Organic adsorbates on metal surfaces: PTCDA and NTCDA on Ag(110)

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To my wife

To my son

To my mother
Bibliographische Beschreibung

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Referat

Polyaromatic molecules functionalized with carboxylic groups have served as model systems for the growth of organic semiconducting films on a large variety of substrates. Most non-reactive substrates allow for a growth mode compatible with the bulk phase of the molecular crystal with two molecules in the unit cell, but some more reactive substrates including Ag(111) and Ag(110) can induce substantial changes in the first monolayer (ML). In the specific case of Ag(110), the adsorbate unit cell of both NTCDA and PTCDA resembles a brickwall structure, with a single molecule in the unit cell. From this finding, it can be concluded that the adsorbate-substrate interaction is stronger than typical inter-molecular binding energies in the respective bulk phases.

In the present work, the interactions between small Ag(110) clusters and a single NTCDA or PTCDA molecule are investigated with different \textit{ab initio} techniques. Four major ingredients contribute to the binding between adsorbate and substrate: Directional bonds between Ag atoms in the topmost layer and the oxygen atoms of the molecule, Pauli repulsion between filled orbitals of molecule and substrate, an attractive van-der-Waals interaction, and a negative net charge on the molecule inducing positive image charges in the substrate, resulting therefore in an attractive Coulomb interaction between these opposite charges. As both Hartree-Fock theory and density functional theory with typical gradient-corrected density functional do not contain any long range correlation energy required for dispersion interactions, we compare these approaches with the fastest numerical technique where the leading term of the van-der-Waals interaction is included, i.e. second order Møller-Plesset theory (MP2). Both Hartree-Fock and density functional theory result in bended optimized geometries where the adsorbate is interacting mainly via the oxygen atoms, with the core of the molecule repelled from the substrate. Only at the MP2 level, the inclusion of the major part of the attractive van-der-Waals interaction brings the adsorbate back to an arrangement close to parallel to the substrate, with very small differences in height between the different subunits. With respect to experimental data obtained on Ag(111), the calculated distance between adsorbate and substrate is somewhat smaller, indicating that the open Ag(110) surface interacts more strongly with the organic compounds. This is consistent with the fact that only Ag(110) induces a brickwall unit cell.
of the adsorbate, a clear sign for a particularly large adsorption energy. The resulting model geometries are analysed in terms of cohesive energy, Mulliken charges, core level shifts, and vibrational properties.

Schlagwörter

*Ab initio*, Organic semiconductor, Adsorption, PTCDA, NTCDA, Ag(110) surface, Møller-Plesset theory.
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<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>B3LYP</td>
<td>Becke’s three-parameter hybrid density functional</td>
</tr>
<tr>
<td>BSSE</td>
<td>basis set superposition error</td>
</tr>
<tr>
<td>CC</td>
<td>coupled-cluster</td>
</tr>
<tr>
<td>CCSD(T)</td>
<td>coupled-cluster singles and doubles with perturbative triples</td>
</tr>
<tr>
<td>CI</td>
<td>configuration interaction</td>
</tr>
<tr>
<td>CP</td>
<td>counterpoise</td>
</tr>
<tr>
<td>DFT</td>
<td>density functional theory</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform infrared</td>
</tr>
<tr>
<td>GGA</td>
<td>generalized gradient approximation</td>
</tr>
<tr>
<td>HF</td>
<td>Hartree-Fock</td>
</tr>
<tr>
<td>HOMO</td>
<td>highest occupied molecular orbital</td>
</tr>
<tr>
<td>HREEL</td>
<td>high-resolution electron energy loss spectroscopy</td>
</tr>
<tr>
<td>KS</td>
<td>Kohn-Sham</td>
</tr>
<tr>
<td>LDA</td>
<td>local density approximation</td>
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<tr>
<td>LEED</td>
<td>low energy electron diffraction</td>
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<tr>
<td>LUMO</td>
<td>lowest unoccupied molecular orbital</td>
</tr>
<tr>
<td>ML</td>
<td>monolayer</td>
</tr>
<tr>
<td>MP2</td>
<td>Møller-Plesset perturbation theory</td>
</tr>
<tr>
<td>NEXAFS</td>
<td>near-edge X-ray absorption fine structure</td>
</tr>
<tr>
<td>NTCDA</td>
<td>1,4,5,8-naphthalene tetracarboxylic acid dianhydride</td>
</tr>
<tr>
<td>PBE</td>
<td>Perdew-Burke-Ernzerhof GGA functional</td>
</tr>
<tr>
<td>PTCDA</td>
<td>3,4,9,10-perylene tetracarboxylic acid dianhydride</td>
</tr>
<tr>
<td>PES</td>
<td>potential energy surface</td>
</tr>
<tr>
<td>RI</td>
<td>resolution of identity</td>
</tr>
<tr>
<td>SCF</td>
<td>self-consistent field</td>
</tr>
<tr>
<td>STM</td>
<td>scanning tunneling microscope</td>
</tr>
<tr>
<td>STS</td>
<td>scanning tunneling spectroscopy</td>
</tr>
<tr>
<td>UPS</td>
<td>ultraviolet photoelectron spectroscopy</td>
</tr>
<tr>
<td>vdW</td>
<td>van-der-Waals</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>XSW</td>
<td>X-ray standing wave</td>
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</table>
Chapter 1

Introduction

1.1 Organic nanoscience and organic/inorganic interfaces

In the last few decades, several studies have focused on organic semiconductors due to their potentially interesting properties for electronic and optoelectronic applications such as organic light emitting diodes (OLED) [1, 2], organic field effect transistors (OFET) [3, 4] and organic solar cells [5].

In all such devices, molecule-metal contacts and interfaces are rather important. The basic knowledge especially about the interfaces involved is still limited. Therefore, the methods of surface science have to be applied in order to improve the knowledge about organic/inorganic interfaces. It is possible to prepare highly pure, ultrathin layers of large π-conjugated molecules by organic molecular beam deposition (OMBD) on various substrates. This allows to study the interaction of molecules with the surface of single crystals used as model substrates [6–8]. The interaction between the inorganic surface and the first organic molecular layer plays a dominant role for the properties of an organic/inorganic system. This kind of interaction determines the orientation and ordering of the first layer of the adsorbed molecules and the subsequent growth behavior of the following layers, so that it plays a key role for the electronic interface properties such as orbital level alignment and charge transport [9–12].

The term adsorption denotes a process occurring when a gas or liquid solute (adsorbate) accumulates on the surface of a solid or a liquid (adsorbent). The adsorption can either occur by chemical or by physical bonding. In chemisorption, there are well oriented chemical bonds between adsorbate and adsorbent in contrast to physisorption, referring to adsorption based on the dispersion interaction.

Many experimental techniques are applied to the study of organic/inorganic interfaces. Low energy electron diffraction (LEED) patterns show the degree of structural order and allow the determination of the adsorbate unit cell [13–15]. Real-space structural models can be deduced from LEED patterns in combination with scanning tunnel microscope (STM) images of monolayer films. Information about frontier orbitals can
be obtained from ultraviolet photoelectron spectroscopy (UPS) and X-ray photoelectron spectroscopy (XPS) [16,17]. Normal incidence X-ray standing wave (XSW) technique is frequently used to obtain the precise distances between atoms or molecules and the topmost substrate layer [18–20].

Despite the wide range of techniques that have been used to understand the adsorption process, there are still a lot of open questions which could only be answered based on a precise theoretical model for the adsorption geometry. In the next section we give some examples of the challenges for surface science where quantifying theoretical models could help to elucidate the open questions.

1.2 PTCDA on Ag substrates as a model system for organic/metal interfaces

Perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA) (Fig. 1.1) is one of the best studied π-conjugated organic molecules and it has become a model system for various benchmark studies. PTCDA belongs to a class of pigments showing an intensive color with excellent light-fastness [21,22]. More recently, the semiconducting properties of the crystalline phase have received increasing attention [3]. PTCDA has a planar structure and in the crystalline phase it exhibits a finite overlap between the π-systems of adjacent molecules [23–25]. PTCDA provides very pure and highly ordered films with very nice epitaxial properties on several metals [26–41]. It contains four carboxylic groups and two anhydride groups which have different prospects of bonding than the perylene core of the molecule. The PTCDA molecule is easily processable, stable under electron and photon bombardment, and therefore amenable to surface science studies.

The LEED and STM technique have been used to study the superstructure of PTCDA monolayers on different substrates [26–41]. Due to the epitaxial growth of PTCDA on Ag(111), this interface is more interesting to surface scientists than other interfaces, and it allows to study details of the bonding phenomena. Even though the superstructure of PTCDA on surfaces can easily be determined by LEEDs, a detailed knowledge of the bonding requires further studies with complementary techniques.

1.2.1 Vibrational spectra of PTCDA adsorbed on silver surfaces

High-resolution electron energy loss (HREEL) and Fourier transform infrared (FTIR) spectroscopy were used for the investigation of PTCDA films on Ag(110) and Ag(111) surfaces [35, 36]. While these two techniques present complementarity information about the vibrational modes of adsorbed molecules, HREELS has an advantage over FTIR spectroscopy consisting in the excessively high surface sensitivity of much less than 0.1 monolayer (ML) and the ready accessibility of the complete spectral area, consequentially starting at about 2.5 meV and extending into the eV range of electronic
Figure 1.1: Atomic structure of NTCDA and PTCDA. Orange spheres - carbon atoms, red spheres - oxygen atoms, white spheres - hydrogen atoms. NTCDA has an aromatic naphthalene core and is terminated by two anhydride side groups at both ends. Similarly, PTCDA has an aromatic perylene core and is terminated by two anhydride side groups at both ends. Each number shows atoms in equivalent positions.
transitions. F. S. Tautz et al. [35, 36] recorded HREEL spectra of PTCDA multilayers (3.5, 4.5 and 11 ML) on the Ag(110) surface. Figure 1.2 shows a HREEL spectrum of a PTCDA multilayer (4.5 ML) on the Ag(110) surface. It was shown that with increasing layer thickness certain modes like the modes at 382, 436 cm$^{-1}$ and all modes above 900 cm$^{-1}$, become more prominent in comparison with the modes at 572, 736, 810, and 867 cm$^{-1}$, while the intensities of the latter modes are equivalent for all film thicknesses. These facts were described in the framework of the surface selection rule if the peaks at 382, 436 cm$^{-1}$, and above 900 cm$^{-1}$ were assigned to parallel polarized modes and the strong modes at 572, 736, 810, and 867 cm$^{-1}$ were assigned to vertical polarized modes. This conclusion is corroborated by off-specular HREELS measurements and by density functional theory (DFT) calculations of a single molecule. In dipole scattering from metallic surfaces, dynamical dipoles oriented parallel to the surfaces are fully screened by their image charges, such that parallel polarized modes are not excited by this scattering mechanism. In contrast, dynamical dipoles oriented normal to the surface are enhanced by a factor of 2 by their image dipole.

Figure 1.3 shows the results of specular and off-specular HREELS experiments of the submonolayer PTCDA film on Ag(110), and also HREELS of the 4.5 ML PTCDA on Ag(110) [36]. Comparing the multilayer with the submonolayer in specular detection, one observes dramatic differences. The specular HREELS data of PTCDA molecules adsorbed on Ag surfaces are modified very strongly as compared to free molecules or a multilayer. Some of these differences are a direct result of the strict validity of the surface selection rule for the submonolayer, e.g., the strongly reduced scattering intensity above 900 cm$^{-1}$. In some cases the places of the modes in multilayer were strongly changed in the submonolayer dipole spectrum. This indicates large changes of the force constants within the molecule, resulting from the interaction with the metal. For example the three modes which in the multilayer occur at 736, 810, and 867 cm$^{-1}$ (Fig. 1.3 a) appear at 716, 781, 808 cm$^{-1}$ in the sub-monolayer spectrum of PTCDA on Ag(110). This cannot be explained by any argument based on selection rules, since for the monolayer the specular (dipole) and the off-specular (impact) spectrum are identical in this frequency range. The multilayer spectra presented [36] correspond very well to the theoretical calculations for the free molecule, except for small frequency splittings detectable in FTIR due to intermolecular interactions. However, a deeper understanding of the monolayer spectra would require calculations of the surface-bound molecule before they can be interpreted unambiguously.

### 1.2.2 Effect of frontier orbitals on the chemical bonding

The UPS/IPES techniques give information of the PTCDA frontier orbitals. UPS spectra of PTCDA are strongly affected by the presence of the substrate. Submolecular STM contrast and scanning tunneling spectroscopy (STS) imaging show that in the adsorption of PTCDA on Ag(111) the lowest unoccupied molecular orbital (LUMO) of the molecule becomes partially occupied [6, 17, 42, 43]. Near edge X-ray absorption
Figure 1.2: HREEL spectrum of PTCDA multilayer on Ag(110). (a) HREEL spectrum of 4.5 ML, (b) deconvoluted HREEL spectrum of 4.5 ML which has been obtained by deconvolution routin, (c) FTIR spectrum corresponding with more than 10 ML PTCDA on Ag(111). (b) Frequency labels in cm$^{-1}$ have been included for the stronger peaks that are also clearly visible in the as-measured data of (a).
Figure 1.3: (a) HREELS data for the 4.5-ML PTCDA film on Ag(110), (b) off-specular and (c) specular HREELS data for the submonolayer film of 0.3-ML thickness. x, y, and z labels denote the polarization of the respective modes.
Figure 1.4: Model of the chemical bonding of PTCDA on Ag(110) (left) and Ag(111) (right). A schematic energy diagram of the pure Ag metal consisting of a 5s-band and the 4d-band is depicted in the left-hand side of each panel, and the HOMO and the LUMO of a free PTCDA molecule are shown on the right-hand side of each panel. Orbitals labelled A, B, C, and D are new hybridized orbitals which are derived from the interaction of molecular HOMO (A and B) and LUMO (C and D) with substrate.

Fine structure (NEXAFS) data in the range of the binding energy of the C 1s core state also give a clear indication of the occupation of the former LUMO [17]. The (partial) occupation of the previously unoccupied LUMO state and the resulting charge transfer is indicative of chemical bonding. Fig. 1.4 represents a schematic energy level diagram for PTCDA/Ag system which was taken from Ref. [17]. The left side represents a model for the energy levels for the PTCDA/Ag(110) and the right hand side for PTCDA/Ag(111). It shows that the highest occupied molecular orbital (HOMO) of the molecule interacts with the substrate forming a bonding and an anti-bonding hybrid orbital denoted with A and B, respectively. In principle, it is possible to validate this model with experimental techniques like angle-resolved ultraviolet photoelectron spectroscopy, but a detailed picture requires a precise calculation which takes the local bonding geometry into account.

### 1.2.3 Molecular distortion

Normal incidence XSW techniques have been used to obtain precise information concerning the height of the adsorbed species with respect to the topmost substrate layer, including reference cases like PTCDA [44–46] and NTCDA [20] deposited on Ag(111) (Table 1.1). Both compounds form closed monolayers with the molecular plane oriented parallel to the substrate surface, allowing for the determination of the activation
energy for thermal desorption [47], tunneling spectra, and shifts of the core levels with respect to thicker polycrystalline films [32, 45, 48]. The XSW measurements have revealed that the carboxylic oxygens are closer to the substrate than the aromatic core, indicating the formation of strong chemical bonds between the functional groups and the substrate. Possible height modulations within the carbon backbone are more difficult to track, so that the evaluation of the experimental data remains restricted to an average height, where a reduced coherent fraction represents destructive interference of C atoms placed at different distances from the topmost substrate layer [20]. In a first attempt, DFT calculations seemed to reproduce the XSW geometry obtained for PTCDA on Ag(111) [44], but in a revised calculation with more extended variational orbitals, a much too shallow potential minimum occurred at an adsorbate-substrate distance of about 0.5 Å above the experimentally determined height [49, 50] (Fig. 1.5).

1.3 Superstructure models of adsorbed PTCDA and NTCDA on Ag(111) and Ag(110) surfaces

The atomic structures of NTCDA and PTCDA are shown in Fig. 1.1. NTCDA has a naphthalene aromatic core which is terminated on both sides by two carboxylic anhydride side groups. Similarly, PTCDA has a perylene core which is terminated by the same side groups. Both molecules have a $D_{2h}$ point symmetry. Despite the difference...
### Table 1.1: Experimental height (Å) of different parts of the NTCDA and PTCDA above the topmost ML of the different substrates.

<table>
<thead>
<tr>
<th>Adsorption system</th>
<th>$z_C$</th>
<th>$z_O$</th>
<th>$z_O$(carb)</th>
<th>$z_O$(anh)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTCDA/Cu(111) [45]</td>
<td>2.66</td>
<td>2.81</td>
<td>2.73</td>
<td>2.89</td>
</tr>
<tr>
<td>PTCDA/Ag(111) [44]</td>
<td>2.86</td>
<td>2.78</td>
<td>2.68</td>
<td>2.97</td>
</tr>
<tr>
<td>PTCDA/Au(111) [46]</td>
<td>3.27</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PTCDA/Ag(110) [51]</td>
<td>2.59</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NTCDA/Ag(111) [20]</td>
<td>3.00</td>
<td>2.83</td>
<td>2.75</td>
<td>3.00</td>
</tr>
</tbody>
</table>

$z_C$ and $z_O$ denote to the average height of carbons and oxygens above the topmost ML of substrat and $z_O$(carb) and $z_O$(anh) are height of carboxylic and anhydride oxyegen.

