the surface, experiences a substantial charge transfer from Au



Figure 6.4: Calculated binding energy scheme for CHO (left) and HMC (right) with respect to the parent molecule coronene (center). Binding energies (referred to the vacuum level) have been calculated by means of Δ SCF. Full and dashed lines denote orbitals with π - and σ -symmetry (for HMC π - and σ like symmetry), respectively. Dotted lines for HMC denote orbitals that strongly deviate from π - and σ -symmetry. All E-orbitals are double degenerate. Equivalent orbitals are connected by lines or labeled by $\alpha - \delta$. Blue bold lines show the experimental electron binding energies measured by UPS.

showing up in terms of a new interface state [52]. For comparison with the theory, the UPS data refers to a higher CHO coverage, where the interface state has disappeared in the spectra. In the multilayer coverage regime two signals appear in the region below 11 eV. As shown in Table 6.1, the first signal corresponds to the HOMO and appears at 8.8 eV in very good agreement with the Δ SCF calculation (8.78 eV). This value is similar to TCNQ which is a strong classical acceptor(Figure 6.2). The binding energy of electrons in the HOMO of CHO has increased by more than 2 eV with respect to coronene because of the electronegative keto groups. HOMO-1 and HOMO-2 as well as HOMO-4 and HOMO-5 are weak signals in the experimental spectra since they are derived from the oxygen $2p_{x,y}$ orbitals that are aligned in the molecular plane. HOMO-6 and HOMO-7 (π symmetry) constitute the second UPS signal at 10.3 eV in the measured spectra. The Δ SCF calculation again shows good agreement. Obviously the six carbonyl groups strongly alter the electronic structure of CHO compared to the unfunctionalized coronene, and make CHO a strong acceptor.

6.6 Binding energies of pyrene derivatives

For tetramethoxypyrene (TMP) and tetracyanoquinodimethane (TCNQ), the theoretical binding energies are smaller than the experimental values. For the HOMO of TMP the difference is 0.42 eV. The same discrepancy occurs for the overlapping HOMO-1 and HOMO-2 signals. HOMO-3 to HOMO-4 and HOMO-9 to HOMO-10 have σ -like symmetry and appear weakly in the experimental spectra due to a large oxygen 2p content. The π -like group HOMO-6 to HOMO-8 can not be resolved experimentally and shows up as one signal centered at 9.2 eV.

	$PTO(D_{2h})$					$\mathrm{TMP}(\mathrm{D}_2)$			$TCNQ(D_{2h})$			
MOs	Symmetry	\mathbf{KT}	ΔSCF	UPS	Symmetry	\mathbf{KT}	ΔSCF	UPS	Symmetry	ΚT	ΔSCF	UPS
HOMO	$B_{2u}(\sigma)$	9.32	8.70		$B_1(\pi)$	6.88	6.18	6.7	$B_{3u}(\pi)$	9.65	8.87	9.3
HOMO-1	$A_g(\sigma)$	10.14	8.90		$B_3(\pi)$	7.99	7.09] 7 7	$B_{1g}(\pi)$	9.65	10.49	$\int_{10.8}$
HOMO-2	$B_{2g}(\pi)$	10.35	8.92		$B_2(\pi)$	8.83	7.30	<i>```</i>	$B_{2g}(\pi)$	11.98	10.91	10.8
HOMO-3	$A_u(\pi)$	11.39	9.50		A (π)	9.67	8.03		$B_{3g}(\sigma)$	12.30	11.56	
HOMO-4	$B_{1g}(\pi)$	11.50	9.67		$B_3(\sigma)$	10.73	8.06		$B_{2u}(\sigma)$	13.76	11.58	
HOMO-5	$B_{3g}(\sigma)$	11.58	9.96		$A(\pi)$	11.58	8.28		$A_u(\sigma)$	13.77	11.87	
HOMO-6	$B_{1u}(\sigma)$	13.38	10.26		$B_1(\pi)$	11.64	8.66		$B_{1g}(\pi)$	14.12	11.88	
HOMO-7	$B_{3u}(\pi)$	13.70	10.60		$B_2(\pi)$	11.66	8.72	9.3	$B_{1u}(\pi)$	14.13	11.89	
HOMO-8	$B_{2g}(\pi)$	13.97	11.66		$B_2(\pi)$	12.36	8.96	J	$A_g(\sigma)$	14.18	12.01	
HOMO-9	$B_{3g}(\sigma)$	14.74	12.08		$B_1(\pi)$	12.72	9.42		$B_{3g}(\sigma)$	14.33	12.34	
HOMO-10	$A_g(\sigma)$	14.77	12.10		$B_2(\sigma)$	13.06	9.71		$B_{2u}(\sigma)$	14.65	12.38	

Table 6.2: Same as table 6.1, but for pyrene derivatives and TCNQ.

For **pyrene-tetraone** (PTO) reliable UPS binding energies could not be determined due to charging. Charging was also observed for thick CHO films (above 10 nm thickness). For TCNQ, HOMO-1 and HOMO-2 agree fairly well with the experimental signal centered at 10.6 eV. HOMO-3 to HOMO-5 have σ -symmetry and appear only weakly in UPS spectra. Therefore, most of the states in the Table 6.2 are found by the calculation, and measurement is not straightforward in the case of pyrene-tetraone.

6.7 LUMO and electron affinity

The strength of an acceptor molecule is measured by its electron affinity (EA) which is the energy released when adding one electron to the lowest unoccupied molecular orbital. An acceptor must have a high electron affinity, while low electron affinity is required for effective donor molecules. Since EA depends on the lowest unoccupied molecular orbital (LUMO), it can be calculated more accurately by considering the final state (anion). In order to describe the anion with an extra electron sufficiently, a diffuse basis set is required. We use the B3LYP/6-311++G(d,2p) basis to study donor and acceptor molecules.

The calculated EA of coronene is 0.48 eV which is in good agreement with the reported experimental value of 0.470 ± 0.009 eV [68]. A high electron affinity is the major characteristic of strong acceptors like TCNQ. Reported values for the EA of TCNQ vary with the applied measurement technique [69, 70, 71, 72]. Calculated values of EA are in the range of 3.4 ± 4 eV [73]. Using B3LYP/6-311++G^{**}, an EA of 3.62 eV is obtained, while B. Milián et al. report a value of 3.42 eV calculated with B3LYP/ccpVDZ and 3.28 eV calculated with CCSD/aug-cc-pVDZ. All these values are close to the reported experimental value of $EA=3.3\pm0.3 \text{ eV}$ [72, 70].

The electron affinity of CHO is 3.5 eV (see first column of Table 6.3) which is close to the electron affinity of TCNQ (3.62 eV). Therefore, CHO is expected to be a strong electron acceptor. CHO has a large electron affinity and an extended π system which makes it an interesting alternative to common acceptors. In Table 6.3 the experimental

Table 6.3: Δ SCF electron affinity (EA) calculated using 6-311++G^{**} basis set. Moreover the HOMO-LUMO gaps are calculated using TD-DFT/6-31G* (singlet excitation), second column and B3LYP/6-311++G** (LUMO-HOMO eigenvalue differences) third column. All values are given in eV.

Molecule	\mathbf{EA}	\mathbf{EA}	Gap	Gap	Gap
	(B3LYP)	(Exp)	(TD-DFT)	$(\varepsilon_{LUMO} - \varepsilon_{HOMO})$	(Exp)
Coronene	0.48	0.47^{a}	3.99	3.23	3.54^{c}
Coronene-Hexaone	3.50		2.98	2.57	3.20^{c}
Hexamethoxycoronene	0.51		3.81	3.09	3.30^{c}
Pyrene-Tetraone	2.48		3.48	2.22	
Tetramethoxypyrene	0.41		3.67	3.58	
TCNQ	3.62	3.3^{b}	2.54	3.04	3.10^{d}
^a Ref. [68]					

^b Ref. [72, 70] ^c Ref. [59] ^d Ref. [74]

gaps are compared with the theoretical calculations. To estimate the LUMO-HOMO gap, both TD-DFT and the difference of B3LYP eigenvalues are used and the results are listed in the second and third column of Table 6.3 respectively. In the case of large molecules there is a good agreement between the eigenvalue differences and the measured optical gap. In the earlier study, it is shown that there is a large deviation between the calculated gap using B3LYP and experimental results [22]. In the same paper, discrepancy depends to the size of molecule and it decreases by increasing the size of hydrocarbons. Therefore, one can conclude the good agreement in our calculations should be attributed to the large size of the hydrocarbons. For all compounds, the calculated HOMO-LUMO eigenvalue differences are smaller than the measured gaps. The gaps obtained from TD-DFT are spread symmetrically around the experimental values. In general, the calculated gaps from TD-DFT and the HOMO-LUMO eigenvalues deviate less than 20% from the experimental gaps, which is a reasonable result for this quantity. The fair agreement between the experimental values and the results calculated with $B3LYP/6-31G^*$ indicates that this calculation method may be used also for the larger molecules of this family called nanographenes, for which more correlated methods like post Hartree-Fock or even DFT with the diffuse basis sets are difficult or not applicable.