...in size, the electronic structure of isolated NTCDA and PTCDA is rather similar.

NTCDA and PTCDA molecules possess an electric quadrupole moment and have strong electron accepting properties. Keeping this similarity in mind, it is justified to compare the behaviour of these two molecules on metal surfaces and to review the experimental results together. In many cases, similar behaviour has been proved experimentally. However, there exist much more experimental data for PTCDA than for NTCDA. Both adsorbates show a long-range ordered monolayer structure at room temperature. The lateral superstructures of both adsorbate systems have been well investigated with various techniques. In the case of PTCDA adsorbed on Ag(111), the molecular arrangement in the monolayer fits well to that of the (102) plane in crystalline PTCDA, and well-oriented homogeneous films with a thickness of about 1000 layers were realized. On this specific substrate, the self-organization of organic monolayers is largely determined by the molecular mobility and the intermolecular interaction, a prototypical behaviour observed on several inert substrates. The weak interaction with the substrate may lead to the formation of incommensurate monolayers and polycrystalline films. The superstructures can define by the analysis of the LEED data. In the conventional matrix notation, the superstructures are given as

$$\begin{pmatrix} \vec{b}_1 \\ \vec{b}_2 \end{pmatrix} = M \begin{pmatrix} \vec{a}_1 \\ \vec{a}_2 \end{pmatrix}$$  \hspace{1cm} (1.1)$$

where $\vec{b}_1$ and $\vec{b}_2$ are basis vectors of the superstructure, $\vec{a}_1$ and $\vec{a}_2$ are unit vectors, and $M$ is a transformation matrix defined as:

$$M = \begin{pmatrix} m_{11} & m_{12} \\ m_{21} & m_{22} \end{pmatrix}$$  \hspace{1cm} (1.2)$$

The superstructures are commensurate with the substrate, when all numbers $m_{ij}$,
Table 1.2: LEED pattern for PTCDA and NTCDA monolayers on Ag(111) and Ag(110) surfaces. \( \gamma \) is the angle between \( \vec{b}_1 \) and \( \vec{b}_2 \), \( \phi \) is the angle between the long molecular axis and the unit vector \( \vec{b}_1 \) of the unit cell, and \( \alpha \) is the angle between \( \vec{b}_1 \) and \( \vec{a}_1 \) (vectors of the substrate unit cell).

\[
M = \left( \begin{array}{cc}
+6 & +1 \\
-3 & +5 \\
\end{array} \right), \quad \left( \begin{array}{cc}
+2 & +3 \\
-2 & +3 \\
\end{array} \right), \quad \left( \begin{array}{cc}
+4 & 0 \\
+3 & +6 \\
\end{array} \right), \quad \left( \begin{array}{cc}
+6 & -1 \\
+1 & +7 \\
\end{array} \right), \quad \left( \begin{array}{cc}
+3 & 0 \\
+1 & +3 \\
\end{array} \right)
\]

The matrix elements \((i,j)\) of the matrix \(M\) are integer. Since in all cases the substrate spots could be observed simultaneously, the numbers of the derived crystallographic data are accurate to at least 5%. The analysis of the LEED pattern for PTCDA and NTCDA monolayers on Ag(111) and Ag(110) are summarized in Table 1.2. STM and LEED investigations for NTCDA monolayers on Ag(111) substrate reveal two different superstructures, a relaxed superstructure with two molecules in a unit cell and a compressed one with four molecules in each unit cell. For NTCDA on Ag(110) a very similar structure to PTCDA/Ag(110) was found, so that each adsorbate unit cell contains one NTCDA molecule (Fig. 1.7) [52, 53].

For PTCDA, the adsorption site was determined by a manipulation of Ag adatoms [54], whereas the preferred position of NTCDA within the adsorbate unit cell was deduced from DFT calculations [55].

Fig. 1.6 shows the orientation of the PTCDA molecules with respect to an Ag substrate which has been derived from STM images with submolecular resolution [32]. For NTCDA, Alkauskas [55] used DFT methods to study four different possible adsorption geometries as presented in Fig. 1.7. From the energetic point of view the T site is the best structure for NTCDA adsorbed on Ag(110) surface, and a real space model can be derived from this calculation.

## 1.4 Ab initio study of structure and bonding of large aromatic molecules on noble metal surfaces

Due to the fast development of computers and numerical algorithms, molecular quantum calculations have become one of the largest branches of computational physics and
Figure 1.6: (a) Left: narrow-scan STM picture of a PTCDA monolayer on Ag(111). Right: real-space model of PTCDA adsorbed on Ag(111). Ag atoms are represented by dots, and PTCDA molecules by their vdW radii. A unit cell containing two inequivalent molecules is indicated in both parts. (b) Left: narrow-scan STM picture of a PTCDA monolayer on Ag(110). Right: real-space model of PTCDA adsorbed on Ag(110). Ag atoms are represented by circles, and PTCDA molecules by their vdW radii. A unit cell containing one molecule is indicated in both parts [32].

Figure 1.7: (a) Local adsorption geometries studied [55]: T (top), SB (short bridge), LB (long bridge) and H (hollow). The names refer to the position of the midpoint of the central C=C bond with respect to the underlying Ag(110) surface. (b) Real space model of NTCDA on Ag(110).
chemistry. Many quantitative and qualitative properties of the molecules like ground-state electronic structure of the system and vibrational modes can be obtained from the molecular quantum calculations. Due to the lack of correlation terms in the Hartree-Fock (HF) approach, post HF methods like Møller-Plesset perturbation theory (MP2) and configuration interaction (CI) are widely used. These methods are using the HF wave functions as the zeroth-order approximation to the total wave function. The computational cost of such schemes grows extremely fast with system size. DFT methods are widely used in solid state physics since they are well suited for describing periodic systems in a crystalline structure. Moreover DFT methods have a lower computational cost than post HF methods, and they can calculate the short range part of the correlation energy.

Although much work has been devoted to the theoretical understanding of the interfaces between large organic semiconductor and metal surfaces they still constitute a big challenge to theory, for two reasons. On the one hand, this is due to the height numerical requirements of carrying out calculations for systems of this size and complexity. On the other hand, due to the limitation of DFT methods on short range correlations, calculating the van-der-Waals (vdW) interactions still remain beyond common DFT schemes.

S. Picozzi et al. [57] used a generalized gradient approximation (GGA), density functional to study the adsorption geometry of PTCDA on the Ag(111) and Al(111) surfaces. In this study the adsorbed PTCDA was kept parallel to the metal (111) surface during the geometry optimization. Hence they had lost the main feature concerning the molecular distortion on the adsorbed molecule.

Kraft et al. used DFT in the local density approximation (LDA) and GGA approaches to study the lateral adsorption geometry and the site-specific electronic structure of PTCDA on a Ag(111) surface [43]. They investigated the adsorption energy of different adsorption sites of PTCDA on a Ag(111) surface to find the best adsorption geometry. They found large differences between the adsorption energies obtained with LDA and GGA approaches.

Rohlfing et al. [58] used DFT-LDA calculations of a monolayer of PTCDA on the Ag(111) surface, to discuss the bond lengths inside the molecules, the distortion of the molecules due to adsorption, their position and orientation relative to the substrate, and the geometric arrangement of the two molecules in the adsorbate unit cell with respect to each other. Based on the geometric and electronic structures, they calculated scanning tunneling microscopy and spectroscopy data.

Alkauskas et al. [55] studied the adsorption geometry of NTCDA on an Ag(110) surface using a DFT-GGA functional and a plane wave code, identifying the most stable adsorption site within the shown unit cell containing a single NTCDA molecule Fig. 1.7.
1.5 Limitations of density functional theory

The adsorption of small molecules on the surface of transition metals has been analyzed in great detail with DFT, resulting in a quantitative understanding of the chemical bonding and of subsequent reactions catalyzed by the metal [59, 60]. The success of these studies depends crucially on the large binding energy of the adsorbate, so that the absence of dispersion interactions in standard DFT does not induce significant shortcomings. For aromatic molecules adsorbed to transition metals, DFT can reproduce the large chemisorption energies resulting from the interaction of the adsorbate with a partly filled \( d \) band [61–64].

In sharp contrast to this behaviour, the binding potential of aromatic molecules on noble metals is rather shallow, so that the attractive vDW interaction between adsorbate and substrate may give a major contribution to the adsorption energy. For pentacene on gold, it was found that DFT with the gradient-corrected PBE (Perdew-Burke-Ernzerhof) functional [65] underestimates the adsorption energy by a factor of four, and plane waves and localized basis sets give equivalent results once a calculation with the latter accounts for the counterpoise (CP) correction of the basis set superposition error (BSSE) according to the Boys-Bernardi scheme [65–67].

An analysis of the density-density response function constructed within the random phase approximation, provides the vDW interaction resembling the experimental situation [68]. This work demonstrates that DFT-LDA results in a substantial overbinding, with an interaction potential resembling erroneously a realistic dispersion interaction, whereas functionals employing the well tested GGA underestimate the absorption energy. Hybrid functionals like B3LYP cannot cure this deficiency because both the underlying GGA functional and the HF part result in similar failures of the interaction potential. In reference cases where dispersion interactions dominate, it was found that 25 common density functionals fail completely to predict both reasonable geometries and interaction energies [69], just like HF. Therefore, it was suggested that HF or DFT augmented by dispersion interactions included in the form of a sum over pair potentials may give a significant improvement with respect to standard DFT [70, 71]. Even though it cannot be denied that these semi-empirical schemes reduce systematic deviations of DFT, they become questionable even for dimers of rare gas atoms where a pair potential for the dispersion interaction should be adequate [71]. For polyaromatic molecules, it is evident that the calculated dispersion interaction has to be based on molecular orbitals, as opposed to a sum over pair potentials whose validity cannot be guaranteed.

An alternative computational approach to dispersion interactions arises naturally from post-HF methods, including configuration interaction (CI) or coupled-cluster (CC) schemes. As these approaches scale very steeply with the system size, they can only be applied to rather small systems, including e.g. pairs of small aromatic molecules like benzene, naphthalene or anthracene [72–76]. Second order Møller-Plesset perturbation theory (MP2) still keeps track of the leading order of the vDW attraction arising from double excitations, and with respect to the more advanced
schemes, its scaling with the fifth power of the system size remains moderate. Therefore, for very small systems, its range of applicability can be tested with more expensive methods like CC techniques including single and double excitations together with a perturbative treatment of triple excitations (CCSD(T)) scaling as \( N^7 \). For rather large systems, MP2 emerges as a suitable compromise including the main part of the dispersion interactions at affordable cost.

### 1.6 Outline

The remaining part of the thesis is organized as follows. In chapter 2 we describe the theoretical basis of different *ab initio* schemes. First we discuss the HF approximation as one of the essential *ab initio* methods. Due to the lack of correlation terms in this scheme the development of post HF methods has become the main topic of quantum chemistry. We discuss MP2 and CC methods as examples of two possible strategies quantifying the correlation terms. Then, we discuss resolution of identity (RI) approaches as a method to reduce the cost of the numerical calculation. We shall discuss the basic ingredients of DFT, an *ab initio* technique widely used in chemistry and solid state physics. A brief discussion of the basis sets is presented in Sec. 2.9. Then, we discuss the BSSE and the standard method for correcting this error. The last section of chapter 2 is devoted to model cluster calculation. There we will show advantages and disadvantages of the cluster calculations compared to periodic boundary approaches.

Chapter 3 deals with *ab initio* calculations of the dispersion interaction between the PTCDA molecule and an Ag(110) substrate. In Sec. 3.2, we investigate the suitability of different *ab initio* methods to the intermolecular interactions in \( \alpha \)-PTCDA, and in Sec. 3.3, two of them are applied to the optimization of a PTCDA molecule interacting with an Ag(110) substrate. Sec. 3.4 is devoted to an analysis of the charge distribution in the adsorbate, interpreted in more detail in Sec. 3.5 in terms of specific orbitals highlighting selected interaction mechanisms and distance dependence of orbital energies in Sec. 3.6. In Sec. 3.7, we analyse the shifts of the core levels with respect to the free molecule, and Sec. 3.8 presents the modified vibrational fingerprint of adsorbate modes producing a dipole moment along the substrate normal. The main achievements of this chapter are summarized in Sec. 3.9.

Chapter 4 concerns the influence of dispersion interactions on the adsorption of NTCDA on Ag(110). There we apply MP2 and the B3LYP hybrid functional to an investigation of the adsorption geometry of NTCDA on the Ag(110) surface. Sec. 4.2 introduces the theoretical approaches applied in this work and motivates the choice of the used substrate clusters. Sec. 4.3 is devoted to the optimized geometries found on these clusters. Sec. 4.4 dealing with the cluster size dependence of the adsorption energy of NTCDA on the Ag(110) surface. In Sec. 4.5, we interpret the bonding mechanism based on the MOs and distance dependence of MOs energies. In Sec. 4.6, we study the adsorption geometry of naphthalene on the Ag(110) surface to find the effect of functional groups on the adsorption of NTCDA on Ag(110). The main
findings of this work are summarized in Sec. 4.7.

The achievements of the present work will be summarized in Chapter 5.
Chapter 2

Electronic structure calculation

2.1 Schrödinger equation

The first objective of electronic structure calculation is to solve the time-independent
Schrödinger equation for electrons in molecules. The exact solution of the Schrödinger
equation can only be done just for a very small numbers of simple model systems.
However there are several levels of sophisticated approximations allowing rather pre-
cise computations. The first approximation which separates the Schrödinger equation
into one part which describes the electronic wave function for a fixed nuclear geom-
etry and another part which describes the wave function of nuclear motion is called
the Born-Oppenheimer approximation (BO) \cite{77}. The electronic wave function plays
the role of a potential for the nuclear motion. The electronic part of the Schrödinger
equation is given by:

\[ H \psi(r; R) = E(R) \psi(r; R) \]  

(2.1)

where the Hamiltonian for N electrons and M nuclei is defined as

\[ H = -\frac{1}{2} \sum_i^N \nabla_i^2 - \sum_i^N \sum_A^M Z_A \frac{1}{r_{iA}} + \frac{1}{2} \sum_i^N \sum_{i,j}^N \frac{1}{r_{ij}} \]  

(2.2)

In the above equation, \( Z_A \) is atomic number of nucleus \( A \), \( r_{iA} \) is the distance between the
\( i \)th electron and the \( A \)th nucleus and \( r_{ij} \) is the distance between the \( i \)th and \( j \)th electrons.
The first term represents the kinetic energy of electrons and the second and third terms
show the electron-nuclei and electron-electron Coulomb interaction respectively. All
terms in the above equation and the remaining part of this work are represented in
atomic units. There are many approximation methods to solve Eq. (2.1). In an \textit{ab initio}
calculation, Eq. (2.1) is solved using the values of fundamental constants and
the atomic number of the nuclei as the only input. However, for large systems, the
electron-electron interaction cannot be solved exactly, so that it has to be simplified
with some approximation, the starting point being the HF method.
2.2 The Hartree-Fock method

The HF method is an approximate theory where each electron feels an average Coulomb repulsion due to the presence of the other electrons in an \( N \) electron wave function \( \psi(x_1, x_2, x_3, \ldots, x_N) \) depending on coordinates \((x_1, x_2, x_3, \ldots, x_N)\) of electrons \(1, 2, 3 \ldots N\), where \( x_i \) represents both the spatial \((r_i)\) and spin \((\omega = \alpha \text{ or } \beta)\) coordinates of the \(i\)th electron. In HF theory, this wave function is expressed as a single Slater determinant,

\[
\psi_{HF} = \frac{1}{\sqrt{N!}} \left| \begin{array}{cccc}
\chi_1(x_1) & \chi_2(x_1) & \ldots & \chi_N(x_1) \\
\chi_1(x_2) & \chi_2(x_2) & \ldots & \chi_N(x_2) \\
\vdots & \vdots & \ddots & \vdots \\
\chi_1(x_N) & \chi_2(x_N) & \ldots & \chi_N(x_N)
\end{array} \right|
\] (2.3)

where \( \chi_i(x_j) \) represents an electron with coordinates \( x_j \) in a spin orbital \( \chi_i \). The factor \( \sqrt{N!} \) is a normalization factor. This Slater determinant has \( N \) electrons occupying \( N \) spin orbitals \((\chi_1, \chi_2, \ldots, \chi_N)\) without specifying which electron is in which orbital.

The Slater determinant is an expression for the many-particle wave function respecting the indistinguishability of electrons. It also satisfies the antisymmetry principle, which states that the wave function should be antisymmetric under the interchange of any two electrons. The HF method is based on variational theory which defines the best \( N \)-electron determinantal wave function by minimizing the Rayleigh ratio

\[
E = \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle}
\] (2.4)

Without discussing the details of the derivations, the total HF energy can be written in terms of one and two-electron integrals and nuclear repulsion energy, as

\[
E_{HF} = \sum_{i=1}^{N} \langle \chi_i | h | \chi_i \rangle + \frac{1}{2} \sum_{i<j}^{N} (J_{ij} - K_{ij}) + V_{nn}
\] (2.5)

where the first term is a summation over the one-electron integrals. i.e. the integration is over the coordinates of a single electron, as

\[
\langle \chi_i | h | \chi_i \rangle = \int dx_1 \chi_i^* (x_1) h(x_1) \chi_i (x_1)
\] (2.6)

the variables of integration are, by convention, chosen to be the coordinates of electron one and \( h(x_1) \) is the single particle Hamiltonian for electron 1:

\[
h(x_1) = -\frac{1}{2} \nabla_1^2 - \sum_{A} \frac{Z_A}{r_{1A}}
\] (2.7)

The second term in the Eq. 2.5 is the summation over the two-electron Coulomb integrals \( J_{ij} \) and exchange integrals \( K_{ij} \).
\[ J_{ij} = \int d\mathbf{x}_1 d\mathbf{x}_2 \chi_i^*(\mathbf{x}_1) \chi_i^*(\mathbf{x}_2) \frac{1}{r_{12}} \chi_j(\mathbf{x}_1) \chi_j(\mathbf{x}_2) \]  
(2.8)

\[ K_{ij} = \int d\mathbf{x}_1 d\mathbf{x}_2 \chi_i^*(\mathbf{x}_1) \chi_i^*(\mathbf{x}_2) \frac{1}{r_{12}} \chi_j(\mathbf{x}_1) \chi_i(\mathbf{x}_2) \]  
(2.9)

The integrals in the above expressions are examples of two-electron integrals, i.e., the integration is over the space and spin coordinates of electron 1 and 2. It is conventional always to choose the dummy variables of integration in a two-electron integral to be the coordinate of electrons 1 and 2.

The HF method involves determining the orbitals that minimize the expression of the HF energy (Eq. 2.5). This is achieved through the Lagrange method of undetermined multipliers. The application of this procedure leads to HF equations [78, 79] based on single particle orbitals \( \chi_i(\mathbf{x}_1) \) with

\[ f(\mathbf{x}_1) | \chi_i(\mathbf{x}_1) \rangle = \varepsilon_i | \chi_i(\mathbf{x}_1) \rangle \]  
(2.10)

where \( \varepsilon_i \) is the orbital energy of the single particle orbital \( \chi_i \) and \( f \) is the Fock operator defined as:

\[ f(\mathbf{x}_1) = h(\mathbf{x}_1) + \sum_i [J_i(\mathbf{x}_1) - K_i(\mathbf{x}_1)] \]  
(2.11)

The **Coulomb operator** \( J_i \), and the **exchange operator** \( K_i \), arise from the Coulomb interaction between the electrons, defined as:

\[ J_i(\mathbf{x}_1) | \chi_j(\mathbf{x}_1) \rangle = \left\langle \chi_i(\mathbf{x}_2) \left| \frac{1}{r_{12}} \right| \chi_j(\mathbf{x}_2) \right\rangle | \chi_j(\mathbf{x}_1) \rangle \]  
(2.12)

\[ K_i(\mathbf{x}_1) | \chi_j(\mathbf{x}_1) \rangle = \left\langle \chi_i(\mathbf{x}_2) \left| \frac{1}{r_{12}} \right| \chi_j(\mathbf{x}_2) \right\rangle | \chi_i(\mathbf{x}_1) \rangle \]  
(2.13)

The Coulomb operator takes into account the electrostatic repulsion between pairs of electrons. There is no classical equivalent for the exchange operator arising from the indistinguishable electrons with parallel spins but the exchange guarantees that two electrons with the same spin cannot be found in the same single particle orbital (Pauli principle). Electrons with the same spin thus tend to avoid each other so that they experience a smaller Coulomb repulsion. To solve the HF equation (Eq. 2.10) it is necessary to know the value of the Coulomb and exchange operators which depend on the spin orbitals. Clearly, to construct the HF equation, one should know some aspects of the solution in advance. The procedure requires an initial guess of spin orbitals defining starting values for the Fock operator. The HF equations are solved, giving an improved solution of spin orbitals, which are used for the next iteration. This procedure is eventually repeated until the difference among successive iterations fall below a sufficient small threshold. Therefore, this solution of the HF approximation is called self-consistent field (SCF) method.
2.3 The closed-shell HF equations

It is possible to eliminate the spin from the Eq. 2.11, by writing spin orbitals based on their spin and spatial parts in the form

$$\chi_i(x_1) = \begin{cases} \Psi_j(r_1)\alpha_\omega \\ \Psi_j(r_1)\beta_\omega \end{cases}$$

(2.14)

The HF equation for closed-shell and doubly-occupied (restricted) sets of orbitals, is

$$f(r_1) = h(r_1) + \sum_{i}^{N/2} 2J_i(r_1) - K_i(r_1)$$

(2.15)

where the sum runs over the $N/2$ occupied orbitals. In this case closed-shell Coulomb and exchange operators are defined in terms of spatial orbitals as

$$J_i(r_1)|\Psi_j(r_1)\rangle = \left\langle \Psi_i(r_2)\frac{1}{r_{12}}|\Psi_j(r_2)\right\rangle |\Psi_j(r_1)\rangle$$

(2.16)

$$K_i(r_1)|\Psi_j(r_1)\rangle = \left\langle \Psi_i(r_2)\frac{1}{r_{12}}|\Psi_j(r_2)\right\rangle |\Psi_i(r_1)\rangle$$

(2.17)

The new form of the energy expression for the restricted HF equation in terms of spatial orbitals is

$$E_{HF} = 2 \sum_i^{N/2} \langle \Psi_i|h|\Psi_i\rangle + \sum_{ij}^{N/2} 2 \left\langle \Psi_i\Psi_i|\frac{1}{r_{12}}\Psi_j\Psi_j\right\rangle - \left\langle \Psi_i\Psi_j|\frac{1}{r_{12}}\Psi_j\Psi_i\right\rangle$$

(2.18)

For the rest of this chapter of the thesis we mainly use the restricted closed-shell HF formalism.

2.3.1 The Roothaan equations

As the exact form of the molecular orbitals for most atoms and molecules is not known, we introduce a set of $K$ known spatial basis functions $\phi_\mu$ and express each of the unknown spatial orbitals as a linear combination of these basis function.

$$\Psi_i = \sum_{\mu=1}^{K} C_{\mu i} \phi_\mu$$

(2.19)

where the $C_{\mu i}$ represent a set of unknown coefficients. If the set of $\phi_\mu$ was complete, it would become an exact expansion, and any complete set could be used. However, due to computational limitations, one is restricted to a finite set of basis functions. Here it is important to choose a basis which is as large as possible to a complete basis. A reasonably accurate expansion for the exact spatial orbitals $\Psi_i$ substituted into Eq. 2.15.
yields a set of \( K \) equations known as the Roothaan equations. The matrix notation of this equation is

\[
FC = SC\varepsilon
\]

(2.20)

where the Fock matrix \( F \) is a Hermitian \( K \times K \) matrix, and its elements are

\[
F_{\mu\nu} = \langle \phi_{\mu}(r_1)|f(r_1)|\phi_{\nu}(r_1) \rangle
\]

(2.21)

and the coefficient matrix \( C \) is a \( K \times K \) square matrix. The \( S \) matrix, called the overlap matrix, is also a Hermitian \( K \times K \) square matrix with elements given by

\[
S_{\mu\nu} = \langle \phi_{\mu}(r_1)|\phi_{\nu}(r_1) \rangle
\]

(2.22)

and \( \varepsilon \) is a \( K \times K \) diagonal matrix containing the single-particle orbital energies \( \varepsilon_i \). From the Eq. 2.21 we can derive a form of the Fock matrix by writing the Fock operator in terms of one and two-electron operators (the algebraic step to obtain this equation is skipped):

\[
F_{\mu\nu} = H_{\mu\nu}^{\text{core}} + \sum_{\lambda\sigma} P_{\lambda\sigma} \left\{ \langle \mu|\lambda\sigma \rangle - \frac{1}{2} \langle \mu\lambda|\nu\sigma \rangle \right\}
\]

(2.23)

where \( H_{\mu\nu}^{\text{core}} \) is the core-Hamiltonian matrix

\[
H_{\mu\nu}^{\text{core}} = \langle \phi_{\mu}(r_1)|h(r_1)|\phi_{\nu}(r_1) \rangle
\]

(2.24)

and \( P_{\lambda\sigma} \) are called the density matrix elements defined by

\[
P_{\lambda\sigma} = 2 \sum_{i} \frac{N/2}{C_{\lambda i}^* C_{\sigma i}}
\]

(2.25)

It is now clear that the Fock matrix elements \( F_{\mu\nu} \) depend on the expansion coefficient \( C_{\mu i} \) and hence the wave function. In this case the Roothaan equations must be solved iteratively starting with a set of expansion coefficients \( C_{\mu i} \) and testing for the convergence at each iteration step.

### 2.4 Electron correlation

The main drawback of HF theory is that it cannot represent electron correlation. The instantaneous position of an electron is influenced by its neighboring electrons while in the SCF method the electrons are assumed to be moving in an average potential of the other electrons. Often, neglecting electron correlation leads to unphysical results, especially in the study of intermolecular interactions, where electron correlation is crucial.
2.5 The coupled-cluster methods

The idea of coupled-cluster method was proposed by Bartlett (1989). Before going to the discussion of this method, let $i, j, l, \ldots$ denote the occupied spin-orbitals in the ground-state HF function $|\Psi_0\rangle$ and let $a, b, c, d, \ldots$ denote the unoccupied (virtual) spin-orbitals. Each unperturbed wave function can be classified by the number of virtual spin-orbitals it contains; this number is called the excitation level. Let $|\Psi_i^a\rangle$ denote the singly excited determinant that differs from $|\Psi_0\rangle$ by replacement of $\chi_i$ by the virtual spin-orbital $\chi_a$ and $|\Psi_{ij}^{ab}\rangle$ denote the doubly excited determinant formed from $|\Psi_0\rangle$ by replacement of $\chi_i$ by $\chi_a$ and $\chi_j$ by $\chi_b$; and so on. In the CC method the wave function is written as

$$\Psi_{cc} = e^{\hat{T}} \Psi_{HF}$$  (2.26)

where $\Psi_{HF}$ is the ground-state HF wave function and the operator $e^{\hat{T}}$ is defined as

$$e^{\hat{T}} = 1 + \hat{T} + \frac{\hat{T}^2}{2!} + \frac{\hat{T}^3}{3!} + \ldots = \sum_{k=0}^{\infty} \frac{\hat{T}^k}{k!}$$  (2.27)

$\hat{T}$ is an operator acting on the HF wave function that has the effect of generating all the excited Slater determinants. For a molecule with $N$ electrons, these can be classified according to the number of excitations,

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \ldots + \hat{T}_N$$  (2.28)

In this equation $\hat{T}_1$ is defined by

$$\hat{T}_1 \Psi_{HF} = \sum_{i} \sum_{a} t_{i}^{a} \Psi_{i}^{a}$$  (2.29)

and is an operator generating single excitations from the HF reference, and $\hat{T}_2$

$$\hat{T}_2 \Psi_{HF} = \sum_{i} \sum_{a<v} t_{ij}^{ab} \Psi_{ij}^{ab}$$  (2.30)

generates double excitations and so on. The expansion coefficients $t_{i}^{a}$ and $t_{ij}^{ab}$ are called the $t$-amplitudes. By expanding the exponential,

$$e^{\hat{T}} = \hat{1} + \hat{T}_1 + \left(\hat{T}_2 + \frac{1}{2} \hat{T}_1^2\right) + \left(\hat{T}_3 + \hat{T}_2 \hat{T}_1 + \frac{1}{6} \hat{T}_1^3\right) + \ldots,$$  (2.31)

the CC wave function comprises all the excited Slater determinants. For instance, the second order term will involve connected doubles through $\hat{T}_2$, and disconnected doubles through $\hat{T}_1^2$. In the CC singles and doubles approximation (CCSD), both the $\hat{T}_1$ and $\hat{T}_1^2$ operators are exerted in constructing $\Psi_{CC}$, and the wave function is written as
\[ \Psi_{CCSD} = \{ 1 + \hat{T}_1 + \hat{T}_2 + \frac{1}{2} (\hat{T}_1^2 + \hat{T}_1 \hat{T}_2 + \hat{T}_2 \hat{T}_1 + \hat{T}_2^2) + \frac{1}{6} (\hat{T}_1^3 + \hat{T}_1^2 \hat{T}_2 + \hat{T}_1 \hat{T}_2^2 + \hat{T}_2 \hat{T}_1^2 + \hat{T}_2^3 + \ldots) \} \Psi_{HF} \] (2.32)

From this equation, apparently disconnected higher order excitations can be obtained from the lower order connected excitations. As \( \hat{T}_1 \) commutes with the \( \hat{T}_2 \) operator, a part of the above expansion can be simplified. For example, the product \( \hat{T}_1 \hat{T}_2 \hat{T}_1 \) can be written as \( \hat{T}_2 \hat{T}_1^2 \). By inserting the CC wave function into the time-independent Schrödinger equation

\[ \hat{H} e^{\hat{T}} \Psi_{HF} = E_{cc} e^{\hat{T}} \Psi_{HF} \] (2.33)

multiplying by \( \Psi_{HF} \) and integrating gives

\[ \left\langle \Psi_{HF} | \hat{H} e^{\hat{T}} | \Psi_{HF} \right\rangle = E_{cc} \left\langle \Psi_{HF} | e^{\hat{T}} \Psi_{HF} \right\rangle \] (2.34)

Using the intermediate normalization (\( \langle \Psi_{HF} | \Psi_{cc} \rangle = 1 \)) and an expansion of \( \hat{T} \) in the above equation in terms of \( \hat{T}_1 \) and \( \hat{T}_2 \) gives \( E_{cc} \) as

\[ E_{cc} = \left\langle \Psi_{HF} | \hat{H} e^{\hat{T}} | \Psi_{HF} \right\rangle = \left\langle \Psi_{HF} | \hat{H} (1 + \hat{T}_1 + \hat{T}_2 + \frac{1}{2} \hat{T}_1^2 + \ldots) | \Psi_{HF} \right\rangle \] (2.35)

Since HF orbitals are used as a reference, Brillouin’s theorem holds. Additionally, because the Hamiltonian contains one- and two-particle operators, terms like \( \hat{T}_1 \hat{T}_2 \) and \( \hat{T}_3 \) will have zero matrix elements with the Hamiltonian in the above equation [78]. By applying these properties to the Hamiltonian, the following energy expression can be obtained

\[ E_{cc} = E_{HF} + \sum_{i<j} \sum_{a<b} \left( t_{ij}^{ab} + t_{ij}^{a} t_{ij}^{b} - t_{ij}^{b} t_{ij}^{a} \right) \left( (ij|ab) - (ab|ij) \right) \] (2.36)

with four-index two-electron integrals \( (ij|kl) \) denoted according to

\[ (ij|kl) = \langle \chi_i \chi_j | \chi_k \chi_l \rangle \] (2.37)

and \( t_{ij}^{a} \) are amplitudes that can be extracted from the truncation of \( \hat{T} \) at some stage. The CC singles and doubles (CCSD) method is obtained by using \( \hat{T} = \hat{T}_1 + \hat{T}_2 \) whereas in CCSDT, the operator \( \hat{T} \) contains single, double and triple excitations, \( \hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 \).

For the CCSD method, amplitudes are generated by projection of the Eq. (2.33) with singly and the doubly excited determinants. The details of the derivations and the set of equations used to find the amplitudes are omitted and can be found in many advanced quantum chemistry books [80]. Computationally the CC method is highly
demanding. The CPU time for a CCSD calculation is proportional to the seventh power and for CCSDT is proportional to the eighth power of the number of basis functions. In CC singles and doubles with perturbative triples CCSD(T) method the contribution of triple excitations to the energy is computed by perturbation theory and added to the CCSD energy. This method still includes the correlation arising from triple excitations perturbatively, but the CPU time scales only with the seventh power of the number of basis functions. Calculations applying the CCSD(T) method with very large basis sets provide accurate intermolecular interaction energies.

2.6 Many-body perturbation theory

CC approach is a systematic procedure to calculate correlation energy and going beyond the HF approximation. Another systematic procedure for finding the correlation energy, is perturbation theory. In this method, the total (exact) Hamiltonian of the system is divided into two parts: a zeroth-order one, $H_0$ which has known eigenvalues and eigenfunctions, and a perturbation part, $V$. The exact energy is then expressed as an infinite sum of contributions. We suppose that the Hamiltonian $H$ is only slightly different from the Hamiltonian $H_0$ (small perturbation).

Suppose we want to solve the Schrödinger equation

$$H|\phi_i\rangle = (H_0 + V)|\phi_i\rangle = \varepsilon_i|\phi_i\rangle$$

(2.38)

where we know the eigenfunctions and eigenvalues of $H_0$,

$$H_0|i\rangle = E_i^{(0)}|i\rangle$$

(2.39)

where $|i\rangle = |\psi_i^{(0)}\rangle$. If the perturbation, $V$, is small, we expect $|\phi_i\rangle$ and $\varepsilon_i$ to be reasonably close to $|i\rangle$ and $E_i^{(0)}$, respectively. To construct a procedure by which we can systematically improve the eigenfunctions and eigenvalues of $H_0$ so that they step by step become closer to the eigenvalues and eigenfunctions of the exact Hamiltonian, $H$, we can introduce an ordering parameter $\lambda$.

$$H = H_0 + \lambda V$$

(2.40)

$\lambda$ is a parameter that can vary between zero and one and it is equal to unity for the exact Hamiltonian. The eigenfunctions $\phi_i$ and eigenvalues $\varepsilon_i$ of $H$ can be expanded in powers of $\lambda$ in a Taylor series.

$$|\phi_i\rangle = |\psi_i^{(0)}\rangle + \lambda|\psi_i^{(1)}\rangle + \lambda^2|\psi_i^{(2)}\rangle + \ldots = \sum_{n=0}^{\infty} \lambda^n|\psi_i^{(n)}\rangle$$

(2.41)

$$\varepsilon_i = E_i^{(0)} + \lambda E_i^{(1)} + \lambda^2 E_i^{(2)} + \ldots = \sum_{n=0}^{\infty} \lambda^n E_i^{(n)}$$

(2.42)
\( \Psi_i^{(0)} \) are the eigenfunctions of the zero-order Hamiltonian with energies \( E_i^{(0)} \). The ground-state wave function is thus \( \Psi_0^{(0)} \) with energy \( E_0^{(0)} \). \( E_i^{(1)} \) is the first-order correction to the energy, \( E_i^{(2)} \) is the second-order correction, and so on.