6.8 Discussion

When comparing theoretical and experimental electron binding energies, one has to take into consideration that they correspond to different situations. The calculations have been performed for single isolated molecules (equivalent to a gas phase experiment), whereas the UPS data have been taken for condensed multi layers on a metal surface. Thus, systematic differences in the binding energies must be expected, the main contribution being the polarization screening of the ionized molecule by its neighbors. The ultrafast polarization of the neighboring molecules leads to an effective screening of the Coulomb attraction of the photo-hole and, in turn, to a decrease of the binding energy. Photoemission from condensed layers should thus reveal lower binding energies than measurements or calculations of free molecules.

Table 6.1 and 6.2 reveal that the theoretical Δ SCF binding energies agree well with the measured UPS-values for the condensed films. For the pyrene-derived donor TMP and the acceptor TCNQ the deviation is slightly larger than 0.4 eV. For the large disctype donor HMC and acceptor CHO as well as for their parent molecule coronene even less than 250 meV. The good quantitative agreement between theoretical and experimental binding energies in Table 6.1 and 6.2 suggests that the polarization and screening in the film is partially canceled by other effects.

It is known from angular resolved UPS that the molecular orientation affects the peak

profiles of the UPS signals. This effect can be interpreted in terms of an orientationdependent ionization energy [75]. For hexabenzocoronene the surface induces a special growth mode with the molecular layers being oriented parallel to the surface up to a coverage of about 4 multilayer. Assuming the same orientation for our large PAHs one may conclude that signals in a direction perpendicular to the molecular plane were observed, because the spectra were taken under normal emission. This geometry may be in favor of high binding energy values which might explain part of the fact that spectroscopy measurement of the film match well for calculations for isolated molecules.

In addition to this intermolecular screening there is a further contribution by the image-charge screening of the metal surface. This, however, affects only the first 2-3 atomic or molecular layers as reported for adsorbed Xe [76]. The thickness of the condensed films corresponding to Table 6.1,6.2 was in the few-nm range thus excluding this contribution of image-charge screening. For thinner films towards a monolayer, one indeed observes a shift of UPS signals to lower binding energies [52].

The optical measurements are not influenced by the polarization energy. The measured gaps agree quite well with the calculation. Indeed, the solvatochromic effect leads to a shift in the absorption band. The difference between the gap calculated by timedependent DFT and the gap determined using the difference of the LUMO-HOMO eigenvalues is not large, and most experimental values are located between these two values.

The good quantitative agreement between the Δ SCF calculation and the UPS data taken from multilayer films of the coronene derivatives reflects the fact that the B3LYP functional provides a good quantitative description for substituted large PAHs. Moreover, extra molecular screening does not seem to play an important role for these large PAHs in the condensed film. B3LYP also shows a good agreement for the optical gap and EA. B3LYP can thus be used even for the larger PAHs in which the post Hartree-Fock methods are not applicable.

6.9 Summary

In this chapter, theoretical and experimental electron binding energies of different MOs for coronene, pyrene and their methoxy and keton-derivatives are reported. The electronic structure of the acceptors are compared with TCNQ as a well-known classical acceptor. The studied compounds demonstrate how the functional groups can tune the molecules' electronic state, providing moderate donor or strong acceptor properties.

Comparison of electron structure calculations and photoelectron spectroscopy data provides detailed insights into the electronic structure of the new compounds. The calculated molecular orbitals have been used to identify and complement the experimental results. Calculated IPs for the gas phase are in a good agreement with the UPS measurement on the Au surface. The absence of an energy shift, induced by the metal substrate or the neighboring molecules, is so far not fully understood, but the good agreement between the various UPS signals and the calculated π -type orbitals demonstrates the direct comparability of the molecule's IPs in the condensed and the gas state. In fact, Δ SCF-B3LYP reproduces the whole range of IPs in the measured UPS spectra, while Koopmans' theorem shows a good agreement just for the first IP. The calculated electron affinities allow to rate the donor or acceptor character of the molecules. They confirm that CHO is a strong acceptor. Its high electron affinity (3.5 eV), which characterizes a good acceptor, is almost as large as the affinity of TCNQ (3.62 eV). HMC, coronene and TMP with their low ionization potentials and rich aromatic systems are suitable candidates for donors. HMC is an appropriate choice for surface applications due to its trans isomerism. Especially interesting for the formation of charge transfer complexes are the molecules CHO and HMC. Our results show that they are good acceptor and donor molecules, respectively. With their coronene centers they have a very similar molecular structure. This is analogous to the TTF-TCNQ pair with the benzene core which is studied since a long time. The proposed coronene-based donoracceptor molecules could be the starting point of a new generation of charge transfer salts based on molecular nanographenes.

In the next chapter the electronic structure of donor-acceptor pairs in the charge transfer complexes will be discussed. We present an efficient way for studying the CTC which mainly interact through van der Waals forces. The results will be compared with experimental findings.

7 Donor-Acceptor dimers

7.1 Introduction

Intermolecular charge-transfer (CT) complexes are formed when electron donors (D) and electron acceptors (A) interact. Mulliken [77] considered such complexes to arise from a Lewis acid/Lewis base type of interaction. The bond between the components of the complex is being postulated to arise from the partial transfer of π -electrons from the base (D) to orbitals of the acid (A).

Theoretical investigation of charge transfer (CT) complexes based on face-to-face π -stacked electron donor (D) and electron acceptor (A) dimer, has received more attention in the recent years [42, 43, 78, 79, 80]. Such a A-D pair can be formed by interaction between the electron donor (D) and electron acceptor (A) molecules. Although it has a simple concept, the nature of intermolecular CT complexes has been the subject of many investigations.

In general, energy of interaction between electron donor (D) and electron acceptor (A) moieties can be represented as [81]:

$$E_{\text{tot}} = E_{\text{elec}} + E_{\text{ind}} + E_{\text{vdW}} + E_{\text{rep}} + E_{\text{CT}}$$
(7.1)

The charge-transfer interaction E_{CT} is only important in the excited state, but has a very small contribution to the stability of the ground state of molecular complexes [81, 82]. In the case of non-covalent interactions, the bonding orbitals of the interacting subsystems are occupied by electrons and all antibonding orbitals are unoccupied. The overlaps between the occupied and unoccupied molecular orbitals are not significant (indicating charge transfer in ground state) and interaction between the completely occupied orbitals leads to destabilization (E_{rep}). This repulsion is called exchangerepulsion, that prevents the collapse of the molecule. The attractive parts come from the interaction between the permanent multipoles (E_{elec}), between the permanent and induced multipoles (E_{ind}), and finally between the instantaneous multipole and induced multipole calling London dispersion forces (E_{vdW}). It should be noticed that E_{elec} is either attractive or repulsive depending on mutual orientation of multipoles.

Experimental results also suggest that at the close separation D-A pair is held together mainly by van der Waals type forces [83].

For example, $\pi - \pi$ interaction as for benzene dimers is nowadays considered a typical van der Waals (vdW) complex in which the long range dispersion interaction (dominant R^{-6} dependence of intermolecular energy on the inter-fragment distance R) play a major role [84, 85]. Such a dispersion interaction is purely based on correlation; therefore, the (HF) method is clearly inadequate because of its failure to account for electron correlation and dispersion. The general drawback of all common density functionals including B3LYP, is that they can not describe long-range electron correlations that are responsible for the dispersion forces. Common density functionals fail to locate the stacked minimum energy structure on the potential energy surface [86]. As a result, second Møller-Plesset perturbation theory (MP2) [87] and dispersion corrected density functional theory are recommended. It should be pointed out that MP2 is an expensive method and it is shown that it overestimates $\pi - \pi$ interaction by shortening the distance (15-8 pm) between the layers in π -stacking structure [88]. The opposite behavior is also observed for the DFT method (error up to 15 pm). However, the success of DFT method in production of these very interacting systems in the certain context is still reported [42, 80]. Although $\pi - \pi$ interaction and the effect of dispersion type calculations have been studied widely, little attention has been paid to the contribution of vdW correction of intermolecular distances to the HOMO-LUMO gap of charge transfer complexes.