Let us take the wave function of \( H_0 \) to be normalized (\( \langle i|i \rangle = 1 \)) and then choose the normalization of \( |\phi_i \rangle \) such that \( \langle i|\phi_i \rangle = 1 \). By multiplying Eq. 2.41 by \( \langle i| \) , we have

\[
\langle i|\phi_i \rangle = \langle i|i \rangle + \lambda \langle i|\psi_i^{(1)} \rangle + \lambda^2 \langle i|\psi_i^{(2)} \rangle + \ldots = 1
\]  

(2.43)

The above equation holds for all values of \( \lambda \). Therefore, the coefficients of \( \lambda^n \) on both sides must be equal, and hence

\[
\langle i|\Psi_i^{(n)} \rangle = 0 \quad n = 1, 2, 3, \ldots
\]  

(2.44)

Substituting Eqs. 2.41 and 2.42 into Eq. 2.38,

\[
(H_0 + \lambda V) (|i \rangle + \lambda |\psi_i^{(1)} \rangle + \lambda^2 |\psi_i^{(2)} \rangle + \ldots) = (E_i^{(0)} + \lambda E_i^{(1)} + \lambda^2 E_i^{(2)} + \ldots) (|i \rangle + \lambda |\psi_i^{(1)} \rangle + \lambda^2 |\psi_i^{(2)} \rangle + \ldots)
\]  

(2.45)

and equating coefficients of \( \lambda^n \), we can find

\[
H_0|i \rangle = E_i^{(0)}|i \rangle
\]  

(2.46)

\[
H_0|\psi_i^{(1)} \rangle + V|i \rangle = E_i^{(0)}|\psi_i^{(1)} \rangle + E_i^{(1)}|i \rangle
\]  

(2.47)

\[
H_0|\psi_i^{(2)} \rangle + V|\psi_i^{(1)} \rangle = E_i^{(0)}|\psi_i^{(2)} \rangle + E_i^{(1)}|\psi_i^{(1)} \rangle + E_i^{(2)}|i \rangle
\]  

(2.48)

\[
H_0|\psi_i^{(3)} \rangle + V|\psi_i^{(2)} \rangle = E_i^{(0)}|\psi_i^{(3)} \rangle + E_i^{(1)}|\psi_i^{(2)} \rangle + E_i^{(2)}|\psi_i^{(1)} \rangle + E_i^{(3)}|i \rangle
\]  

(2.49)

and so on. Multiplying each equation by \( \langle i| \) and using the orthogonality relation, we obtain the following expressions for the \( n \)th-order correction of the energies

\[
E_i^{(0)} = \langle i|H_0|i \rangle
\]  

(2.50)

\[
E_i^{(1)} = \langle i|V|i \rangle
\]  

(2.51)

\[
E_i^{(2)} = \langle i|V|\psi_i^{(1)} \rangle
\]  

(2.52)

\[
E_i^{(3)} = \langle i|V|\psi_i^{(2)} \rangle
\]  

(2.53)
All that remains is to solve the set of equations 2.46 - 2.49 for \( |\Psi_i^{(n)}\rangle \) and determine the \( n \)th-order energy using the equation series of 2.50 - 2.52.

Let us consider Eq. 2.47, which gives the first-order wave function \( |\Psi_i^{(1)}\rangle \). This can be rewritten as

\[
\left( E_i^{(0)} - H_0 \right) |\Psi_i^{(1)}\rangle = \left( V - E_{i}^{(1)} \right) |i\rangle = (V - \langle i|V|i \rangle) |i\rangle
\]  

(2.54)

This equation is not an eigenvalue equation but an inhomogeneous differential equation. To solve this equation we can expand \( |\Psi_i^{(1)}\rangle \) in terms of the eigenfunctions of \( H_0 \),

\[
|\Psi_i^{(1)}\rangle = \sum_n c_{i}^{(1)} |n\rangle
\]  

(2.55)

Since the eigenfunctions of \( H_0 \) are orthonormal, multiplying this equation by \( \langle n| \), we find

\[
\langle n|\Psi_i^{(1)}\rangle = c_{n}^{(1)}
\]  

(2.56)

From Eq. 2.44 it is clear that \( c_{i}^{(1)} = 0 \), so we can write

\[
|\Psi_i^{(1)}\rangle = \sum_n' \langle n| \langle n|\Psi_i^{(1)}\rangle
\]  

(2.57)

where the prime on the summation serves as a reminder that the term \( n = i \) is excluded. Multiplying Eq. 2.54 by \( \langle n| \) and using the fact that the zeroth-order wave functions are orthogonal, we have

\[
\left( E_i^{(0)} - E_{n}^{(0)} \right) \langle n|\Psi_i^{(1)}\rangle = \langle n|V|i \rangle
\]  

(2.58)

Using Eq. 2.57 in Eq. 2.52 for the second-order energy, we obtain

\[
E_i^{(2)} = \langle i|V|\Psi_i^{(1)}\rangle = \sum_n \langle i|V|n\rangle \langle n|\Psi_i^{(1)}\rangle
\]  

(2.59)

and hence, using Eq. 2.58, we finally have

\[
E_i^{(2)} = \sum_n' \frac{\langle i|V|n\rangle \langle n|V|i \rangle}{E_i^{(0)} - E_n^{(0)}} = \sum_n' \frac{\langle i|V|n\rangle^2}{E_i^{(0)} - E_n^{(0)}}
\]  

(2.60)

which is the desired expression for the second-order correction to the energy.

### 2.6.1 Møller Plesset perturbation theory

As we discussed before, the problem of HF method is the correlation energy which could not be obtained. We can improve the HF energy of an \( N \)-electron system by
means of perturbation theory. In other words, we hope to obtain the perturbation expansion for the correlation energy [80, 81]. We partition the Hamiltonian as

$$H = H_0 + V$$  \hspace{1cm} (2.61)

where $H_0$ is the HF Hamiltonian (Eq. 2.15),

$$H_0 = \sum_i f(i) = \sum_i [h(i) + \nu^{HF}(i)]$$  \hspace{1cm} (2.62)

$h(i)$ is the single particle Hamiltonian of the form of Eq. 2.7 and $\nu^{HF}(i)$ is

$$\nu^{HF}(i) = \sum_b J(i) - K(i)$$  \hspace{1cm} (2.63)

where $J(i)$ and $K(i)$ are the Coulomb (Eq. 2.12) and the exchange (Eq. 2.13) operators. Hence the perturbation part is

$$V = \sum_{i<j} \frac{1}{r_{ij}} - \nu^{HF} = \sum_{i<j} \frac{1}{r_{ij}} - \sum_i \nu^{HF}(i)$$  \hspace{1cm} (2.64)

The ground-state HF wave function $|\Psi\rangle$ is the Slater determinant of spin-orbitals. This Slater determinant is an antisymmetrized product of the spin-orbitals and, when expanded, is the sum of $n!$ terms, where each term involves a different permutation of the electrons among the spin-orbitals. Each term in the expansion of $|\Psi\rangle$ is an eigenfunction of $H_0$. Hence the HF wave function $|\Psi\rangle$ is an eigenfunction of $H_0$,

$$H_0 |\Psi\rangle = E^{(0)}_0 |\Psi\rangle$$  \hspace{1cm} (2.65)

with the eigenvalue

$$E^{(0)}_0 = \sum_j \epsilon_j$$  \hspace{1cm} (2.66)

The eigenfunctions of the unperturbed Hamiltonian $H_0$ are the zeroth-order wave functions so the HF ground-state function $|\Psi\rangle$ is one of the zeroth-order wave functions. The Hermitian operator $f(i)$ has a complete set of the eigenfunctions, these eigenfunctions being all the possible spin-orbitals of the molecule; the $n$ lowest-energy spin-orbitals are occupied, and there are an infinite number of virtual orbitals. The operator $H_0$ is the sum of the $f(i)$ operators, and so the eigenfunctions of $H_0$ are all possible products of any $n$ of the spin-orbitals. Thus, the zeroth-order wave functions are the possible Slater determinants formed using any $n$ of the infinite number of possible spin-orbitals.

The antisymmetrized two-electron integral is defined as

$$\langle ij|kl \rangle = \langle ij|kl \rangle - \langle ij|lk \rangle$$  \hspace{1cm} (2.67)

Using this notation, we have

36
\begin{equation}
\langle \Psi_0 \left| \sum_{m<n} \frac{1}{r_{mn}} \Psi_{ij}^{ab} \right| \rangle = \langle ij || ab \rangle \quad (2.68)
\end{equation}

and

\begin{equation}
\psi_{HF}^{(1)} \chi_n(x_1) = \sum_j \langle j \left| \frac{1}{r_{12}} \right| j \rangle \chi_n(x_1) - \sum_j \langle j \left| \frac{1}{r_{12}} \right| n \rangle \chi_j(x_1) \quad (2.69)
\end{equation}

Thus

\begin{equation}
\langle m \left| \psi_{HF} \right| n \rangle = \psi_{mn}^{HF} = \sum_j \langle mj || nj \rangle - \sum_j \langle mj || nj \rangle = \sum_j \langle mj || nj \rangle \quad (2.70)
\end{equation}

\begin{equation}
E_0^{(1)} = \langle \Psi_0 | V | \Psi_0 \rangle = \left\langle \Psi_0 \left| \sum_{m<n} \frac{1}{r_{mn}} \Psi_0 \right| \right\rangle - \left\langle \Psi_0 \left| \sum_m \psi_{HF}^{(m)} \right| \Psi_0 \right\rangle = \frac{1}{2} \sum_{ij} \langle ij || ij \rangle - \sum_i \langle i | \psi_{HF} || i \rangle = -\frac{1}{2} \sum_{ij} \langle ij || ij \rangle \quad (2.71)
\end{equation}

The HF energy is the sum of the zeroth and first-order energies,

\begin{equation}
E_0 = E_0^{(0)} + E_0^{(1)} = \sum_i \epsilon_i - \frac{1}{2} \sum_{ij} \langle ij || ij \rangle \quad (2.72)
\end{equation}

Thus the first correction to the HF energy appears in the second order of perturbation theory. The result for the second-order energy (2.60), is

\begin{equation}
E_0^{(2)} = \sum_n \frac{|\langle 0 | V | n \rangle|^2}{E_0^{(0)} - E_n^{(0)}} \quad (2.73)
\end{equation}

where the summation runs over all but the ground state of the system. Clearly, we take \( |0 \rangle = |\Psi_0 \rangle \) but what about \( |n \rangle \)? These states cannot correspond to single excitations since

\begin{equation}
\langle \Psi_0 | V | \Psi_i^{ab} \rangle = \langle \Psi_0 | H - H_0 | \Psi_i^{ab} \rangle = \langle \Psi_0 | H | \Psi_i^{ab} \rangle - f_{ia} = 0 \quad (2.74)
\end{equation}

The first term vanishes because of Brillouin’s theorem and the second because the spin-orbitals are eigenfunctions of Fock operator. In addition, triply exited states do not mix with \( |\Psi_0 \rangle \) because of the two-particle nature of the perturbation. Therefore, we are left with double excitations of the form \( |\Psi_{ij}^{ab} \rangle \).
The doubly excited function $|\Psi_{ij}^{ab}\rangle$ is an eigenfunction of $H_0$ with an eigenvalue that differs from the eigenvalue of $|\Psi_0^{a}\rangle$ only by replacement of $\epsilon_i$ by $\epsilon_a$ and replacement of $\epsilon_j$ by $\epsilon_b$. Hence in Eq. 2.73

$$E_0^{(0)} - E_n^{(0)} = \epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b$$

and so

$$H_0|\Psi_{ij}^{ab}\rangle = \left( E_0^{(0)} - (\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b) \right) |\Psi_{ij}^{ab}\rangle$$

(2.76)

Use of (2.64) for $V$ and of the Condon-Slater rule allows the integrals involving $|\Psi_{ij}^{ab}\rangle$ to be evaluated.

$$E_0^{(2)} = \sum_{a<b} \sum_{i<j} \frac{|\langle ij|ab\rangle|^2}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}$$

(2.77)

Using Eq. 2.67 the second-order energy in terms of regular two-electron integrals is

$$E_0^{(2)} = \sum_{a<b} \sum_{i<j} \frac{|\langle ab|ij\rangle - \langle ab|ji\rangle|^2}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}$$

(2.78)

The second-order energy also can be written as

$$E_0^{(2)} = \sum_{ab} \sum_{ij} \frac{(ia|jb)(2(ia|jb) + (ib|ja))}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}$$

(2.79)

where the notation of the form of 2.37 is used.

Taking the molecular energy as

$$E_0^{(0)} + E_0^{(1)} + E_0^{(2)} = E_{HF} + E_0^{(2)}$$

(2.80)

gives a calculation designated as MP2, where the superscript 2 indicates inclusion of the second order correction energy.

To do a Möller Plesset (MP) electron-correlation calculation, we first choose a basis set and carry out an SCF calculation to obtain $|\Psi_0\rangle$, $E_{HF}$ and virtual orbitals. We then evaluate $E_0^2$ by calculating the integrals over spin-orbitals in Eq. 2.78 in terms of integrals over the basis functions. We have to use a complete set of basis functions to expand the spin-orbitals. So, the SCF calculation will then produce the exact HF energy and will yield an infinite number of terms. Of course we always use a finite, incomplete basis set, which yields a finite number of virtual orbitals and the sums in 2.78 contain only finite number of terms. Thus in addition to the error due to truncation of the MP perturbation energy at $E_0^{(2)}$ we have also a basis-set truncation errors. For the finite number of virtual orbitals there are of the order of $N^4$ integrals which $N$ refers to the number of MOs. Thus the calculation of the energy increases as $N^4$ with the system size. However the transformation of the integrals from molecular orbitals
to the atomic orbital (AO) basis grows as $N^5$. Since the number of such integrals is very height, the performance of such a calculation for a large molecular system needs a huge amount of CPU time and memory.

MP calculations are much faster than CI calculations, and most \textit{ab initio} programs can perform MP calculations. However, MP calculations are not variational and can produce an energy below the true energy.

### 2.6.2 Resolution of identity MP2

Several methods have been developed to simplify the computation and storage of the four-center integrals by computing the integrals in an approximate manner. With the use of the resolution of the identity (RI) [82–84], four-center integrals are replaced by linear combination of three-center integrals through the introduction of an auxiliary basis expansion [82, 85, 86].

\[
(ij|kl) = \sum_m (ijm)(m|kl) \tag{2.81}
\]

where \((ijm)\) is a three-index one-electron overlap integral,

\[
(ijm) = \int \chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_1)\chi_m(\mathbf{x}_1)d\mathbf{x}_1 \tag{2.82}
\]

and \((m|kl)\) is a three-index two-electron repulsion integral,

\[
(m|kl) = \int \chi_m(\mathbf{x}_1)\frac{1}{r_{12}}\chi_k(\mathbf{x}_2)\chi_(\mathbf{x}_2)d\mathbf{x}_1d\mathbf{x}_2 \tag{2.83}
\]

and \(|m\) is the auxiliary basis in the space of the product \(|ij\). We can substitute Eq. (2.81) into Eq. (2.79) to find the RI-MP2 expression

\[
E_{RIMP2} = \frac{1}{2} \sum_{ab} \sum_{ij} \sum_{n,m} (iam)(m|jb)[2(ian)(n|jb) + (ibn)(n|ja)] \varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b \tag{2.84}
\]

The benefits of applying RI come from both the speed of the calculation of the integrals and the size of the resulting integral files. For instance, the three-index overlap integrals, \((ijm)\), are excessively cheap to calculate, while three-index repulsion integrals, \((m|kl)\), are definitively cheaper than the corresponding four-index integrals. Moreover, the volume needed to store the integrals in memory is significantly reduced with respect to four-index terms. For the system of $N$ basis functions and $m$ auxiliary functions, the RI method requires on the order of $N^2m$ words of storage, whereas the conventional methods require on the order of $N^4$ [82].
2.7 Density functional theory

Density functional theory (DFT) is a very efficient method to investigate the electronic structure of many-body systems, so that it is widely used in chemistry and physics. One reason for the growing popularity is that DFT takes electron correlation into account, but computationally, it is less demanding than, for example, CI and MP2. Moreover for transition metals, DFT gives results that very often agree more closely with experiment than HF calculation do. The main idea in DFT (which was suggested by Thomas and Fermi in the 1920s) is that there is a relation between electronic energy and electron density. The modern proof was given by Hohenberg and Kohn [87] who showed that the ground-state energy and all other ground state electronic properties are uniquely determined by the electron density. The next major development was done by Kohn and Sham [88] who showed that a derivation of a set of one-electron equations could be obtained from electron density. The energy $E$ can be defined as a unique functional of the electronic density $\rho(r)$

$$E[\rho(r)] = \int V_{\text{ext}}(r)\rho(r)dr + F[\rho(r)] \tag{2.85}$$

The first term arises from the interaction of the electrons with an external potential $V_{\text{ext}}(r)$. This external potential is due to the Coulomb interaction of nuclei and electrons.

$$V_{\text{ext}} = -\sum_{A=1}^{M} \frac{Z_A}{r_{iA}} \tag{2.86}$$

$F[\rho(r)]$ is the sum of the kinetic energy of the electrons and the contribution from interelectronic interactions. To find the function $F[\rho(r)]$, Kohn and Sham suggested that it should be approximated as a sum of three terms:

$$F[\rho(r)] = E_{KE}[\rho(r)] + E_{H}[\rho(r)] + E_{XC}[\rho(r)] \tag{2.87}$$

where $E_{KE}[\rho(r)]$ is the kinetic energy, $E_{H}[\rho(r)]$ is the electron-electron Coulomb energy, and $E_{XC}[\rho(r)]$ is the term containing the exchange and correlation contributions to the energy. $E_{KE}[\rho(r)]$ is the kinetic energy of a system of non-interacting electrons with the same density $\rho(r)$ as the real system:

$$E_{KE}[\rho(r)] = \sum_{i=1}^{N} \int \psi_i(r)(-\frac{\nabla^2}{2})\psi_i(r)dr \tag{2.88}$$

$E_{H}[\rho(r)]$ is known as the Hartree electrostatic energy which includes the classical interaction between two charge densities:

$$E_{H}[\rho(r)] = \frac{1}{2} \int \int \rho(r_1)\rho(r_2)\frac{1}{r_{12}}d\mathbf{r}_1d\mathbf{r}_2 \tag{2.89}$$

From Eqs. 2.85 - 2.89, the Kohn-Sham (KS) energy of an $N$-electron system is
\[ E[\rho(\mathbf{r})] = \int V_{\text{ext}}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} + \sum_{i=1}^{N} \int \psi_i(\mathbf{r})(-\frac{\nabla^2}{2})\psi_i(\mathbf{r})d\mathbf{r} + \frac{1}{2} \int \int \frac{1}{r_{12}} \rho(\mathbf{r}_1)\rho(\mathbf{r}_2)d\mathbf{r}_1d\mathbf{r}_2 + E_{\text{XC}}[\rho(\mathbf{r})] \] 

(2.90)

We can determine the minimum energy by introducing the Lagrangian multiplier \( \mu \) which gives:

\[ \frac{\delta}{\delta \rho(\mathbf{r})} \left[ E[\rho(\mathbf{r})] - \mu \int \rho(\mathbf{r})d\mathbf{r} \right] = 0 \] 

(2.91)

From this equation we can write:

\[ \left( \frac{\delta E[\rho(\mathbf{r})]}{\delta \rho(\mathbf{r})} \right)_{V_{\text{ext}}} = \mu \] 

(2.92)

The Lagrange multiplier \( \mu \) is known as the chemical potential of an electron cloud. This chemical potential relates to the electronegativity, \( \chi \):

\[ -\chi = \mu = \left( \frac{\delta E}{\delta \rho(\mathbf{r})} \right)_{V_{\text{ext}}} \] 

(2.93)

In the KS approach electron density \( \rho(\mathbf{r}) \) can be defined as:

\[ \rho(\mathbf{r}) = \sum_{i=1}^{N} |\psi_i(\mathbf{r})|^2 \] 

(2.94)

By using this equation and applying the appropriate variational condition, a set of one-electron KS equations can be obtained:

\[ \left\{ -\frac{\nabla^2}{2} - \left( \sum_{A=1}^{M} \frac{Z_A}{r_{1A}} \right) + \int \frac{\rho(\mathbf{r}_2)}{r_{12}}d\mathbf{r}_2 + V_{\text{XC}}[\mathbf{r}_1] \right\} \psi_i(\mathbf{r}_1) = \varepsilon_i \psi_i(\mathbf{r}_1) \] 

(2.95)

In this equation \( \varepsilon_i \) are orbital energies and \( V_{\text{XC}} \) is known as the exchange-correlation functional given by:

\[ V_{\text{XC}}[\mathbf{r}] = \left( \frac{\delta E_{\text{XC}}[\rho(\mathbf{r})]}{\delta \rho(\mathbf{r})} \right) \] 

(2.96)

If \( E_{\text{XC}} \) is known, then \( V_{\text{XC}} \) can readily be obtained. The KS equations are solved in a self-consistent fashion. Initially, we guess the charge density \( \rho(\mathbf{r}) \) (or a good guess of molecular orbitals) and with some approximation for the functional dependence of \( E_{\text{XC}} \) on density, we can compute \( V_{\text{XC}} \) as a function of \( \mathbf{r} \). The KS equations are then
solved to find initial KS orbitals. This iteration is continued until the density and exchange-correlation energy have converged within a small tolerance.

Many different schemes have been developed for obtaining approximate forms for the functional of the exchange-correlation energy. One of the simplest schemes is known as the LDA. This scheme is based on a model called the uniform electron gas, in which the electron density is constant throughout all space. The total exchange-correlation energy can be expressed as:

\[ E_{XC}[\rho(r)] = \int \rho(r) \varepsilon_{XC}(\rho(r)) \, dr \]  

(2.97)

\( \varepsilon_{XC}(\rho(r)) \) is the exchange-correlation energy per electron as a function of the density in the uniform electron gas, a quantity known accurately from various approaches such as quantum Monte Carlo methods. LDA is an excellent approximation for many cases, especially for solid state systems, but, it has been shown to be clearly inadequate for some problems [89]. For example, chemical bonds of molecules are predicted to be too strong and bond lengths too short. To cure this problem, the GGA has been developed which depends on the gradient of the density at each point in space and not just on density itself. These gradient corrections are normally divided into separate exchange and correlation contributions. A variety of GGA functionals have been developed. The BLYP exchange-correlation functional is frequently used for organic molecules. It is a combination of Becke’s exchange functionals [90] and Lee, Yang, and Parr’s correlation functional LYP [91]. B3LYP [92] is a hybrid functional in which the exchange-correlation energy, here from Becke’s exchange functional, is combined with a fraction of the exact non-local exchange from HF theory.

### 2.8 van-der-Waals interaction

The topic of vdW or dispersion interactions is a difficult benchmark in many-body theory that any correlation functional should be able to address [93, 94]. The origin of the vdW interaction between two fragments results from coupling of the electric field generated by fluctuations in the electronic density of one fragment with the density changes induced in the other fragment. This type of correlation conventional local and semi-local functionals like LDA and GGA cannot provide, and it is not related to the exchange. At long distances, the vdW interaction is approaching the classical interaction between fluctuating dipoles, which decays as \( E_{vdW} = -C_6/R^6 \). Standard DFT methods cannot accurately evaluate the vdW energy. A DFT calculation with LDA correlation functional leads to overestimated binding energies in weakly bound systems, and GGA functionals normally underestimate the interaction energy. Furthermore, the commonly used hybrid functional B3LYP cannot reproduce the dispersion interaction. Although this problem now has become a very active field of research, it seems to be very difficult to account for dispersion within the standard Kohn-Sham picture of DFT [69, 95]. All nonempirical attempts to introduce vdW interactions in
DFT will finally end with methods that will be at least as complex as simple wave function methods like MP2. Another empirical strategy is to combine or modify existing density functionals. These approaches cannot yet be considered to be successful because the modified functionals are not applicable for different systems.

In order to find realistic dispersion interactions, highly demanding \textit{ab initio} calculations like CC with a very large basis set are needed. These methods are feasible for relatively small systems while they scale very steeply with the number of basis functions. The MP2 method is computationally less expensive than CC, so that it represents an intermediate level of theory. The success of the MP2 method in describing intermolecular interactions is largely attributable to a kind of compensation of errors involving the size of the basis set employed and the lack of the higher order correlation terms neglected by this method [96,97]. The MP2 method is used extensively in computational chemistry for the treatment of intermolecular and intramolecular non-covalent bonds. MP2 with very extended basis sets overestimates the dispersion energy so that it becomes too attractive. As an example, MP2 calculations were performed for more than 100 stacked structures of DNA base pairs by Jurecka et al. [98]. They found that MP2 calculations with small or medium-sized basis set give accurate stabilization energies and complex geometries.

In the final part of this section, the potential energy surfaces (PESs) of a stacked benzene dimer obtained with different \textit{ab initio} methods are presented, allowing to compare the ability of each method to approximate dispersion interactions. In this specific model system the vdW interactions are the main intermolecular $\pi - \pi$ inter-
actions. Furthermore, the interactions of benzene-based aromatic compounds with metallic substrates are mainly vDW. The accurate evaluation of these interactions requires computationally demanding high-level ab initio calculations. The intermolecular interaction of the benzene dimer ($\pi-\pi$ interaction) was extensively studied with different ab initio methods [72,73,75,95,99–104]. The PES of a stacked dimer of benzene obtained with different levels of theory [99] is depicted in Fig. 2.1. The highly accurate PES produced by the CCSD(T) method is the reference PES for the benzene dimer. Fig. 2.1a shows the PES calculated with DFT-GGA functionals and HF are repulsive. Only PW91 (Perdew and Wang’s 1991 gradient-corrected functionals) gives attractive potentials, however the size of the attraction is not accurate. The PW91 calculations considerably underestimate the attraction in the benzene dimer, as shown in Fig. 2.1a. The attraction calculated by the PW91 method is probably not due to dispersion, since the basis set dependence is negligible [99]. The large difference between the HF and CCSD(T) PES shows that the dispersion interaction is significant for the intermolecular interaction of the benzene dimer and similar aromatic compounds.

Fig. 2.1b shows that MP2 calculation with large basis sets substantially overestimates the attraction compared to the reference PES. However the MP2 calculations with 6-31G** basis (a medium-sized basis set) gives the PES which is very close to the reference PES [104].

### 2.9 Basis sets

In all the self-consistent approaches discussed previously, a complete set of basis functions must be employed to represent the spin orbitals accurately. One of the most common choices of basis sets in quantum mechanical calculations are Gaussian type orbitals (GTO) which can represent atomic functions [105]. A Gaussian function decays as:

$$\phi(\alpha) = x^a y^b z^c e^{-\alpha r^2} \quad (2.98)$$

where $a$, $b$, $c$ are three non-negative integers. The sum over the powers of $a$, $b$ and $c$, determines the type of orbitals. If $a + b + c = 0$ then this function is like a Slater $s$-orbital, a Gaussian function is representing a $p$-orbital if $a + b + c = 1$, and depending which exponent $a$, $b$ or $c$ is non zero, this function transforms like a $p_x$, $p_y$ or $p_z$ orbitals respectively. The other atomic orbitals can be determined in the same ways. It is found that a single Gaussian function is a rather poor approximation for an AO. A construction of a linear combination of elementary Gaussian functions can be used for better representing an atomic orbital [106]. This linear combination has the form of:

$$\phi_\mu = \sum_{i=1}^{L} d_{i\mu} \phi_i(\alpha_{i\mu}) \quad (2.99)$$

44
$d_{\mu}$ is the coefficient of the primitive Gaussian function $\phi_i$, and $\alpha_{\mu}$ is the exponent of this function. It is obvious that the quality of a basis set is improved as the number of functions in the primitive basis set increases. In \textit{ab initio} calculations, it is conventional to use brief notation schemes to denote the basis sets. A \textit{minimal basis set} contains just the number of Gaussian functions that are needed to determine all the filled orbitals. In STO-$n$G notation, $n$ is the number of primitive function for representing each orbital. It is found that the minimum number of primitive functions for properly expressing Slater type orbitals is three [106, 107]. Thus, to construct a STO-3G basis set which forms the smallest possible basis, for hydrogen and helium (1s atoms), three primitive functions should be combined. In double-$\zeta$ (DZ) the number of functions in the minimal basis set are increased by a factor of two. The same procedure is applied for the increased basis size in triple-$\zeta$, quadruple-$\zeta$, and so on. Increasing the number of basis functions in this way does not terribly improve the quality of the results, but this procedure increases the cost of the calculation.

In \textit{split valence} (SV) basis sets, the inner-shell electrons are described with a single Slater orbital, while some diffuse functions are added to the valence shell. For example in the 3-21G basis set [108–113], three basis function are used to represent the core orbitals, the valence electrons are also represented by three Gaussian functions: the contracted part by two Gaussians and the diffuse part by one Gaussian. Another example of this kind is given by the 6-31G basis set [114–117]. In this basis set, each core orbital is constructed by six primary functions, and for valence orbitals, three constructive and one diffuse function are used. To represent hybridization of orbitals, one or more functions of higher momentum (polarizing functions) are added to constructive orbitals. A nominative example of SVP (SV plus polarization) is 6-31G** or 6-31G(d,p), where polarized $p$ functions are added to each $s$ and, $d$ is added as a polarization function to $p$ orbitals. In this work we mainly used the def-SVP basis set. This basis set is a fully optimized SVP basis set (optimization of exponents and contraction coefficients) which was developed by Ahlrichs and his coworkers [118, 119]. This basis set has the advantage that it is less expensive than the 6-31G** basis, reaching however a similar accuracy. This basis set also included an optimized auxiliary basis used in RI calculations.

### 2.10 Basis set superposition error

Concerning the energy of formation of a bimolecular complex $AB$, we expect that this energy can be obtained by using the difference between the energy of the bimolecular complex ($E_{AB}$) and the energy of the isolated molecules $A$ ($E_A$) and $B$ ($E_B$). Normally, the energy difference obtained by such an approach is bigger than the true value. This difference arises from a fact known as the BSSE. When the distance of two molecules $A$ and $B$ is decreasing, the energy of the system falls not only because of the favorable intermolecular interactions, but also because the basis functions of molecule $A$ improve the description of the basis functions of molecule $B$, and vice
versa. Especially for weak intermolecular dispersion interactions, the BSSE can be significant [120, 121]. One of the best ways [122, 123] to estimate the BSSE is via the counterpoise correction method of Boys and Bernardi [105]. In the CP method, the corrected energy $\Delta E_{CP}(AB)$ can be defined as:

$$\Delta E_{CP}(AB) = E_{AB}^A(A) - E_B^B(B) + E_{AB}^A(A) - E_{AB}^B(B) - E_{AB}^B(B) + E_{AB}^A(A) - E_{AB}^A(A) + E_{AB}^B(B)$$

(2.100)

where $E_{Z}^Y(X)$ represents the energy of system X at geometry Y with basis set Z. Here, $E_{AB}^A(A)$ represents the energy of the monomer A in the geometry of the complex AB with the implementation of the ghost orbitals of monomer B, and $E_A^A(A)$ and $E_{AB}^A(A)$ are the energies of the monomer A in its own geometry and in the geometry in the complex AB, respectively.

### 2.11 Cluster models for substrates

Cluster models and periodic boundary conditions have been applied to investigate adsorbed molecule on metal surfaces. Both models have their advantages and disadvantages. If we employ a cluster of a definite number of metal atoms we are never sure if the cluster is big enough to simulate metallic features such as electron delocalization. Moreover, we should choose a cluster large enough to escape boundary effects, which would not appear for an infinite surface. Using a cluster approach has the advantage that a large variety of methods is available in electronic structure programs. For periodic systems already the implementation of HF into plane wave codes is a formidable task. Therefore other post-HF approaches like MP2 and CC methods are not feasible in periodic boundary conditions, with the expection of current development of a computational technique for solving the MP2 equations for periodic systems which is implemented in the CRYSCOR code [124]. However, for surface reactions involving weak interaction of vDW type one would prefer to use post-HF methods in order to obtain adsorption geometry and reaction barriers of stationary points described in a trustworthy way. In addition, a cluster model helps us to examine the behavior of the adsorbate at low coverage, and it precisely predicts local properties like equilibrium geometries and vibrational frequencies. Unluckily, deriving long range properties like absolute values of adsorption energies is a big challenge within the cluster model approach [125–127] and obtaining such values may require a highly symmetric and large cluster [128].

There are plenty of studies attempting an analysis of the impact of cluster-size on reaction energies or the comparison of cluster and supercell calculations. For example a comparison between slab and cluster calculations showed that the experimental adsorption geometries of CO$_2$ on Cu surfaces are better described by hybrid DFT on clusters (Cu$_{18}$) than a supercell approach [129]. Penev et al. [130] demonstrated that a cluster of 15 Si atoms is sufficient to reproduce the adsorption geometry of H$_2$. Gil et al. [131] have analyzed the adsorption of CO on Pt(111). They have shown that supercell models poorly describe the energy differences between different adsorption sites,
but hybrid DFT on small cluster models (Pt$_{13}$, Pt$_{18}$) performs better. Melle-Franco et al. [132] applied B3LYP to slab and cluster approaches for CO$_2$ adsorption on a SnO$_2$ surface. They have shown that both cluster and slab models result in vibrational frequencies close to the experimental observations.