In this chapter, the $\pi - \pi$ interaction has been studied with hybrid functionals (B3LYP) corrected by vdW interaction. Two different cases have been observed. The first category is a typical π -stacking system in which both the moieties are the same. For this case a coronene dimer are chosen. The next category is a charge transfer system. A dimer of coronene hexaone (A) and hexamethoxycoronene (D) have been studied which are a coronene based acceptor and a donor, respectively. Furthermore, a CT system with a hexaazatriphenylene-hexacarboni-trile and a hexamethoxycoronene molecule have been investigated. The vdW correction is used for these two sets of CT dimers (HMC-CHO and HMC-HAT-(CN)₆). HMC and CHO are new coronene based donor and acceptor molecules [59]. The coronene center makes them interesting because coronene has a high symmetry (D_{6h}) and a small band gap. Both D-A dimers (HMC-CHO and HMC-HAT-(CN)₆) have extended π -systems with planar structures.

In a first step, the interaction of D-A dimers without vdW corrections is analyzed. Coronene, hexamethoxycoronene (HMC), hexamethoxypyrene (HMP) and tetramethoxypyrene (TMP) are studied in combination with the acceptors tetracyanoquinodimethane (TCNQ) and hexaazatriphenylene-hexacarboni-trile (HAT-(CN)₆) (see Figure 7.1 and 7.3).



Figure 7.1: Structure of charge transfer molecules.

7.2 Geometry optimization

Electron donor and acceptor molecules chosen for this study are illustrated in Figure 7.1 and related CT complexes are shown in Figure 7.3 along with the inter-planar distances (R_{D-A}) optimized at B3LYP level of theory in the absence of vdW corrections. Indeed without vdW corrections the intermolecular distances are overestimated. Coronene based donor and acceptor molecules (CHO and HMC) are studied because of the interesting chemistry of coronene [89, 90, 91] which is already discussed in the present thesis. HAT-(CN)₆ is an acceptor with six electron-withdrawing cyanide (CN⁻)



Figure 7.2: The three different arrangements of donor-acceptor pair in the studied molecules.

groups. An interesting aspect is that the redox chemistry in acetonitrile consists of two accessible and reversible one-electron reductions [92] suggesting that $[HAT-(CN)_6]^-$ and $[HAT-(CN)_6]^{-2}$ are stable. Therefore, this molecule has attracted lots of interests for charge transfer and molecular magnets [93, 92]. The three molecules HMC, CHO and HAT-(CN)_6 have similar sizes (See Fig. 7.1) and their combinations give the cofacial arrangement (Fig. 7.2) for the related D-A pairs in their optimized structures 7.3. TCNQ which is a known acceptor is used as a benchmark. Pyrene derivatives are chosen in order to investigate the effect of symmetry and size in comparison with coronene based molecules.

In the calculation, D-A dimers were constructed by placing one component above, and parallel to the other component; then all complexes were optimized without any constraint, in order to find the best geometry and arrangement of D-A moieties. As shown in Figure 7.3, the optimized structure for coronene-TCNQ, HMC-CHO, HMC-HAT- $(CN)_6$ are cofacial and parallel. HMC and TCNQ are slipped parallel (see Figure 7.2 for the different arrangements). TMP-TCNQ and HMP-HAT-(CN)₆ show a tilted arrangement (Fig.7.2) in the optimized structure. In other words, coronene based donor molecules lead to parallel arrangement due to their high symmetry and matching sizes. The geometrical matching size of a coronene center with $HAT-(CN)_6$ is demonstrated in Figure 7.1, were the coronene ring can be considered as two triphenylene rings with the C_3 rotation with respect to each other. Hexamethoxycoronene has the D_3 symmetric try with the 3 fold rotation axis which cause a symmetrical repulsion on the acceptor. Therefore, HMC-HAT- $(CN)_6$ and HMC-CHO have a perfectly parallel and cofacial arrangement. The vdW corrections on HMC-HAT-(CN)₆ and CHO-HMC which are parallel dimers are applied. As it is seen, in Figure 7.3, inter-planar distances of CT complexes when HMC is a donor molecule are around 4 Å with B3LYP. As shown in Fig. 7.3 and 7.6 in the case of HMC-CHO and HMC-HAT- $(CN)_6$ vdW correction can change the optimized intermolecular distances drastically. Especially, for the case of HMC-CHO this change is more strong since the Coulomb attraction is weak. The optimized distance after vdW correction for HMC-HAT- $(CN)_6$ and HMC-CHO are 3.27 and 3.6 Å, while for the coronene dimer it is about 3.8 Å. Therefore, the vdW correction is important in the case of CT complexes since the Coulomb interaction is not a dominant interaction. However, it should be pointed out that although the Coulomb interaction can not give the exact distance, it helps to characterize the dimers. At very short distances the steric repulsion of methyl groups with the related acceptors become dominant.



Figure 7.3: CT complexes and inter-planar distances (R_{D-A}) optimized with B3LYP. CT complexes with HMC as a donor are oriented parallel. Because of the steric effect of the methoxy groups in HMC with the related acceptor, CTCs containing this donor, have the larger optimum distances.

7.3 Potential energy surface

As discussed in the introduction π -stacking is dominated by vdW interactions and DFT fails to locate the minimum in the potential energy surface (PES). Experimental results also suggest that at the close separation the D-A pair is held together mainly by vdW-type forces [83].

In order to compare a typical $\pi - \pi$ interaction with the studied CT complexes in which there is a D-A pair, a coronene dimer is compared with HMC-CHO and HMC-HAT-(CN)₆. The coronene dimer is chosen for two reasons. First, it has been studied extensively. Second, it has a same center as HMC-CHO with the same $\pi - \pi$ interactions which allows a direct comparison. Potential energy surfaces (PES) of HMC-CHO and HMC-HAT-(CN)₆ are calculated using B3LYP/6-31G(d) and compared with the coronene dimer. As shown in Figure 7.4, B3LYP/6-31G(d) shows a repulsive interaction for the coronene dimer as reported in the literatures [94, 46]. For the case of CT



Figure 7.4: potential energy surface of the coronene dimer with and without vdW correction. B3LYP shows purely repulsive interaction for the coronene dimer.

complexes (D-A pairs), B3LYP can locate an energy minimum on the potential energy surface (Fig. 7.5). This attraction which is counted in B3LYP is mainly an electrostatic interaction. As shown in Fig. 7.5, if one subtracts the Coulomb part from the total PES (calculated by B3LYP), the remaining part is nearly repulsive. Therefore, one can conclude that in the case of CT complexes, both vdW and Coulomb interactions are important, while for the case of coronene vdW is dominant as seen in the Fig. 7.4. Since coronene dimer does not have any Coulomb attraction, most of hybrid functionals and semi-local methods show a repulsive interaction. B3LYP will underestimate dimer interactions and binding energies at least as much as neglect the long range interactions (see Fig. 7.6). The fastest solution is the vdW correction, since optimized parame-



Figure 7.5: potential energy surface for CHO-HMC and HMC-HAT-(CN)₆ using B3LYP/6-31G(g) and counterpoise corrected BSSE. PES for D-A pairs shows attractive interaction. HMC-HAT-(CN)₆ shows stronger interaction than CHO-HMC. With vdW corrections the binding energy increases and the minimum is shifted towards smaller distances. This effect is smaller in the case of HMC-HAT-(CN)₆

ters have already been obtained for C, H, O and N atoms. The vdW parameters are checked for coronene dimer and minimum of PES is matched very well with the other articles. [46, 90, 94] Calculated binding energies for HMC-CHO and HMC-HAT-(CN)₆ after vdW corrections are -37 and -44 kcal/mol respectively, ~ 2 -3 times larger than the binding energy of the coronene dimer. The effect of correction on the optimized distance is too high because the contribution of the Coulomb attraction is small and B3LYP can find the wrong minimum with the help of Coulomb attraction. As shown in Figure 7.6, the change of the gap versus distance is larger in the interval of vdW corrected distances and distances optimized by the B3LYP. In the further distances the slope of lines are very smooth and molecular orbitals of the CT complex are energetically similar to the isolated molecule. The main change in the calculation of HOMO and LUMO eigenvalues is in the area of vdW correction which hybrid functional and other exchange-correlation in DFT can not account for. Therefore the vdW correction is essential for the study of CT complexes when one is interested in the shift of HOMO and LUMO in the CTC in order to compare with experiment [57].



Figure 7.6: HOMO and LUMO shifts of HMC-CHO and HMC-HAT-(CN)₆ as a function of the intermolecular distances. δ_{shift} shows the shift of the HOMO energy after the vdW corrections.

7.4 Energy investigation

The calculated attraction without vdW interaction is about 2.5 and 4.8 kcal/mol for the HMC-CHO and HMC-HAT-(CN)₆, respectively. In these two D-A pairs the effect of Coulomb attraction is ~ 10% of the total energy of the system, comparing the minima obtained with the vdW corrections, as seen in Fig. 7.5. Although the vdW contribution is additionally larger part of energy, the minimum without vdW attraction (B3LYP) can be used for a rough estimation of the optimum distance of the D-A pairs. Exploring the source the non-vdW attraction provides some new interesting aspects. The main part of the Coulomb attraction is based on the interaction of opposite charges located at the peripheries of the molecules. More precisely, the attraction results from the interaction of hydrogen at the CH₃ of HMC and the negative charge on the O atoms

of CHO. If these charges are neglected, then there is no attraction anymore.