Tautermann et al. [125] compared various ruthenium clusters of different sizes to study the effect of a Ru(0001) surface on the catalytic production cycle of ammonia by using a hybrid density functional method (B3LYP). They showed that a cluster of 12 ruthenium atoms is large enough to reproduce experimental geometries and frequencies of the reactants on the surface. They also concluded that cluster and supercell calculations applying plane waves give comparable barriers for reaction.
Chapter 3

Influence of dispersion interaction on chemisorption of PTCDA on Ag(110)

3.1 Introduction

In the first chapter of this thesis we discussed the importance of the adsorption geometry and the resulting energetics at the molecule-metal interface. We also discussed that the aromatic compound PTCDA analysed in the present work is among the most intensively studied molecular semiconductors. In the present work, we apply MP2 calculations to the interaction of PTCDA with an Ag(110) substrate, and we use DFT calculations without any semi-empirical correction for an analysis of the adsorbate geometry resulting in the absence of dispersion interactions.

3.2 Stacked PTCDA pair

In order to assess the suitability of different \textit{ab initio} approaches for our purposes, we start with an analysis of the interaction between stacked PTCDA molecules in a geometry compatible with the crystalline \(\alpha\)-phase [23]. The substantial molecular quadrupole moments influence the geometric arrangement of adjacent molecules, so that the tilted stack geometry reflects a compromise between vdW interaction, electrostatic contributions, and overlap repulsion. Fig. 3.1 shows the intermolecular potential along the stacking direction of PTCDA, calculated with the TURBOMOLE 5.7 [133] software package and a split-valence basis including polarization functions, def-SV(P) [86,134]. From the comparison between HF, the gradient corrected density functional BLYP, the hybrid functional B3LYP [90,135], and MP2 [85,136], we find clear evidence that only in the latter case the long-range correlations responsible for the vdW interaction are included in an appropriate way, as discussed earlier for rare gas dimers and pairs of benzene molecules [93,101,137].

After applying the counterpoise correction, a more flexible basis triple-\(\zeta\) valence-polarized (TZVP) [138] does not significantly modify the shape of the MP2 potential.
energy surface in Fig. 3.1, so that an def-SV(P) basis turns out to be an adequate compromise for our purposes. For these intermediate size basis sets, we find that the BSSE increases more rapidly than the net interaction after the counterpoise correction. This situation resembles earlier studies of benzene and naphthalene dimers with similar basis sets [72, 75], but independently of the basis size, it is generally accepted that the counterpoise correction is a reliable way of handling the BSSE error, as demonstrated by an analytic proof relying on full CI [122]. In the MP2 calculation of the PTCDA dimer, the def-SV(P) basis is already large enough to produce a small overbinding, so that the minimum of the intermolecular potential occurs at a stacking distance about 2% below the lattice constant in $\alpha$-PTCDA.

### 3.3 Optimized geometries of PTCDA chemisorbed to Ag(110)

#### 3.3.1 Substrate clusters

The Ag atoms in the topmost layer dominate the chemisorption behaviour of PTCDA. The second Ag layer allows a redistribution of excess charges induced by the adsorbate, including favourable image charges compensating the charge distribution in the
adsorbate. Due to the steep scaling of MP2 with system size, it is unavoidable that the substrate cluster has to be a compromise between computational requirements and a fair representation of the surroundings of the Ag atoms in the topmost layer. In the following, we use the two model clusters shown in Fig. 3.2: Ag\textsubscript{22} with 12 atoms in the first layer and 10 in the second, and Ag\textsubscript{32}, where the number of atoms in the second layer is increased to 20. For the silver atoms interacting with the carboxylic groups of PTCDA, the Ag\textsubscript{22} cluster realizes three nearest neighbours and the Ag\textsubscript{32} cluster five, compared to seven for an extended (110) surface.

The def-SV(P) basis set used in the following treats 19 electrons of each silver atom explicitly, whereas the 28 electrons in the core are replaced by pseudopotentials [118, 139]. In a comparison between all-electron calculations and pseudopotential calculations for Ag and Ag\textsuperscript{+}, it was proven that the energetic changes for the electronic configurations of interest (d\textsuperscript{9}s\textsuperscript{2}, d\textsuperscript{10}s\textsuperscript{1}, d\textsuperscript{9}s\textsuperscript{1}, d\textsuperscript{10}) do not vary by more than 0.05 eV, indicating that the use of pseudopotentials has no significant influence on our results [139].

When comparing the mid-gap energies (E\textsubscript{HOMO} + E\textsubscript{LUMO})/2 of the silver clusters with the respective value for PTCDA, we find the molecular energy at a lower value. This misalignment in the region of the frontier orbitals favours transfer of electronic charge from the metal into the molecule, involving especially the former LUMO of the adsorbate, see Sec. 3.5 for details. Nevertheless, due to compensating mechanisms which will be discussed below, the net charge of chemisorbed PTCDA remains rather small.

### 3.3.2 Relaxed adsorbate geometries

Fig. 3.2 visualizes the relaxed geometry of an adsorbed PTCDA molecule obtained at the MP2/def-SV(P) and B3LYP/def-SV(P) levels [85, 136, 140]. In all cases, the geometry of the metal cluster was kept fixed at an Ag-Ag bond length of 2.88 Å as in the bulk crystal. The height of different atoms with respect to the topmost ML of silver are given in Table 3.1, including a rigid shift towards the potential minimum after applying the counterpoise correction, compare Fig. 3.3 for the MP2 calculation of PTCDA on Ag\textsubscript{32}. The distance dependence of the relatively large BSSE found for the correlation part of the MP2 calculation modifies the slope of the BSSE-CP corrected surface, so that the minimum of the potential surface shifts by 0.24 Å to larger distances. Due to the increased curvature of the MP2 potential surface with respect to the PES of the PTCDA dimer in Fig. 3.1, the distance shift arising from the BSSE-CP correction remains somewhat smaller. The BSSE of the HF potential depends only weakly on the distance, so that the shape of the potential surface after the BSSE-CP correction is hardly modified. Similarly, the short range correlations included at the B3LYP level show only a small BSSE depending weakly on the distance between adsorbate and substrate, so that the distance shift of the minimum of the BSSE-CP corrected potential surface remains as small as 0.04 Å, compare Table 3.1.
Figure 3.2: Optimized geometries of PTCDA on a (110)-oriented Ag\textsubscript{22} cluster (left), and on a (110)-oriented Ag\textsubscript{32} cluster (right). The geometries have been optimized with MP2/def-SV(P) or B3LYP/def-SV(P), as annotated. In each case, the distance from the substrate has been shifted rigidly to the minimum of the counterpoise-corrected potential surface, compare Table 3.1 and Fig. 3.3 for the MP2/def-SV(P) calculation of PTCDA on Ag\textsubscript{32}.

3.3.3 B3LYP: Contributions to chemisorption

Similar to the interaction between stack neighbours shown in Fig. 3.1, the counterpoise correction of the BSSE produces a substantial reduction of the binding energy, compare Table 3.1. The B3LYP adsorption energies remain below the cohesive energy in α-PTCDA [25], falling instead into the range of previous DFT calculations for similar systems [44, 55, 141]. The very small adsorption energy found in B3LYP contradicts the known experimental fact that intermolecular interactions in the crystalline phase are so weak that they still allow sublimation without destroying the molecule, but that desorption of intact molecules from the first monolayer chemisorbed to a silver substrate is inhibited by the stronger interaction with the metal substrate.

The deviation between the average height of the carbon atoms above the topmost substrate layer with respect to the measured value of 2.59 ± 0.01 Å [51] is about 0.5 Å, in the same range as the deviation observed for DFT calculations of PTCDA on Ag(111) [44, 49, 50].

As DFT does not include dispersion interactions, only the following four ingredients contribute to the binding between adsorbate and substrate: (i) Charge donation via directional bonds between oxygen atoms and the substrate, (ii) back-donation through a double occupancy of the former LUMO of PTCDA, (iii) a positive image charge in the region below the negatively charged molecule giving an attractive Coulomb contribution, and (iv) exchange repulsion between filled orbitals of molecule and substrate.
Figure 3.3: Scan of the MP2/def-SV(P) adsorption energy of PTCDA on a (110)-oriented Ag$_{32}$ cluster along the distance between molecule and substrate, where the reference distance corresponds to the geometry optimized without counterpoise correction. •: with BSSE-CP correction [67], ○: without BSSE-CP correction, lines without symbols: size of BSSE correction for the different energetic contributions (magenta: HF, blue: correlation at the MP2 level, red: MP2). The minimum of the counterpoise-corrected MP2 potential is indicated by a vertical line.

Due to the lack of a long-range non-local correlation term required for the vdW attraction, the overlap repulsion increases the distance between perylene core and substrate, as in earlier DFT studies of similar systems [55, 141]. Nevertheless, the O-Ag bonds are so strong that they keep the height of the carbon core significantly below the sum of the vdW radii of silver and carbon, $r_{vdW}(C) + r_{vdW}(Ag) = 1.70 \text{ Å} + 1.72 \text{ Å} = 3.42 \text{ Å}$ [142]. This indicates a substantial strength of the chemical interaction, as opposed to physisorption, where the position of the adsorbate would essentially reproduce a value expected from the sum of the vdW radii, a behaviour observed for PTCDA on gold [143].

### 3.3.4 MP2: Influence of dispersion interaction

In the MP2/def-SV(P) calculation, the above phenomena are still included at the HF level, but in addition, the leading term of the dispersion interaction is taken into account. Therefore, exchange repulsion and vdW attraction compensate each other to a large extent, resulting in nearly flat geometries and large binding energies, compare Fig. 3.2 and Table 3.1. In fact, for the larger substrate cluster, the calculated average height of 2.68 Å of the carbon atoms is in excellent agreement with the measured position of 2.59 ± 0.01 Å [51]. The residual deviation between calculated and measured height can be related to unavoidable shortcomings of our geometry optimization:
Table 3.1: Calculated height (Å) of different atoms above the topmost ML of the Ag substrate, with the distance shift arising from the counterpoise correction of the BSSE included in all entries. The last two lines give the binding energies, without and with counterpoise correction of the BSSE. All calculations have been performed using an def-SV(P) orbital basis, and the calculated average height of the carbon atoms is compared to the measured value of 2.59 ± 0.01 Å [51].

<table>
<thead>
<tr>
<th>substrate method</th>
<th>$Ag_{22}$ B3LYP</th>
<th>$Ag_{22}$ MP2</th>
<th>$Ag_{32}$ B3LYP</th>
<th>$Ag_{32}$ MP2</th>
</tr>
</thead>
<tbody>
<tr>
<td>average C</td>
<td>3.15</td>
<td>2.81</td>
<td>3.05</td>
<td>2.68</td>
</tr>
<tr>
<td>deviation C (calc.-exp. [51])</td>
<td>0.56</td>
<td>0.22</td>
<td>0.46</td>
<td>0.09</td>
</tr>
<tr>
<td>perylene core</td>
<td>3.23</td>
<td>2.83</td>
<td>3.13</td>
<td>2.69</td>
</tr>
<tr>
<td>C central ring</td>
<td>3.33</td>
<td>2.84</td>
<td>3.24</td>
<td>2.62</td>
</tr>
<tr>
<td>C end groups</td>
<td>2.73</td>
<td>2.72</td>
<td>2.66</td>
<td>2.64</td>
</tr>
<tr>
<td>carboxylic O</td>
<td>2.49</td>
<td>2.63</td>
<td>2.37</td>
<td>2.50</td>
</tr>
<tr>
<td>anhydride O</td>
<td>2.57</td>
<td>2.68</td>
<td>2.53</td>
<td>2.63</td>
</tr>
<tr>
<td>average H</td>
<td>3.30</td>
<td>2.98</td>
<td>3.15</td>
<td>2.86</td>
</tr>
<tr>
<td>BSSE distance shift</td>
<td>0.04</td>
<td>0.20</td>
<td>0.04</td>
<td>0.24</td>
</tr>
<tr>
<td>$E$ (eV), including BSSE</td>
<td>−0.99</td>
<td>−5.43</td>
<td>−2.27</td>
<td>−7.94</td>
</tr>
<tr>
<td>$E$ (eV), CP-corrected</td>
<td>−0.27</td>
<td>−2.12</td>
<td>−1.41</td>
<td>−3.74</td>
</tr>
</tbody>
</table>

Obviously, the $Ag_{32}$ cluster is still rather small, so that the precise geometry of the adsorbate may be influenced by boundary effects. Moreover, with the software used, the geometry could not be optimized at the counterpoise-corrected level. Instead, we have performed a counterpoise-corrected scan along the most important configuration coordinate, defined by the distance between adsorbate and substrate, as visualized in Fig. 3.3 for MP2 on the larger silver cluster.

The MP2 geometry shows a bending of the C-H bonds away from the substrate, indicating a substantial repulsion between hydrogen and silver. As the distance between the H atoms and the topmost substrate plane is only 2.86 Å, compare Table 3.1, slightly below the sum of the vdW radii $r_{vdW}(H) + r_{vdW}(Ag) = 1.20 \, \AA + 1.72 \, \AA = 2.92 \, \AA$, such a behaviour has to be expected. In the B3LYP geometry, on the other hand, the H atoms remain at such a large distance that the geometric distortion with respect to the adjacent carbon atoms remains much smaller.

### 3.3.5 Adsorption energies

In B3LYP, the adsorption energy on the $Ag_{32}$ substrate cluster increases by 1.14 eV with respect to $Ag_{22}$, and in MP2 this difference is as large as 1.62 eV. The geometry of the strong O–Ag bonds is very similar on both substrate models, defining in turn a similar contribution to the adsorption energy. However, the larger substrate cluster...
allows a more flexible distribution of favourable image charges, with a large impact on the adsorption energy.

In MP2, the chemisorption energies for both substrate models are much larger than the interaction between stack neighbours in α-PTCDA depicted in Fig. 3.1, rationalizing the observation that the first ML of PTCDA on Ag(110) cannot be desorbed thermally without destroying the molecule. When comparing the two substrate clusters, the HF energy changes only from $+0.10 \text{ eV}$ to $-0.22 \text{ eV}$, but the MP2 correlation energy grows from $-2.22 \text{ eV}$ to $-3.52 \text{ eV}$.

The convergence of the dispersion interaction can be analyzed by a calculation of a sum over pair potentials scaling as the long-range part of the vdW interaction proportional to $1/r^6$. On each substrate cluster, we estimate the dispersion interaction for the reference position in the center of the central aromatic ring of PTCDA. On the Ag$_{22}$ cluster, this gives 83% of the sum over $1/r^6$ pair potentials with respect to a silver substrate of infinite size. For the Ag$_{32}$ cluster, this fraction increases to 87.5%, and due to the significant decrease of the height of the central ring on the larger substrate cluster, the lattice sum over $1/r^6$ is larger by a factor 1.31 when compared to the smaller substrate cluster. The substantially larger increase of the MP2 correlation by a factor of 1.59 indicates that the lower energetic cost for single excitations of the larger silver cluster plays a significant role, underlining the limitations of a simple sum over pair potentials.

The large change of the adsorption energy between different substrate clusters demonstrates that a direct comparison may be problematic. However, in terms of the calculated height above the substrate, in MP2 the deviation between the relaxed geometries on both substrate models remains rather small: 0.13 Å for the average height of the carbon atoms and the carboxylic oxygens, and 0.05 Å for the anhydride oxygens. The strong interaction of the four carboxylic oxygens with the substrate outweighs the attraction between the anhydride groups and the Ag surface, resulting in a height difference of 0.13 Å between the two kinds of O atoms on Ag$_{32}$. In part, this difference in height can be rationalized from the Coulomb interaction between each oxygen atom and the silver atom underneath: Both kinds of oxygen atoms carry a similar negative net charge, but the silver atom below the anhydride oxygen has a particularly large negative charge, so that the respective O–Ag distance is increased by Coulomb repulsion.

### 3.4 Charge balance

The above optimized geometries raise the question how the charge distribution in a chemisorbed molecule differs from the reference of a free molecule. In order to guarantee a comparable interpretation of different reference geometries, we have to choose the same ab initio scheme for all of them, e.g. HF or B3LYP. As the latter hybrid functional is known to be quite reliable for various properties of organic systems, we shall apply it in the following.
Figure 3.4: Partial charges in a free PTCDA molecule (black dashed), in the B3LYP geometry of the adsorbate visualized in Fig. 3.2 (blue), and in the RIMP2 geometry (red). In each case, the partial charges are defined as Mulliken charges obtained at the B3LYP/def-SV(P) level, and the labelling of the atoms is according to the scheme displayed in the inset.

In Fig. 3.4, we show the distribution of Mulliken charges obtained at the B3LYP/def-SV(P) level. In both adsorbate geometries, all atoms in the functional O=C–O–C=O end groups (atoms 1 - 5) increase their net charge, and the fact that there occurs no substantial difference between both adsorbate geometries demonstrates that the Ag-O bonds formed in both cases are very similar. The central region of the perylene core (atoms 13 - 19) shows a small increase of electronic charges corresponding to a decrease of the positive charges close to the long axis, with a very similar behaviour of both adsorbate geometries. In B3LYP, the charges on the hydrogen atoms (atoms 13 and 19) remain essentially unchanged with respect to the free molecule, but in the MP2 geometry, the energetic cost for the repulsion between H atoms and substrate is reduced by a decrease of the electronic charges, reflected in an increased positive charge. In the periphery of the perylene core, the B3LYP geometry of the adsorbate follows the charge distribution of the free molecule, but in MP2, this region is subject to a charge redistribution around the long axis, without major impact on the total charge of the entire group. In MP2, the negative charge on the silver atom below the carbon atoms 9 and 16 is larger than in the B3LYP calculation, indicating an increased influence of C-Ag interactions via hybrid orbitals arising from molecular orbitals mixing with substrate states.
3.5 Electronic orbitals

In the MP2 geometry, the distance between adsorbate and substrate is significantly below the sum of vdW radii, a clear indication of chemisorption. Therefore, in addition to the discussion of the global charge distribution in Sec. 3.4, it is interesting to establish the main interaction mechanisms via an analysis of the electronic orbitals involved. A few key examples are visualized in Fig. 3.5.

The most striking feature is the fact that the LUMO of the free molecule is now occupied by two electrons, resulting in STM pictures of the adsorbate reproducing the LUMO pattern [32]. From this modified occupation of a previously empty molecular orbital, one would expect a large negative charge in the adsorbate. However, the atomic charges visualized in Fig. 3.4 sum to a much smaller net charge of only about $q = -0.41e$ on the entire molecule, indicating several compensating mechanisms transferring electronic charge into the substrate. Similar to the LUMO state of the free molecule, its HOMO state does not form hybrids with the substrate, so that both frontier orbitals of PTCDA are not involved in chemical bonds with the metal.

Due to the reduced point group of the adsorbate, i.e. $C_{2v}$ instead of $D_{2h}$ for the free molecule, pairs of representations in $D_{2h}$ can be superimposed. Among the electronic states visualized in Fig. 3.5, the $b_2$ orbital at $-11.44$ eV has $\sigma$ character in the core region, hybridizing with $\pi$ states on the end groups. Such a hybridization would be forbidden in $D_{2h}$, but in the smaller point group of the adsorbate, it allows to transfer electronic charge from the core region into the oxygen-containing functional groups. In the adsorbate, the reduced electronic charge on the hydrogen atoms shown in Fig. 3.4 can be understood quantitatively from two such $\sigma - \pi$ hybrids transferring electronic charge from the core region towards the end groups.

Besides the occupation of the former LUMO, the main interaction mechanism consists in the formation of bonding hybrid orbitals between the oxygen atoms and the substrate. In the free molecule, $\pi$ orbitals on O atoms occur only in the form of conjugated states extending over a major part of the core region, but in the adsorbate, this conjugation between core region and functional groups is modified, so that $\pi$ orbitals localized mainly on O may occur. These states can then form bonding hybrids with the underlying substrate atoms, involving metal orbitals which would not be occupied in the substrate cluster alone. These bonding orbitals based on previously occupied $\pi$ states on oxygen and previously empty states in the substrate donate electronic charge from the adsorbate into the metal, as visualized for a $b_1$ orbital at $-9.63$ eV, so that these bonding O-Ag orbitals play the dominant role for a reduced net charge of the molecule.

Of course, most of the $\pi$ states still extend over the entire molecule, and in selected cases, the part in the core region of perylene can hybridize with orbitals in silver, as shown for a $b_2$ state at $-10.28$ eV. Among the mechanisms defining the net charge of the molecule, this type of hybridization is the less efficient, mainly because most of these states occur as hybrid pairs, differing only in the signs of the wave function on molecule and substrate. Therefore, when summing over both states in such a pair,
Figure 3.5: Selected occupied orbitals in the MP2 model geometry, calculated with B3LYP/def-SV(P), ordered according to their energy. For each orbital, the representation in the point group $C_{2v}$ is indicated.
a bonding and an anti-bonding one, only a small amount of electronic charge can be accumulated in the region between adsorbate and substrate.

A comparison between the MP2 and B3LYP model geometries raises the question which of the above interaction mechanisms occur both in the flat and in the bended adsorbate geometry, and which are severely modified. In the bended B3LYP geometry, electronic states resembling the orbitals visualized in Fig. 3.5 occur at similar energies, compare Table 3.2. In the B3LYP geometry, states localized mainly on the adsorbate have a significantly lower binding energy with respect to the flat MP2 geometry, a difference related to the larger net charge of \( q = -0.49e \) in the bended adsorbate. Even though the orbitals in both geometries have similar patterns, there may be significant differences. For the \( \sigma - \pi \) hybrid shown at the bottom of Fig. 3.5, in the B3LYP geometry the degree of hybridization in a similar orbital is three times smaller, so that this state is less efficient in transferring electron density from the H atoms and the perylene core towards the end groups. As a further \( \sigma - \pi \) hybrid shows a similar reduced hybridization, these minor differences between the orbitals in both model geometries have a major impact on the net charge of the H atoms shown in Fig. 3.4: In the bended adsorbate geometry, this type of hybridization is so small that the electron density around the H atoms resembles the free molecule. Concerning \( \pi \) states hybridizing with substrate states via their core region, it is clear that the much larger distance in the bended geometry strongly reduces this specific hybridization mechanism, contributing in turn to a smaller transfer of electronic charge towards the substrate, so that the negative charge on the adsorbate remains somewhat larger.

Due to the negative net charge of PTCDA in both adsorbate geometries, all orbitals localized mainly on the molecule have a reduced binding energy with respect to a free molecule, compare Table 3.2, with the obvious exception of the former LUMO, moving far below the Fermi energy of the substrate.

In the MP2 model geometry, the redistribution of charge in the periphery of the perylene core (atoms 8, 9, 10 in Fig. 3.4) seems to be related to a larger hybridization

<table>
<thead>
<tr>
<th>substrate model geometry</th>
<th>( \text{Ag}_{32} ) MP2</th>
<th>( \text{Ag}_{32} ) B3LYP</th>
<th>B3LYP</th>
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</thead>
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<tr>
<td>( b_2 ) LUMO(PTCDA)</td>
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<tr>
<td>( a_2 ) HOMO(PTCDA)</td>
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<td>-5.88</td>
<td>-6.57</td>
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<td>-9.62</td>
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<td>( b_2 ) ( \pi(\text{core})-\text{Ag hybrid} )</td>
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<td>-10.20</td>
<td>-10.72</td>
</tr>
<tr>
<td>( b_2 ) ( \sigma - \pi ) hybrid</td>
<td>-11.44</td>
<td>-11.18</td>
<td>-11.77</td>
</tr>
</tbody>
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Table 3.2: Kohn-Sham energies of the orbitals in the MP2 geometry visualized in Fig. 3.5, in eV, of similar electronic states occurring in the bended B3LYP model geometry, and of the respective states in a free molecule in \( D_{2h} \) symmetry. In all model geometries, the electronic states have been calculated with B3LYP/def-SV(P).
of the core region of molecular π states with the substrate. However, this region of the adsorbate is involved in so many σ and π states that a clear assignment of this modified charge distribution to a small number of electronic states could not be achieved, as opposed to the orbitals visualized in Fig. 3.5 where a clear correspondence between orbitals, charge distribution and interaction mechanisms can easily be established.

### 3.6 Distance dependence of orbital energies

Figure 3.6 shows the energies of the all occupied MOs of PTCDA/Ag	extsubscript{32} which have the energy larger than −14eV calculated with B3LYP/def-SV(P) as a function of height, defined with respect to the geometry optimized at the MP2/def-SV(P) level. Most eigenstates resemble molecular orbitals of the free molecule or the free metal cluster, but their energies have a different slope as a function of the distance between adsorbate and substrate: The energy of molecular states increases with distance, but the energy of metallic states decreases with distance. Both slopes arise from the surprising fact that the charge of the molecule becomes more negative with increasing distance. The reason for this counterintuitive distance dependence arises from the breaking of Ag-O bonds: The O atoms donate electronic charge into the substrate, so that the large negative excess charge arising from the double occupancy of the former molecular LUMO is strongly reduced. For the intermediate distance range shown, this doubly occupied LUMO remains below the Fermi energy of the entire system, but at much larger distance, eventually the electronic configuration with neutral subunits becomes more favourable, so that the LUMO of PTCDA will be emptied again.

### 3.7 Core levels

The core levels of PTCDA multilayers have been investigated with X-ray photoemission spectroscopy (XPS), revealing significant differences between the two kinds of oxygen atoms and between the carbons interacting with oxygen and in the central region of the molecule [144]. In chemisorbed PTCDA, this fingerprint of the 1s levels is modified by the negative net charge of the adsorbate, so that the binding energies of these core states with respect to vacuum decrease.

In Table 3.3, we report B3LYP/def-SV(P) core levels calculated for a free PTCDA molecule and for the MP2/def-SV(P) -based geometry on Ag	extsubscript{32}. Our results reveal that the B3LYP/def-SV(P) calculations of the core levels give systematic deviations of about 6 eV for carbon, and 10 eV for oxygen, in both cases far below deviations occurring in HF. This underlines the fact that the short range correlations included in the B3LYP functional constitute a substantial improvement.

For free PTCDA, the calculated difference ΔO= 1.66 eV between the core levels in the oxygen atoms is in excellent agreement with the XPS result ΔO= 1.76 eV [144]. In the adsorbate, the experiment reveals an increase of this difference to 2.4 eV, qualita-
Figure 3.6: B3LYP/def-SV(P) MO energies of PTCDA/Ag$_{32}$ adsorption system versus distance between PTCDA and substrate. The MP2 relaxed geometry of PTCDA is used and the relaxed MP2 distance between PTCDA and substrate is used as reference point. The minimum of the counterpoise-corrected MP2 potential is indicated by vertical dashed line.
Calculation experimental

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<tr>
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<td>−531.65</td>
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<td>δO(O=O=O)</td>
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<td>δO(C=O-O-C)</td>
<td>−0.07</td>
<td>−0.09(10)</td>
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Table 3.3: Binding energy of the core levels in a free PTCDA molecule and in PTCDA chemisorbed to Ag(110). Calculation: B3LYP/def-SV(P), for a free molecule optimized with the same method, and for the MP2/def-SV(P) geometry obtained on Ag32. Experimental: Film of several PTCDA layers [144], and sub-monolayer chemisorbed to Ag(110) [145]. ΔO denotes the energetic difference between the core levels of the two types of oxygens, and δO and δC the energetic shifts in chemisorbed PTCDA.

The geometry found from the MP2 optimization and the scan towards the potential minimum of the BSSE-corrected potential energy surface can serve as a starting point for further investigations. As an example, we have performed a B3LYP/def-SV(P) calculation of the vibrational properties, and in Fig. 3.7 we compare the results for a free PTCDA molecule and the chemisorbed species (on Ag22 silver cluster). The shift of the three dominating out-of-plane modes compares favourably with measured HREELS data [36]. Concerning the adsorbate mode at 1579 cm⁻¹ with its large out-of-plane dipolar activity, there is clear evidence that it corresponds to a breathing mode of the free molecule at 1572 cm⁻¹ resembling an optical phonon of graphite [146, 147], with negligible contribution of the oxygen atoms. The dipole moment along the substrate normal results from a small admixture of out-of-plane motion related to the

3.8 Vibrational properties

The geometry found from the MP2 optimization and the scan towards the potential minimum of the BSSE-corrected potential energy surface can serve as a starting point for further investigations. As an example, we have performed a B3LYP/def-SV(P) calculation of the vibrational properties, and in Fig. 3.7 we compare the results for a free PTCDA molecule and the chemisorbed species (on Ag22 silver cluster). The shift of the three dominating out-of-plane modes compares favourably with measured HREELS data [36]. Concerning the adsorbate mode at 1579 cm⁻¹ with its large out-of-plane dipolar activity, there is clear evidence that it corresponds to a breathing mode of the free molecule at 1572 cm⁻¹ resembling an optical phonon of graphite [146, 147], with negligible contribution of the oxygen atoms. The dipole moment along the substrate normal results from a small admixture of out-of-plane motion related to the
Figure 3.7: Dipole activity of internal vibrations of a free PTCDA molecule (top), and out-of-plane modes of PTCDA adsorbed on a (110)-oriented Ag$_{22}$ substrate cluster, in the MP2/def-SV(P) geometry as defined in Figs. 3.2, 3.3 and in Table 3.1. The vibrational frequencies obtained at the B3LYP/def-SV(P) level have been scaled by a factor of 0.97.
small bending of the molecule in the MP2 geometry. The fact that this dipole activity is overestimated with respect to the measured data [36] indicates that our MP2 adsorbate geometry is still more bended than in reality.

3.9 Conclusion

In conclusion, the chemisorption of PTCDA on Ag(110) occurs via charge donation from the oxygen atoms into the metal substrate, back-donation from the metal into the former LUMO of the free molecule, and Coulomb attraction between the small negative net charge of the adsorbate and the induced positive image charge in the substrate. The occupation of the former LUMO with two electrons does not favour a specific geometric configuration with respect to the topmost substrate atoms, in sharp contrast with the formation of bonding orbitals between oxygen atoms and silver, playing a decisive role for the definition of the adsorption site.

The compensation between vdW attraction and overlap repulsion is responsible for a nearly flat adsorption geometry, and in the present work, this dispersion part of the interaction was quantified for the first time with an \textit{ab initio} method, resulting in a deviation between calculated and measured height of only 0.1 Å.

MP2 calculations like the one presented can serve as a benchmark for the test of improved density functionals accounting explicitly for non-local correlations required for the vdW interaction [148, 149]. If these tests for small substrate clusters would be convincing, such improved DFT schemes would eventually allow to circumvent the unavoidable size limits arising from the $N^5$ scaling of MP2, so that in the future, density functionals including non-local correlation might help to elucidate the impact of dispersion interactions on chemisorption of large molecules on metallic substrates.
Chapter 4

Influence of dispersion interaction on chemisorption of NTCDA on Ag(110)

4.1 Introduction

In the present chapter, we apply MP2 and the B3LYP hybrid functional to an investigation of the adsorption geometry of NTCDA on the Ag(110) surface. The rather (110)-oriented silver surface was chosen because it is known that the adsorbate unit cell of both NTCDA and PTCDA contain only a single molecule, indicating that the adsorbate-substrate interaction is much stronger than intermolecular interactions in the adsorbate layer. Moreover, for NTCDA, previous DFT studies have already determined the preferential adsorption site, allowing to handle all numerical calculations within the adsorbate point group $C_2v$ [55]. The rather large intermolecular distances between adjacent chemisorbed NTCDA molecules underpin the fact that they interact only via electric multipoles.

4.2 Computational methods

4.2.1 MP2 versus B3LYP

In the present study, we have applied MP2 using the resolution-of-identity approximation for the evaluation of two-electron integrals (RIMP2) [85], as implemented in the TURBOMOLE 5.7 software package [133]. For comparison with a method excluding dispersion interactions, we have applied DFT using the hybrid functional B3LYP with an exchange-correlation energy calculated on an integration grid of medium density (m4). A def-SV(P) basis set [118] was chosen for the atoms in NTCDA, whereas silver was treated with an effective core potential based on 28 core electrons, accounting for scalar relativistic effects (ECP-28-MWB [139]). In order to obtain the relaxed structure of NTCDA adsorbed on the Ag(110) surface we start from a geometry in keeping with the known adsorption site [55]. Since the positions of the silver atoms on
Figure 4.1: (a) Molecular structure of NTCDA. Orange spheres - carbon atoms, red spheres - oxygen atoms, white spheres - hydrogen atoms. Each index addresses atoms in equivalent positions. (b) Highest occupied molecular orbital (HOMO) and (c) lowest unoccupied molecular orbital (LUMO) of a free NTCDA molecule.
the metal surface are not expected to change strongly due to the interaction with the adsorbate, it is convenient to fix the position of all silver atoms during the geometry optimization of the adsorbate.

4.2.2 Substrate models

In the present work, five different silver clusters were used to model the Ag(110) surface, compare Fig. 4.2. The smallest cluster has 9 atoms in the first layer, corresponding exactly to the unit cell required by chemisorbed NTCDA on Ag(110), and 4 and 3 atoms in the second and third layers, respectively, summing to 16 silver atoms. In the following, we will denote the different substrate clusters by their total number of atoms and by the number of atoms in each layer, e.g. Ag$_{16}$(9,4,3) for this specific case. In order to speed up the calculations, we investigate only Ag(110) clusters with $C_{2v}$ symmetry, coinciding with the largest point group a $D_{2h}$-symmetric molecule can realize as an adsorbate.

![Cluster models for Ag(110)](image)

Figure 4.2: Cluster models for Ag(110) used in the present work.

4.3 Adsorbate geometry

In the TURBOMOLE 5.7 code used, the optimization is still subject to the BSSE. As the distance between adsorbate and substrate is the most important configuration coordi-
nate, we have used the optimized adsorbate geometry and scanned the interaction energy along the distance between adsorbate and substrate cluster. By applying the Boys-Bernardi counterpoise scheme [150], such a scan reveals the energetic influence of the BSSE onto the interaction potential. For all substrate clusters, the BSSE-CP scheme reduces the adsorption energy substantially. Moreover, the distance dependences of the raw data including the BSSE and the BSSE-CP corrected potential energy surfaces (PES) differ, so that the position of the energetic minimum of the BSSE-CP corrected PES is shifted to a larger distance. As an example, Fig. 4.3 visualizes the PES of the interaction between NTCDA and a Ag$_{22}$(9,4,9) substrate cluster obtained at the MP2/def-SV(P) level. The counterpoise correction of the BSSE produces a substantial reduction of the adsorption energy, and the minimum of the counterpoise-corrected PES shifts by 0.18 Å to larger distance from the substrate.