The amount of Coulomb attraction directly depends on the accepting power of the acceptor moiety. The reason why the Coulomb interaction is related to the accepting power lies within functional groups, which can turn the coronene into either a good acceptor or a donor. When the functional groups placed at the periphery of a coronene ring have a very high electronegativity then more negative charges will be located on the periphery, which leads to a strong Coulomb attraction. Therefore one can conclude that the HAT-(CN)₆ is a stronger acceptor than CHO which is true according to experimental evidence described in 7.1. The van der Waals interaction has a strong indirect



Figure 7.7: Molecular orbital correlation diagrams for HMC-HAT-(CN)₆ and the related subunits (a) and HMC-CHO and the related subunits (b). HMC (a) has a strong shift in HOMO energy after complexation with HAT-(CN)₆. In addition, HMC-HAT-(CN)₆ has a LUMO with degeneracy 2 and LUMO+1 close to it, rather than degenerate HOMO. Having 3 unoccupied molecular orbitals with the nearly same energies is a unique feature between the studied molecules.

Table 7.1: HOMO, LUMO, gap and binding energies with BSSE correction is shown in this table. In addition, the shift of HOMO and LUMO of complexes with respect to isolated subunits (acceptor and donor) is given in parentheses.

			E_{bind} (kca	l/mol)
Dimer	HOMO $(shift^1[eV])$	LUMO $(shift^1[eV])$	gap (eV)	BE
HMC-CHO	-5.33(-0.18)	-4.17(0.13)	1.16	-1.42
HMC-HAT- $(CN)_6$	-5.65(-0.49)	-4.19(0.42)	1.46	-3.19
Coronene-TCNQ	-5.75(-0.30)	-4.53(0.33)	1.22	-3.35
HMC-TCNQ	-5.41(-0.28)	-4.40(0.45)	1.01	-0.58
HMP-HAT- $(CN)_6$	-5.67(-0.65)	-4.29(0.32)	1.38	-5.02
TMP-TCNQ	-5.27(-0.22)	-4.60(0.26)	0.67	-0.83

impact on the perturbation of HOMO and LUMO of donor and acceptor molecules after

complexation. This perturbation is strongly dependent on the optimum distance which is changed by the vdW correction. Without vdW correction the B3LYP will underestimate HOMO and LUMO shifts of CT dimers. This underestimation is 112 meV and 250 meV for HMC-CHO and HMC-HAT-(CN)₆, respectively. This error makes about 50% of the change of the HOMO-LUMO gap as shown in Fig. 7.6. Such a change in energy is measured for the TMP-TCNQ dimer by UPS [57].

Due to the weakness of the D-A interaction, only minor perturbations can be observed in the energy of the subunit orbitals, which generally show small upward shift of the acceptor orbitals coupled with a small down-shift of donor orbitals. As shown in Figure 7.7, the HOMO of HMC has a strong down-shift around -744 meV when the acceptor is HAT-(CN)₆, while for the same donor the down-shift is -292 meV in the HMC-CHO complex. The strongest down-shift of the HOMO is found for the HMP-HAT-(CN)₆ complex. The induced shift by HAT-(CN)₆ is the same as that of TCNQ which is a well-known classical acceptor as shown in Table 7.1.

HMC has a D_3 symmetry with a 3 fold rotation axis and higher symmetry than HMP. This 3 fold rotation axis of HMC leads to a degeneracy of two (E) for the HOMO, while pyrene based donors (HMP and TMP) have the degeneracy of 1. HMC also shows cofacial and parallel arrangement with different acceptors.

Altogether, the HMC-HAT- $(CN)_6$ dimer builds a specially strong charge transfer complex. On one hand, their strong interaction leads to a very good cofacial arrangement. On the other hand, not only the HOMO of HMC has a degeneracy of two (E) but also the LUMO of HAT- $(CN)_6$ has an E symmetry with the LUMO+1 level which is only 0.046 eV higher than the LUMO as seen in Figure 7.7. This unique feature of frontier orbitals in HMC-HAT- $(CN)_6$ can increase the charge transfer in the excited state of CTC. This excitation from HOMO to LUMO leads to a new absorption band, absent in either of the monomers.

7.5 CTC: experiment vs theory

Figure 7.8 summarizes the measured and calculated level positions for the acceptor molecule TCNQ (left column), the donor molecule TMP (right column) and their CT complex (center column). In order to be able to compare experiment and theory, the energy scale is referenced to the vacuum level. Calculation is done without vdW correction for this dimer. In principle, the comparison with the experiment is very difficult for a dimer for which there is not enough information about the arrangement of the molecules on the surface. As discussed before and shown in Figure 7.6 the HOMO and LUMO positions depend strongly on the intermolecular distances as well as the configuration of the dimers. Therefore, without having this information, the calculations provide only trends of the electronic structure of the dimers in the experiment. Furthermore, the calculation refers to the gas phase while the measurements are performed for the multilayer and on Au substrate.

The energy levels of the molecules are "biased" by the surface dipole. For TCNQ the CT from the metal to the first layers of the film leads to an interface dipole and the work function increases. For TMP the push-back effect (Pauli repulsion) acting on the spill-out electrons in front of the surface by the molecular electrons leads to a reduction of the metal surface dipole so that the work function decreases. The change of the interface dipole cannot be modeled by theory. Therefore, these work function changes are not taken into account in Figure 7.8. In the following the calculated results with the different experiments will be compared.

For the complex, the difference between the scanning tunneling spectroscopy (STS) and UPS HOMO positions (distance 0.6 eV) is somewhat larger than for TMP (see Figure 7.8). The Δ SCF binding energy prediction (cyan line) lies close to the UPS signal. The calculated LUMO eigenvalue (upper purple line) shows good agreement with the STS LUMO position, similar to the case of TCNQ. The HOMO eigenvalue is substantially too high, i.e. the calculated gap of 0.6 eV is about a factor of 2 smaller than the experimental gap ($\Delta_{exp} = 1.25 \text{ eV}$). This can be improved by using the vdW correction as shown in Figure 7.7. The reason for the underestimation of the gap and HOMO and LUMO eigenvalues is an overestimation of intermolecular distance in the DFT calculation. The vdW correction decreases this distance and as a result, improves the band gap and other related properties.

For the CT complex STS produces a distinctly smaller gap than TMP ($\Delta_{exp} = 1.25 \text{ eV}$) due to an upward shift of the energy of the HOMO by 1.0 eV and a smaller downward shift of the LUMO (compared with TCNQ) by 0.3 eV. The calculation shows that the HOMO (LUMO) of the complex is derived from the respective orbitals of TMP (TCNQ). The upward shift of the HOMO is also visible in UPS (thick lines). Since STS values have been taken at low coverage, Figure 7.8 shows the low-coverage UPS signal. For the complex the difference between the STS and UPS HOMO positions (distance 0.6 eV) is somewhat larger than for TMP. The Δ SCF binding energy prediction (cyan line) lies close to the UPS signal. The calculated LUMO eigenvalue (upper magenta line) shows good agreement with the STS LUMO position, similar as in the case of TCNQ. The HOMO eigenvalue is substantially too high, i. e. the calculated gap of 0.6 eV is about a factor of 2 smaller than the experimental gap ($\Delta_{exp} = 1.25 \text{ eV}$) because of overestimation of intermolecular distances in DFT. The HOMO of TCNQ becomes HOMO-3 in the complex; it is not shown in Figure 7.8.

For the donor, TMP the calculated level positions deviate considerably from the measured results. The LUMO (HOMO) eigenvalues lie 2.5 eV (2 eV) higher than the measured STS values. The measured UPS HOMO position lies rather close to the STS value (0.3 eV difference). The calculated Δ SCF binding energy is about 0.6 eV smaller



Figure 7.8: Energy scheme of the TCNQ-TMP complex (center) in comparison with the pure phases of TCNQ (left) and TMP (right). In order to compare with theory, the binding energy scale is referenced to the vacuum level. Thick, thin and dotted lines denote the experimental UPS, STS and CV results, chain and dashed lines represent theoretical molecular orbital eigenvalues and Δ SCF binding energies, respectively. Δ_{opt} is the experimental value [95] for the optical gap of TCNQ, adapted at the STS LUMO level [96]. Δ_{exp} denotes the gaps determined by STS for TMP and the complex.

than the STS/UPS signals. The cyclic voltammetry (CV) result for the HOMO lies 1.8 eV above the STS/UPS signals, but quite close to the calculated HOMO eigenvalue. Obviously there is a substantial difference between the measurements for the condensed phase (STS, UPS) of TMP on the one hand and the calculation for free molecules and the CV measurement in liquid environment on the other hand. The size of the gap as determined by STS ($\Delta_{exp} = 3.5 \text{ eV}$) compares well with the measured optical gap [97] of 3.16 eV and agrees well with the difference of the HOMO-LUMO eigenvalues (3.6 eV). For the CT complex STS reveals a strong reduction of the gap to $\Delta_{exp} = 1.25 \text{ eV}$ due to an upward shift of the energy of the HOMO (compared with TMP) by 1.0 eV and a smaller downward shift of the LUMO (compared with TCNQ) by 0.3 eV. The calcu-

lation shows that the HOMO (LUMO) of the complex is derived from the respective orbitals of TMP (TCNQ).

For the acceptor TCNQ the LUMO determined by the STS-measurement [64] (green line) and the CV result [96] (blue line) agree very well and lie close to the prediction of the molecular orbital calculation (purple line). The HOMO position observed in UPS (red line) agrees quite well with the calculated Δ SCF binding energy (cyan line). The measured optical gap [98] $\Delta_{opt} = 3.2 \text{ eV}$ is significantly larger than the difference of the HOMO-LUMO eigenvalues (purple lines, distance 2.4 eV), although using the first excitation of TD-DFT gives 3.04 eV which is in good agreement with the experimental results. Due to its large distance from the Fermi level, the HOMO of TCNQ could not be observed in STS. The HOMO position denoted by the green line at 7.5 eV was derived from the LUMO position measured by STS, adding the value of the optical gap Δ opt.

7.6 Summary

It is shown that the attractive interactions in charge transfer complexes (D-A pairs) based on PAHs are not restricted to van der Waals (vdW) forces. Therefore, B3LYP provides a minimum in the potential energy surface (PES) for the CT complexes, whereas for the coronene dimer only repulsive interaction exists. Although B3LYP can locate the minima on the PES, the vdW correction is crucial for the electronic structure calculation of the D-A dimer. The vdW correction decreases the intermolecular distances and the HOMO and LUMO positions depend strongly on these distances. Comparison with the experiment shows that the vdW correction increases the band gap in CTC. Coronene dimer as a π -stacking system has a vdW dominant interaction, while for the D-A pairs like CHO-HMC (with the coronene center) vdW is the main interaction but the Coulomb attraction is either important. Among all the CT complexes, HMC-HAT-(CN)₆ and HMP-HAT-(CN)₆ show the stronger interaction than the other studied CT complexes. It is shown that even thought without vdW the deviation is too high, it can indicate the trend of band gap and MO shifts in different complexes.

8 Rb₄O₆ at high pressure

8.1 Introduction

Almost eighty years ago, Bernal predicted that any nonmetallic solid should ultimately become metallic at high pressure due to the electron delocalization [99]. Among the simple diatomic molecules, oxygen is of particular interest because it shows a triplet ground state with collective magnetic behavior. At a pressure of 6.2 GPa oxygen transforms from an antiferromagnetic phase to a phase with ferromagnetic stacking of antiferromagnetic planes [100, 101], and at 96 GPa it becomes metallic associated with a structural phase transition [102]. At about 100 GPa, it looses its magnetism and becomes a superconductor [103].

From the scientific point of view the alkali metal oxides are of fundamental interest because of their unique ability of incorporating oxygen in a variety of electronic states, i.e., as atomic oxygen, peroxide, hyperoxide, and ozonide [104, 105, 106].

Correlation is typically the domain of materials with 3d and 4f orbitals, comparatively little attention has been paid to the local correlations in *p*-orbital systems. Rb₄O₆ is an important example because two different oxygen molecules (hyperoxide and peroxide) are located inside the lattice. Therefore, Rb₄O₆ can be considered as a molecular solid. In the ground state, Rubidium sesquioxide contains two open shell hyperoxide anions and one closed shell peroxide anion. In the hyperoxide, the single unpaired electron is localized on the antibonding π^* orbital as depicted in Figure 8.1. It causes anionogenic magnetic order below about 3.4 K with a frustrated noncollinear magnetic configuration [107]. Anionic mixed-valent Rb₄O₆ is an insulator with a resistivity of 0.04 MΩm [108]. However, electronic structure calculations based on LSDA predict a half-metallic state for this open shell 2*p* system [109]. The disagreement between experiment and LSDA calculations is caused by the half occupied band of the oxygen π^* state which is strongly correlated in this system.

The simplest treatment of local correlation by LDA+U method [17] result to an insulating state in a reasonable gap of 1 eV for a rather large value of U = 8.1 eV. Analogous situation is encountered by using the hybrid functional B3LYP implemented in CRYS-TAL06 [34]. For further details see Reference [17]. U = 8.1 eV is obtained by fitting the gap to gap calculated by B3LYP.

In this study, the effect of pressure on the magnetic and electronic properties of

 Rb_4O_6 is investigated.

8.2 Optimization

As shown in Figure 8.1 the peroxide molecule has four electrons in antibonding states (π^*) . Therefore, the peroxide molecule has a closed shell, nonmagnetic and with the bond order 1. The antibonding state of the hyperoxide molecule is filled with 3 electrons which makes this molecule magnetic with the bond order 1.5. Therefore a larger bond length is expected for the peroxide with the bond order 1 than for the hyperoxide molecules. There are 6 anionic oxygen molecules in the unit cell in which there are two O_2^- and three O_2^{2-} . A suitable symmetric crystal should distinguish these two types of the anionic oxygen molecules.

The calculated electronic structure of Rb_4O_6 depends strongly on the choice of the symmetry of the system. Cubic symmetry keeps the peroxide and hyperoxide molecules equivalent with the same bond lengths. Therefore the charge is delocalized over the system since oxygen molecules are indistinguishable.

For this reason a metallic ground state was obtained with space group $I\bar{4}3d$ where all dioxygen anions are symmetrically equivalent [109]. In order to obtain the correct ground state, a geometry optimization was performed on the structure with the help of B3LYP implemented in CRYSTAL06. A full optimization of the fractional coordinates was performed in the symmetry broken structure. In this symmetry $(I\bar{4}2d)$ the two hyperoxide molecules are symmetrically independent from the remaining peroxide molecules. Fractional optimization deliver two different bond lengths for peroxide and hyperoxide molecules. In order to study the magnetic order the optimization has been repeated for an even lower symmetry with the space group $I2_12_12_1$ for the antiferromagnetically ordered system. In the $I2_12_12_1$ all the oxygen molecules are symmetrically independent.

Both the ferro- and antiferromagnetic states are insulators with distinguished bond lengths for hyperoxide and peroxide. As shown in Figure 8.1, the hyperoxide anions are aligned along one Cartesian axis and the peroxide anions along the remaining two, orthogonal axes. Optimization in the ferro and antiferromagnetic state results in a bond length of 1.54 Å for hyperoxide and 1.34 Å for peroxide which is in good agreement with the experimental data [110, 111].

8.3 Electronic structure in ambient pressure

The first step is getting the insulating ground state and it can not be achieved if one does not distinguish between the peroxide and hyperoxide molecules in the solid. This shows clearly that the cubic symmetry is not the correct symmetry for this system. Since the



Figure 8.1: The crystallographic cell of Rb_4O_6 which is obtained for the antiferromagnetic setup in space group $I2_12_12_1$ is shown in (a). Differently oriented dioxygen anions are represented by different colors. The nonmagnetic peroxides (red) are assumed along the x axis. In accordance with the calculation, the green and blue colors are hyperoxide anions having spin up and spin down, respectively. In (b) and (c) the molecular orbital diagrams for the peroxide and hyperoxide molecules are shown.

distances between oxygen molecules are 3.6 Å, there is no strong overlap between them and thus the unpaired electron is strictly localized on the peroxide molecules which have a magnetic moment of 1 $\mu_{\rm B}$. This symmetry leads to the ferromagnetic ground state. Therefore, the gap will open as a result of localization caused by difference in the bond lengths between the hyperoxide and peroxide molecules. In the rubidium family, RbO₂ is already known as an antiferromagnetic Mott-insulator [112].

For the antiferromagnetic ground state, the highest possible symmetry is $I2_12_12_1$ with there are three different oxygen molecules (two hyperoxides with anti-parallel moments hyperoxide and a non-magnetic peroxide molecule). At ambient pressure, the ferromagnetic state is 12 meV per cell higher than antiferromagnetic one; however, both phases are insulating in agreement with the experimental results [107]. The frustrated antiferromagnetically ordered structure of Rb_4O_6 has been already indicated [107]. Here only a single collinear case of the magnetization is assumed, where the pairs of hyperoxide anions oriented in different directions coupled antiferromagnetically. In both ferro- and antiferromagnetic cases the hyperoxide molecules have the magnetic moments of approximately 1 μ_B ; the magnetic moment of peroxide is strictly zero at ambient pressure. Figure 8.2 shows the relevant projections of DOS curves for the oxygen molecules in the antiferromagnetically ordered system.

The highest occupied state in the insulator is the $\pi_q^*(2p)$ state of the nonmagnetic



Figure 8.2: Partial density of states for the sublattice of Rb_4O_6 at ambient pressure within the antiferromagnetic regime.

peroxide in agreement with previous calculations [17]. At ambient pressure all σ (2*p*) orbitals are too far below the Fermi energy to affect the electronic properties of Rb₄O₆. The small bandwidth of (about 0.28 eV) the peroxide π^* states indicates strong local correlation in this system. Indeed, calculations using LDA+U (U_{eff} =8 eV) provide the same ground state properties as B3LYP [17].

The interesting point is that Rb does not have a direct effect on the electronic structure of the system. The ground state properties of this system are mainly controlled by the oxygen molecules; as seen in Figure 8.2 the Rb states are far from the Fermi level. The same calculations were carried out for the Cs_4O_6 and the similar situation is found. Similarity between these two systems has been observed in a recent experiment as well [108].

The next part is limited to the effect of pressure on Rb_4O_6 and Cs_4O_6 is not reported. The reason of similarities between these two systems is that the electronic structure of the system has been characterized by oxygen molecules not alkali metals.

8.4 Electronic structure at high pressures

Pressure is an excellent parameter to tune U/W ratio, where U is Coulomb correlation and W is the band width. As discussed already, the electronic structure of this compound is controlled by the oxygen p states of the hyperoxide and peroxide molecules. Thus, of particular interest are the changes of the bond lengths of peroxide and the hyperoxide molecules and their influences on the electronic and magnetic structure as a function of pressure.

In Figure 8.3(c), the typical DOS plot for the different pressures is shown. By increasing the pressure the bandwidth of all oxygen states increases strongly and the bands start to overlap. Decreasing U/W ratio the correlation in the system decreases and the density functional theory within the local spin density approximation becomes more appropriate to describe the electronic structure of the system. At least, the high pressure results support the early prediction of de Groot [109] who did not distinguish between peroxide and hyperoxide molecules in the ambient pressure calculation. The increase of the bandwidth is a result of decreasing the atomic spacing. Indeed the distances between the oxygen dumbbells decrease from 3.6 Å at ambient pressure to 2.6 Å at higher pressures.

As shown in Figure 8.4, the gap and the charge ordering hold up to 75 GPa for



Figure 8.3: The sublattice density of states for Rb_4O_6 calculated with the B3LYP functional for the antiferromagnetic configuration of O_2^- anions at ambient pressure (a). The density of states for the ferromagnetic ordering of O_2^- anions at 14, 75, and 160 GPa are shown in (b), (c), and (d), respectively. Red marks the magnetic O_2^- anions and blue the nonmagnetic O_2^{2-} anions. The dashed black line indicates Rb p states. The positive values correspond to spin-up and negative to spin-down.

both the ferromagnetic and antiferromagnetic states and Rb_4O_6 stays insulating. Figure 8.3(b) shows the density of states for the ferromagnetic ground state at 14 GPa. Compared to ambient pressure the gap slightly decreases and the band widths of all states increase. Between 0 and 60 GPa the energy difference between ferromagnetic and antiferromagnetic states is less than 20 meV (Fig. 8.4). However, with increasing pressure the antiferromagnetic phase becomes unstable; at about 60 GPa the insulating ferromagnetic state is more stable by about 20 meV compared to the antiferromagnetic state. Around 70 GPa there is a drastic energy split between ferro- and antiferromagnetic states which indicates the phase transition from insulator to a half-metallic ferromagnet. This sharp change in the stability of the ferromagnetic phase at 70 GPa is a result of the drastic change in the bond length of peroxide and hyperoxide molecules as shown in Figure 8.5(a).

Since O_2^{2-} has the larger bond length, its compressibility is higher than that of



Figure 8.4: The total energy of Rb_4O_6 as a function of pressure. The energy of the antiferromagnet, shown as dashed line is taken as reference. The stability of the ferromagnetic state dramatically increases in the half-metallic regime. The difference in energy remains up to 160 GPa where the nonmagnetic metallic state appears.

 O_2^- . The differences in the bond lengths of the peroxide and hyperoxide molecules at ambient pressure and at 70 GPa are 0.2 Å and 0.13 Å, respectively. In the ferromagnet at 70 GPa the peroxides (1.38 Å) and hyperoxides (1.25 Å) carry magnetic moments of 0.11 μ_B and 0.85 μ_B , respectively, while in the antiferromagnetic regime the peroxide has a zero magnetic moment. As shown in Figure 8.5, above 70 GPa the bond lengths and magnetic moments of both peroxide and hyperoxide ions converge to almost the same values. Once the bond-length of peroxide under pressure becomes comparable to the bond length of O_2^- at ambient pressure, it acquires a magnetic moment. The critical bond length is 1.34 Å. This delocalization leads to half-metallic ferromagnetic regime between 75 GPa up to 160 GPa. At 160 GPa, third phase appears, where the oxygen molecules become equivalent and their magnetic moments vanish (Fig. 8.5). Above this pressure the nonmagnetic metallic state appears.

Such pressure-driven phase transition from an insulating to a metallic ground state



Figure 8.5: The bond length (a) and magnetic moment (b) for hyperoxide and peroxide anions at different pressure. At 160 GPa the magnetic moment for both peroxide and hyperoxide anions collapses to zero. A drastic change in the bond length of peroxide and hyperoxide molecules takes place at 75 GPa where the half-metallic ferromagnetic phase appears.

was also observed in transition metal oxides such as MnO at similar pressures [113]. However the transition from a frustrated antiferromagnet to a half-metallic ferromagnet with increasing pressure is surprising. For example in MnO, the Mott transition is driven by a collapse of the magnetic moment, which means by a transition from a high spin to a low spin state [113]. From the present knowledge Rb_4O_6 is the only compound where a ferromagnetic order is induced by increasing pressure. This is possible because of the anionic mixed valence of hyperoxide and peroxide molecules at low pressure and increasing band width with increasing pressure.

From the density of states in Figure 8.3(c) it follows that in the half-metallic regime the Rb 4p states partially hybridize with the p orbitals of the oxygen molecules. Furthermore, the $p(\sigma \text{ and } \pi)$ molecular orbitals of hyperoxide and peroxide overlap weakly. By increasing the pressure, the overlap increases and finally at 160 GPa causes delocalization and a second phase transition into a nonmagnetic metal.

8.5 Summary

In summary, the effect of external pressure on the electronic structure of the sesquioxide Rb_4O_6 was investigated and two pressure-driven phase transitions were distinguished. The electronic structure of alkali sesquioxides is controlled by anionic oxygen molecules; therefore, having the optimized structure is a prerequisite for further studying these correlated systems. The calculations deliver the insulating to the half-metallic phase transition at about 70 GPa. It was shown that anionic oxygen molecules built into a solid to a large extend behave similar to molecular oxygen. Except for the half-metallic ferromagnetic phase that appears because of anionic oxygen molecules, there are similarities in the behavior of molecular oxygen and anionic oxygen molecules under pressure. Therefore the intriguing question is whether there is a superconducting phase in Rb_4O_6 at high pressure where the metallic phase concurrents with the suppression of magnetism.

9 FeSe in the hexagonal phase

9.1 Introduction

The discovery of superconductivity in the iron-arsenide (FeAs) family has attracted interest because most of Fe-based compounds exhibit a strong magnetic behavior [114, 115, 116, 117, 118, 119, 120]. The study of these materials is complicated by the fact that their magnetic and superconducting states are competing at similar conditions. For this reason the experiments under pressure gain special importance since the magnetism is typically suppressed by decreasing the volume. In addition, the pressure is a well-controlled tuning parameter that allows to study the electronic structure by *ab initio* methods.

The simplest Fe-based superconductor has a PbO-type structure (α -FeSe), and consists of layers of edge-sharing FeSe tetrahedrals. Upon cooling the tetragonal phase undergoes a slight orthorhombic distortion by lowering its symmetry to Cmma (Group No. 67) [121, 122]. This phase transition takes place within a broad temperature range centered at about 100 K depending on the crystal size and the stoichiometry [123]. FeSe becomes superconducting at ambient pressure with a $T_{\rm c} \approx 8.5 \,\mathrm{K}$ [124]. The interesting point is that T_c raises with pressure. The highest reported T_c for iron selenide is 36.7 K at 8.9 GPa [125]. At first glance, the pressure dependence of $T_{\rm c}$ in FeSe is reminiscent of the superconducting dome observed in many unconventional superconductors, such as cuprates, heavy fermions and, of course, pnictides [125]. There is, however, a clear difference: the vanishing of superconductivity in FeSe at very high pressure is related to a first-order structural phase transition to a more densely packed hexagonal $(P6_3 mmc, NiAs-type)$ [125, 126] or its very similar orthorhombic phase (Pbnm,MnP-type) [125, 127]. Such a phase transition has been also observed in other transition metal chalcogenides (e.g., FeS) under ambient conditions [128, 129, 130]. The corresponding structures are shown in Figure 9.1. At the same time the stoichiometric tetragonal or hexagonal phases are reported to non-magnetic over the whole pressure range proved by Mössbauer spectroscopy [125]. A small amount of a NiAs-phase appears already at 7 GPa and gradually substitutes the superconducting Cmma phase until it fully converts into the NiAs-type at about 30 GPa [125]. At about 15 GPa superconductivity is suppressed where the sample is a mixture of hexagonal and tetragonal phases [125, 126]. This indicates that at least the pressure range of the superconduct-



Figure 9.1: Phase transition from the tetragonal P4/nmm to hexagonal NiAs-type structure by increasing pressure and compressing in c direction is shown in (a).The NiAs-type structure can transform to MnP-phase as shown in (b).

ing dome could be extended if this structural phase transition is avoided. The central aspect in this direction is the knowledge of the electronic structure of the NiAs-type phase and its related properties. Unfortunately there are no systematic studies on this system. However, several experiments figure few important issues which indicate that it might be an insulator. Indeed, at 25 GPa [125] when the amount of NiAs-phase in FeSe is significant, the thermal behavior of the resistivity clearly shows the semiconducting state.

A crucial aspect of FeSe is the stoichiometry. For example, while the tetragonal lowtemperature $Fe_{1.01}Se$ is superconducting, a small increase of Fe up to $Fe_{1.03}Se$ already leads to strong magnetic fluctuations which destroy the superconductivity [122, 131]. The analogous situation occurs by substituting Fe with a small amount of Cu [132, 133]. Early experiments report about various magnetic orders or paramagnetic states in nonstoichiometric low-pressure hexagonal phases of FeSe and related systems [134, 135]. At the same time the stoichiometric (very close to stoichiometric) tetragonal or hexagonal phases are reported as totally non-magnetic even at ambient pressure.

In spite of the fact that superconducting phases of FeSe have been investigated by *ab initio* methods in detail [136, 137], up to now, the electronic structure for the stoichiometric form of hexagonal (NiAs-type) iron selenide has not been studied. Here, he hybrid functional B3LYP was performed to calculate the electronic structure of NiAs-type iron selenide, and the results are compared with local density approxima-
tion (LDA). It has been shown that hybrid functionals like B3LYP give surprisingly good values for the band gap of such correlated systems, where GGA and LDA-based exchange correlation functionals fail [17, 18, 19, 20, 21, 22]. Calculations show the semiconducting ground state for the MnP-phase similar to the NiAs-phase. This study gives the opportunity to illustrate the high pressure phases of FeSe which cause the dropping of T_c .

9.2 Optimization

A structural optimization was first performed for the NiAs-type and MnP-type structure to determine whether the calculated lattice parameters at high pressures are in agreement with experimental ones. B3LYP implemented in CRYSTAL06 was used to optimize the structures. Full geometry optimization was used without any constraint, that is, lattice parameters and internal coordinates were optimized together. For the starting values, the experimental structural data was used [127, 138]. Figure 9.2 (b) demonstrates a very close agreement of the optimized structures for both MnP- and NiAs-type structures with experiment. As it follows from comparison of total energies (Figure 9.2 (a)) the high-symmetric NiAs-type structure is more stable at low pressures, while at high pressures the symmetry is reduced to more general MnP case. Since this change is caused by a slight distortion, it does not influence the electronic structure as indicated by comparison of the DOS curves on Figure 9.3. The experimental values



Figure 9.2: (a) Difference of the total energies (per atom) of NiAs- and MnP-type structures calculated as a function of pressure. (b) The pressure driven evolution of the corresponding lattice parameters. The results of optimization are displayed by squares. Red circles mark the experimental data [127, 138].

for the lattice constants at ambient pressure are $a_{\exp} = 3.62$ Å and $b_{\exp} = 5.88$ Å. The optimized values for the stoichiometric hexagonal structure are $a_{\text{theo}} = 3.62$ Å and $b_{\text{theo}} = 5.97$ Å, which are in a good agreement with the experimental results. The results of

optimization for the hexagonal NiAs-phase are listed and plotted in Table 9.1 and Figure 9.2 respectively. It shows that, in the case of the B3LYP, the optimization results are in an excellent agreement with the experiment for a wide range of pressures for the both MnP and NiAs-type structures.

Figure 9.2 shows that at the high pressure MnP-type phase is more stable than

Table 9.1: Optimization of the tetragonal (P4/nmm) [125, 122] and hexagonal [127] at the different pressures using the B3LYP (CRYSTAL06) and GGA (WIEN2K) exchange correlation functionals. Experimental results are from the references [125, 122] and [127]. "w" means GGA using WIEN2K and "c" is the B3LYP by CRYSTAL06.

	Ambient pressure			1.5 GPa			$12 { m ~Gpa}$		
P4/nmm	Exp.	Theo.(w)	Theo.(c)	Exp.	Theo.(w)	Theo.(c)	Expe.	Theo.(w)	Theo.(c)
a (Å)	3.77	3.74	3.74	3.68	3.62	3.69	3.58	3.54	3.62
c (Å)	5.53	5.62	5.79	5.22	5.32	5.18	4.9	5.02	4.78
Volume $(Å^3)$	78.652	const	const	70.69	const	const	62.80	const	const
Se z	0.2668	0.243	0.241	NO	0.266	0.258	NO	0.285	0.284

	0.25 GPa			$4 {\rm ~Gpa}$			9 GPa		
$P6_3/mmc$	Exp.	Theo.(w)	Theo.(c)	Exp.	Theo.(w)	Theo.(c)	Expe.	Theo.(w)	Theo.(c)
a (Å)	3.590	3.746	3.585	3.509	3.634	3.502	3.439	3.53	3.427
c (Å)	5.866	5.387	5.88	5.684	5.298	5.705	5.463	5.108	5.501
Volume $(Å^3)$	65.489	const	const	60.61	const	const	55.95	const	const

the NiAs-phase about 25 meV/atom, while in the low pressures (~ 9 GPa) NiAs is a dominant phase. Interestingly, the optimization of the low-pressure MnP-type structure delivers the same hexagonal NiAs-type phase. This result reasonably agrees with the experimental findings [127].

9.3 Electronic Structure calculation with B3LYP

The electronic structure of NiAs- and MnP-type phases of FeSe was calculated using the hybrid functional B3LYP and compared to GGA results. As shown in Fig. 9.3, B3LYP shows a semiconducting ground state for both the MnP- and NiAs-type structure. Plain GGA fails by predicting a metallic state as a ground state 9.4. The calculated band gap for the hexagonal phase is about 1.8 eV at 9 GPa as can be seen in Figure. 9.3. Although semiconducting and stoichiometric hexagonal FeSe at ambient conditions has not been observed, a thin film with a hexagonal phase has been reported as a semiconductor with a band gap of 1.23 eV [139].

B3LYP also shows a metallic ground state for the superconducting tetragonal (P4/nmm) and orthorhombic (Cmma) phases similar to LDA [124].



Figure 9.3: (a) The total DOS curves for the MnP and NiAs-phase of FeSe are shown.(b) Corresponding band structure for the hexagonal NiAs phase is shown.Both the phases are insulating using hybrid functional (B3LYP) at the about 9 GPa.

9.4 Electronic Structure Calculation with GGA

The correlation-induced origin of the gap can be verified by applying alternative approaches which account for the local correlations explicitly, as e.g. the GGA+U method. In the following, the GGA and GGA+U based band structures are analyzed. These calculations were performed by WIEN2K using the same lattice parameters as obtained from previous geometry optimizations. As follows from Figure 9.4, the origin of the band gap delivered by B3LYP could be indeed explained on the basis of static approximation to the local on-site electron correlation, as provided by GGA+U.

The plain GGA description, which lacks the proper treatment of strong correlation, delivers a metallic state. The band gap is opened due to the strong Coulomb repulsion which splits the correlated Fe d-shell into lower and upper Hubbard bands.

As shown in Figure. 9.4, the plain GGA description $(U_{\rm eff} = 0)$ is indeed rather inadequate and total DOS shows an metallic state. $U_{\rm eff} \approx 7 \,\mathrm{eV}$ shows the band gap about $1.2 \,\mathrm{eV}$.

At the first glance this value appears to be very high. On the other hand, qualitatively it is clear that the local Coulomb interaction in strongly correlated systems such as Mott insulators, is screened substantially weaker than in metals. Indeed, the adequate results for these systems have been typically obtained at very high U values [140, 141]. Despite the different band gaps (about 1.1 eV within GGA+U (at



Figure 9.4: DOS curves calculated with the plain GGA (gray area), GGA+U with $U_{\text{eff}} = 4 \text{ eV}$ (pink area) and $U_{\text{eff}} = 7 \text{ eV}$ (blue line) are shown.

 $U_{\rm eff} = 7 \,\mathrm{eV}$) and 1.8 eV within the B3LYP) at 10 GPa, the similarity between the Hartree-Fock and GGA+U exchange-correlation functionals lead to a qualitatively similar behavior of the system under pressure.

9.5 Effect of pressure on NiAs phase

By increasing the pressure, the band gap gradually shrinks (see Figure 9.5) indicating the possibility of insulator-metal transition at very high pressure. Calculations predict such transition at about 60 GPa. Such behavior suggests a strongly-correlated origin of the band gap analogical to the situation encountered e.g. in transition metal oxides, including the known high-T_c superconductors [142, 143, 144, 145, 146] which exhibit a pressure driven insulator-metal transition accompanied by a competition of the localized-itinerant electron contributions. As shown in Figure 9.5, $U_{\text{eff}} = 4 \text{ eV}$ is not adequate for this system since in the experiment, up to 25 GPa the NiAs-type is in an insulating phase [125]. The ban gap is closed at around 60 GPa.

As seen in the Figure 9.5, the pressure increases the band width in the orbitals aligned along the c axes, which are the d_{z^2} orbitals. Fe-Fe distances in the xy-plane are too large to have a strong overlap of the orbitals located in this plane even at high pressure. Along the c axis the Fe-Fe distance is 2.9 Å at the low pressure regime where the system is an insulator. By increasing the pressure, the Fe-Fe distance decreases to 2.52 Å and the overlap between the d_{z^2} orbitals increases, which lead to a strong disper-



Figure 9.5: (a) the effect of pressure on the band gap is shown. With GGA+U ($Ue_{eff} = 4 \text{ eV}$) the gap will be close at 20 GPa which is in contrast with the experiment [125] and $Ue_{eff} > 4 \text{ eV}$ is needed to keep the gap open at higher pressures. B3LYP shows an insulating state up to 60 GPa. (b) shows that the pressure mainly influences the d_{z^2} and dispersion in this band will increase.

sion and an insulator-metal transition. Therefore, d_{z^2} has a density of electrons at the Fermi energy, while other orbitals do not have one (See Fig. 9.5). One has the opposite situation for FeSe in the tetragonal phase which is metallic. In this phase, the Fe-Fe distances along the z axis are about 5.4 Å and in the xy plane about 2.57 Å. Therefore, the overlap of the in xy-plane is strong, while d_{z^2} is completely intact because of large Fe-Fe distance along the c direction (5.4 Å). As a result, the Fe-Fe distance in the xy plane for tetragonal and along the z axis in hexagonal controls the electronic structure.

9.6 Summary

The hexagonal phase of FeSe, which substitutes the tetragonal superconducting phase at high pressures is found to be strongly correlated. These local correlations lead to an insulating state. The corresponding band gap reduces due to increasing delocalization with pressure up to the insulator-metal transition which occurs at roughly above 60 GPa. These results reasonably connect the scattered partial experiences from different experiments on FeSe and the series of related systems within a single picture. Moreover, optimization of MnP-phase at low pressures deliver NiAs structure which is experimentally observed in the earlier studies. It is shown that the Fe-Fe distance influences the correlation strength which cause the insulator-metal transition.

10 Summary

The electronic structure of several molecular and crystalline systems have been studied. This work emphasizes the potential of hybrid functionals (B3LYP) in the correlated systems. Obtained results with hybrid functionals agree well with the experiment for both the disk-shape donor and acceptor molecules and the strongly correlated crystalline systems. By taking advantage of the exact Hartree-Fock exchange, these functionals work well for both molecular and crystalline systems.

Chapter 6 is dedicated to functionalized polycyclic aromatic hydrocarbons. The electronic structure of the PAHs has been studied with the help of B3LYP hybrid density functionals. Using the Δ SCF method, electron binding energies have been determined which affirm, specify and complement the experiment results measured by UPS. Symmetry properties of molecular orbitals are analyzed for a categorization and an estimate of the related signal strength. While σ -like orbitals are difficult to detect by UPS measurements of condensed films, calculations provide a detailed insight into the hidden parts of the spectra. In addition, a diffuse basis set (6-311++G^{**}) has been used to calculate the electron affinity and LUMO eigenvalues. The calculated electron affinity (EA) provides a quantitative classification of the donor/acceptor properties of the studied molecules. Coronene-hexaone shows a high EA, comparable to TCNQ, which is a well-known classical acceptor. HOMO-LUMO gaps (the lowest excitation energies) are calculated by both the time-dependent and the time-independent B3LYP method. The results obtained from the calculated LUMO-HOMO gap agree with the measured optical gaps.

Chapter 7 reports about the $\pi - \pi$ complexes formed by several donor and acceptor molecules based on polycyclic aromatic hydrocarbons. Density functional theory (DFT) calculations were carried out to determine the geometric structure of complexes. For the coronene dimers, the attraction is based on vdW interaction while all other interactions are repulsive. Therefore, the pure DFT calculations provide a purely repulsive interaction. For the charge transfer complexes, the DFT calculation provide minimum one the potential energy surface. This attraction is caused by Coulomb interactions. However, the attraction based on Coulomb interaction is not the strongest interaction in CTCs. The vdW corrections improve the intermolecular distances as well as the binding energy. Decreasing the intermolecular distances leads to large shifts in the HOMO and LUMO energies. As a results, B3LYP with the vdW correction is a fast and accurate approach for the study of CTCs based on PAHs.

Chapter 8 shows that the strongly correlated open-shell $2p \text{ Rb}_4\text{O}_6$ exhibits a variety of interesting physical phenomena under high pressure. There are two different kinds of anionic oxygen molecules in the solid simultaneously, hyperoxides and peroxides; at ambient pressure the former carry magnetic moments and the latter are strictly nonmagnetic. Around 75 GPa a transition from an insulating antiferromagnetic phase to a half-metallic ferromagnetic phase takes place. The change of the structure is smooth, so that one could assume a second order transition with a quantum critical point. At pressures higher than 75 GPa, all anionic oxygen molecules (peroxide and hyperoxide) carry magnetic moments, yet still showing a small difference in the bond length. Finally, above 160 GPa a metallic phase appears, where all oxygen molecules show the same bond length without magnetic moment. It is shown that the bond length differences of O_2^{2-} and O_2^{-} have a vital effect on magnetism and the conductivity of rubidium sesquioxide.

Chapter 9 reports a systematic study of the high-pressure FeSe phase performed by means of first-principle electronic structure calculations. Based on available experimental information about the unit cell geometry, the band structure is calculated and the related properties during pressure driven evolution are characterized. Full geometry optimizations agree well with reported experiments at high pressures for both the NiAs- and MnP-type structures. Description of Phase transition between the NiAs- to MnP-type structure agrees with the observed experiment. NiAs is a dominant phase in low pressures and in the high pressures (more than 10 GPa) MnP-phase is a stable phase with about 100 meV energy difference. The electronic structure calculation with the hybrid functional B3LYP leads to the correct semiconducting ground state for hexagonal stoichiometric FeSe. The role of correlation, stoichiometry and the borderline to magnetism are discussed. In particular, it is shown that the NiAs-phase structure exhibits strong local correlations which lead to a semiconducting state within the broad pressure range.

List of Abbreviations

DFT	density functional theory
GGA	generalised gradient approximation
LDA	local density approximation
MP2	second Møller-Plesset perturbation theory
IP	ionization potential
$\mathbf{E}\mathbf{A}$	electron affinity
UPS	ultraviolet photoelectron spectroscopy
vdW	van der Waals
μ_B	Bohr magneton
Å	angstrom
eV	electron volt
Κ	kelvin, unit of temperature
GPa	gigapascal
$T_{ m c}$	critical temperature
DOS	density of states
W	band width
GTO	Gaussian type orbitals
STO	Slater type orbitals
HOMO	highest occupied molecular orbital
LUMO	lowest unoccupied molecular orbital
LCAO	linear combination of atomic orbitals
PAHs	polycyclic aromatic hydrocarbons
MO	molecular orbital
HMC	hexamethoxycoronene
CHO	coronene-hexaone
TMP	tetramethoxypyrene
PTO	pyrene-tetraone
OMe	methoxy
TCNQ	tetracyanoquinodimethane
$HAT-(CN)_6$	hexaazatriphenylene-hexacarboni-trile
CTC	charge transfer complex

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