### 4.3.1 Effect of cluster size on adsorption geometry

For several substrate clusters (Fig. 4.4), Table 4.1 summarizes the heights of different atoms in NTCDA with respect to the topmost silver layer. In all entries, the tabulated distances were obtained from the minimum of the BSSE-CP corrected PES, occurring typically at about 0.14 - 0.18 Å larger distance with respect to the optimized RIMP2 geometries without BSSE-CP correction. During this scan, all internal geometry pa-
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<th>$z_{O\text{(carb)}}$</th>
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Table 4.1: Height (Å) of different atoms above the topmost ML of the Ag substrate, with atoms labeled as in Fig. 4.1. The distance shift arising from the counterpoise correction of the BSSE is included in all entries. The last columns give the BSSE-CP corrected binding energy $E_{\text{ads}}$ (eV) at the minimum of the scan along the distance and the distance shift $\Delta z$ (Å) between the minimum of the CP corrected potential surface with respect to the optimized adsorbate geometry.

$^a$ Calculation using a periodic supercell and the PBE functional [55,65].

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<td>0.13</td>
<td>−</td>
</tr>
<tr>
<td>Ag$_{32}$(15,16,1)</td>
<td>0.17</td>
<td>−0.17</td>
<td>0.28</td>
<td>0.07</td>
<td>−</td>
</tr>
<tr>
<td>Ag$_{34}$(9,16,9)</td>
<td>0.25</td>
<td>−0.14</td>
<td>0.29</td>
<td>0.15</td>
<td>−</td>
</tr>
<tr>
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<td>0.22</td>
<td>−0.16</td>
<td>0.31</td>
<td>0.15</td>
<td>−</td>
</tr>
<tr>
<td>PBE$^a$ [55]</td>
<td>0.10</td>
<td></td>
<td></td>
<td></td>
<td>0.07</td>
</tr>
</tbody>
</table>

Table 4.2: Height differences (Å) between selected atoms in the adsorbate. $\delta_O$ is the difference between the heights of the anhydride and carboxylic oxygens, and $\delta_{C1}$ the difference between a carbon atom in one of the end groups and the average over the naphthalene core. The bending along the long axis is defined as $\delta_{\text{long}} = z_{C1} - z_{C3}$, and the lateral bending as $\delta_{\text{short}} = z_{C4} - z_{C3}$. For a periodic calculation with the PBE functional, it was found that the Ag atoms below the carboxylic atoms are raised out of the topmost substrate plane [55], a phenomenon ignored in our approach based on rigid substrate clusters (last column).
Figure 4.4: Optimized geometries of NTCDA on different cluster models of Ag(110) surface. Top row: B3LYP/def-SV(P) geometries. Second row: MP2 geometries. Third row, from left to right: Top view of NTCDA adsorbed on Ag$_{16}$(9,4,3), Ag$_{22}$(9,4,9), Ag$_{32}$(15,16,1), and Ag$_{34}$(9,16,9), respectively. B3LYP geometry of NTCDA on Ag$_{50}$(25,16,9) cluster model: (m) side view and (n) top view.

Parameters of the adsorbate were kept fixed. In the B3LYP calculation, the BSSE is rather small, so that the distance shifts obtained from the BSSE-CP corrected potential minimum remain below 0.1 Å. Irrespective of computational scheme and cluster size, the two types of oxygen atoms occur at different heights, and this difference δO is tabulated in Table 4.2 together with other geometric parameters revealing distortions from planarity. The height difference between both kinds of oxygen atoms gives a direct measure for the different strength of the respective interactions with the substrate. In principle, this height difference is accessible to XSW measurements, as demonstrated for PTCDA and NTCDA on Ag(111) [20, 44, 46, 151].

The results in Tables 4.1 and 4.2 demonstrate that calculations based on the smallest cluster with only 16 Ag atoms cannot be trusted, mainly because the most important
silver atoms directly below the carboxylic groups have only two nearest neighbours. Such a small number of neighbouring metal atoms defines a rather poor representation of a closed Ag surface where the surface atoms should have 7 nearest neighbours, including 2 in the topmost layer, 4 in the second, and 1 in the third layer, respectively. The convergence of the computed heights can directly be related to the number of Ag atoms surrounding the region of the directional Ag-O bonds: The Ag$_{32}$(15,16,1) and Ag$_{34}$(9,16,9) clusters include six nearest neighbours around the relevant site, whereas the Ag$_{50}$(15,16,9) cluster accounts for all seven neighbours required for an extended surface. However, the memory limitations inhibit a treatment of the largest cluster with RIMP2, so that the RIMP2 calculations using the Ag$_{32}$(15,16,1) and Ag$_{34}$(9,16,9) substrate models define the best converged results. The larger of these two substrate clusters shows a particularly high difference $\delta_O = 0.18 \text{Å}$, significantly larger than the value of $\delta_O = 0.14 \text{Å}$ obtained for the Ag$_{32}$(15,16,1) substrate model.

In previous DFT calculations of NTCDA on Ag(110) allowing for geometric changes of substrate atoms, it was found that the Ag atoms directly below the carboxylic oxygens are raised by 0.07 Å, reducing in turn the distortion within the adsorbate [55]. As our approach does not allow for such changes of the substrate geometry, we expect that the height difference between carboxylic and anhydride oxygens is overestimated by about 0.07 Å, so that the RIMP2 figures in Table 4.2 would correspond to smaller values of $\delta_O = 0.11 \text{Å}$ on Ag$_{34}$(9,16,9) and of $\delta_O = 0.07 \text{Å}$ on Ag$_{32}$(15,16,1), the first of these values being closer to the previous DFT estimate of 0.10 Å [55].

The larger number of silver atoms in the third layer of the Ag$_{34}$ cluster seems to be important for an increased dispersion interaction, so that the entire core region moves down by 0.05 Å. From the different RIMP2 adsorbate geometries obtained on the various substrate models, including especially the rather small changes between the relaxed geometries on the two largest silver clusters, we deduce that on the Ag$_{34}$(9,16,9) cluster, the adsorbate height is converged within a residual deviation of about 0.1 Å.

Previous DFT calculations of a periodic supercell with the PBE functional have resulted in an adsorbate geometry close to our RIMP2 geometry on the Ag$_{34}$ substrate cluster. On first sight, this seems to indicate that the PBE functional yields quantitative agreement with an \textit{ab initio} method like RIMP2 including the largest contribution to the dispersion interaction. However, in studies of PTCDA on Ag(111) applying the same functional, a much too shallow minimum of the interaction potential was found at a height exceeding the experimental findings by 0.5 Å [49, 50], a shortcoming interpreted as the complete lack of dispersion interactions in the PBE functional. Therefore, the good agreement of previous studies of NTCDA on Ag(110) with our RIMP2 geometry accounting for dispersion interactions cannot be understood from known properties of the PBE functional. Instead, the geometry found in the supercell calculation might have been influenced substantially by the specific type of pseudopotentials used. From an analysis of the influence of the density-density response on dispersion interactions implemented in an advanced DFT scheme, it turned out that a seemingly good correspondence of DFT results without dispersion interactions with a realistic shape of the vdW attraction is purely fortuitous [68].
<table>
<thead>
<tr>
<th>optimized geometry</th>
<th>$E_{MP2}$</th>
<th>$E_{HF}$</th>
<th>$E_{corr}^{MP2}$</th>
<th>$E_{B3LYP}$</th>
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</thead>
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<tr>
<td>Ag$_{16}$(9,4,3)</td>
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<td>2.05</td>
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<td>1.86</td>
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<td>1.36</td>
<td>−5.22</td>
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</tr>
<tr>
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<td></td>
<td></td>
<td></td>
<td>−0.74</td>
</tr>
<tr>
<td>BSSE-CP corrected</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
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<td>Ag$_{16}$(9,4,3)</td>
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<td>1.97</td>
<td>−2.97</td>
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<td>Ag$_{22}$(9,4,9)</td>
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<td>−0.97</td>
<td>−1.48</td>
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<tr>
<td>Ag$_{32}$(15,16,1)</td>
<td>−1.52</td>
<td>1.64</td>
<td>−3.16</td>
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<td>Ag$_{34}$(9,16,9)</td>
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<td>−1.62</td>
<td>−0.52</td>
</tr>
<tr>
<td>Ag$_{50}$(15,16,9)</td>
<td></td>
<td></td>
<td></td>
<td>0.05 ??</td>
</tr>
</tbody>
</table>

Table 4.3: Upper: Total energy of NTCDA on different Ag clusters, in the optimized geometries obtained with MP2 or B3LYP, without BSSE-CP correction. The total MP2 energy $E_{MP2}$ is decomposed into the HF contribution $E_{HF}$ and the correlation energy $E_{corr}^{MP2}$. Lower: BSSE-CP corrected energies in the geometry corresponding to the potential minimum when moving the optimized adsorbate geometry rigidly along the distance towards the substrate cluster.

4.3.2 Impact of van der Waals interaction on adsorption geometry

In order to assess the influence of the lack of dispersion interactions, we have optimized the geometry of the NTCDA adsorbate with the B3LYP hybrid functional. Similarly to the PBE functional, this approach does not account for any long range dispersion interactions. From the respective entries of Table 4.1, we find that the length of the Ag-O bonds is similar to RIMP2, but in the center of the molecule, the unavoidable overlap repulsion is no more counterbalanced by the vdW attraction, so that the adsorbate minimizes the repulsive overlap contribution by an increased distance between molecular core and substrate surface, generating in turn a substantial energetic cost for the bended geometry.

The adsorption geometries obtained with DFT and MP2 on the same model clusters show substantial discrepancies. First, in B3LYP, the average height of NTCDA above the topmost ML of the substrate is much larger than in MP2. For the largest Ag$_{34}$(9,16,9) cluster we can handle with both methods, on average B3LYP places the C atoms at a height of 2.88 Å, significantly above the respective value of 2.57 Å obtained with MP2. Second, the adsorption geometry obtained with DFT is strongly bended, a phenomenon occurring not just along the long axis in order to reduce the energetic impact of the overlap repulsion involving atoms in the naphthalene core, but also along the short axis: All hydrogens are repelled more than the carbon atom they are attached to. From the comparison of the substrate models Ag$_{34}$(9,16,9) and Ag$_{50}$(15,16,9), it is clear that the repulsion of the hydrogen atoms cannot be related to the edge of the
substrate cluster: Both substrate models result in exactly the same height difference of \(0.15\) Å between H atoms and adjacent C atoms. In the MP2 geometry, the overlap repulsion is counterbalanced by attractive dispersion interactions, resulting eventually in a nearly flat adsorbate geometry.

### 4.4 Adsorption energy

In sharp contrast to the adsorbate geometries which we consider to be reasonably converged for the largest substrate clusters, the MP2 adsorption energies do not follow any simple rule. This finding indicates that unavoidable boundary effects arising from the finite size of the metal clusters inhibit the definition of a converged adsorption energy. Nevertheless, the RIMP2 calculations allow an estimate of the relative influence of HF energy and dispersion interactions on the total energy.

In Table 4.3, we analyse the HF contribution and the dispersion interaction on different substrate models. For all Ag clusters excluding \(\text{Ag}_{22}(9,4,9)\), the HF energy \(E_{\text{HF}}\) is repulsive. After moving to the minimum of the BSSE-CP corrected MP2 potential, this repulsion is slightly reduced, a combined effect of a larger distance towards the substrate and the subtraction of a small but positive BSSE. Interestingly, also for the B3LYP optimized geometries, the \(\text{Ag}_{22}(9,4,9)\) shows a particularly favourable total energy, revealing that this specific cluster has rather different electronic properties than the other substrate models.

The MP2 correlation energy \(E_{\text{corr}}^{\text{MP2}}\) depends mainly on the number of Ag atoms in the topmost layer: Only for the \(\text{Ag}_{32}(15,16,1)\) cluster with a larger number of Ag atoms at the metal-organic interface, the dispersion contribution to the correlation energy is increased substantially. However, after the BSSE-CP correction, the quite different BSSE occurring for different substrate models spoils the apparent systematic trend observed when the BSSE was still included, so that the total MP2 energy \(E_{\text{MP2}} = E_{\text{HF}} + E_{\text{corr}}^{\text{MP2}}\) shows no systematic dependence on cluster size, apart from the fact that the interaction of NTCDA with \(\text{Ag}_{22}(9,4,9)\) remains particularly favourable. As opposed to the small BSSE occurring for the HF energy, the long range dispersion interaction included in \(E_{\text{corr}}^{\text{MP2}}\) is subject to a substantial BSSE. When combined with the distance shift obtained from the minimum of the CP-corrected potential surface, the attractive correlation energy is reduced substantially by 1.94 eV on \(\text{Ag}_{16}(9,4,3)\) up to 3.6 eV on \(\text{Ag}_{34}(9,16,9)\).

The short-range correlation energy included in B3LYP shows a relatively small BSSE. For all substrate models excluding the smallest cluster, the interaction energy at the CP-corrected distance remains attractive, but the resulting binding energy is significantly below a previous estimate of \(-0.92\) eV obtained for an extended substrate model [55]. Due to the short-range nature of exchange and correlation included at the B3LYP level, the scatter of the interaction energy between different substrate models remains much smaller than in the MP2 results, but due to the complete lack of dispersion interactions in B3LYP, the underlying adsorbate geometries are not expected to
be reliable.

4.5 Bonding mechanism

The chemical interactions involved in adsorption of NTCDA on Ag(110) can be better understood from a careful investigation of the involved molecular orbitals. Although the adsorption geometry obtained with MP2 should be more reliable than the respective B3LYP result, MP2 is not able to provide reasonable MOs since the electronic eigenstates are simply obtained from a HF calculation. Therefore, for an analysis of a given geometry, the short range correlations included in DFT should improve the reliability of the obtained MOs. In the following, we use the adsorption geometry obtained at the MP2 level, but the discussion of electronic orbitals will be based on the B3LYP functional. Scanning the relaxed MP2 geometry of NTCDA along different heights above the substrate, we can investigate the dependence of the orbital energies along that coordinate.

Fig. 4.5 shows the energies of the 50 highest occupied MOs of NTCDA/Ag\(_{22}\) calculated with B3LYP/def-SV(P) as a function of height, defined with respect to the geometry optimized at the MP2/def-SV(P) level. This graph is very similar to that we have seen for PTCDA/Ag\(_{32}\) (Fig. 3.6). Hence the resembling of charge transfer mechanism is expected for NTCDA/Ag(110) system.

Figs. 4.5b and 4.5c show the side view and the top view of the NTCDA LUMO at the geometry of the minimum of the counterpoise-corrected MP2 potential. It can be seen that NTCDA LUMO is strongly hybridized with the metal MOs and Fig. 4.5a shows that there are two MOs of this kind. For this reason NTCDA LUMO is one of the basic MOs in the chemical reaction between NTCDA and substrate. This MO has nodes directly at the center carbons (C1). So, these carbons represent lower contribution to the interaction with substrate atoms and they have higher distance than the sides carbons.

4.6 Effect of the functional groups on the adsorption geometry

In order to study the effect of functional groups on the adsorption of NTCDA on the Ag(110) surface, the adsorption structure of the aromatic core of the NTCDA (naphthalene) on Ag(110) was investigated. In this case the structure of naphthalene on a Ag\(_{22}\) cluster was relaxed using the same methodology which we have discussed for PTCDA and NTCDCA molecules. The adsorption geometry of NTCDA on Ag(110) surface was used to determine the first adsorption geometry of naphthalene on Ag(110). Fig. 4.6 shows the top view of the first adsorption geometry of naphthalene on Ag(110), it can be seen that the position of naphthalene on Ag(110) is exactly the same as the position of naphthalene core of NTCDA on the Ag(110) surface.
Figure 4.5: B3LYP/def-SV(P) MO energies of NTCDA/Ag$_{22}$ adsorption system versus distance between NTCDA and substrate (a). MP2 relaxed geometry of NTCDA is used and the relaxed MP2 distance between NTCDA and substrate is used as reference point. The minimum of the counterpoise-corrected MP2 potential is indicated by vertical line. Side view (b) and top view (c) of hybridized NTCDA LUMO.
Figure 4.6: Top view of naphthalene (a) and NTCDA (b) on Ag$_{22}$. The adsorption model of naphthalene has been based on the adsorption site of NTCDA on the Ag(110) surface which has been investigated in this study.

We should clarify that we are not going to obtain the best adsorption site of naphthalene on the Ag(110) surface and we do not claim that this adsorption geometry is the best energetic possible adsorption geometry of naphthalene on the Ag(110) surface. However this adsorption geometry was selected to better compare the naphthalene adsorption with the NTCDA adsorption on Ag(110). The C average distance heights ($z_C$) are 4.48 Å and 3.23 Å at DFT and MP2 level of theory respectively. The adsorption energies which are obtained at DFT and MP2 are 0.00 eV and -1.87 eV respectively. These large differences between the adsorption geometries and the energies obtained at these two levels show that the shortcoming of DFT methods to study the adsorption geometry of non-functionalized aromatic compounds on metal surfaces is more significant. We can also conclude that the attractive PES of the NTCDA on Ag(110) obtained at DFT level is coming from the anhydride functional groups.

The approximate value of adsorption energy which has arisen from the anhydride part of the NTCDA molecule can be determined by subtracting the adsorption energies of NTCDA and naphthalene on Ag(110) which is -0.57 eV. This value is not exactly equal to the DFT $E_{ads}$ for NTCDA on Ag$_{22}$ (-0.35 eV). The difference between these two values is coming from the energy which require to deform NTCDA toward the adsorption.

4.7 Conclusion

In this work we have employed MP2 and DFT calculation to study the adsorption of the organic semiconductors on the metal surface. We have used cluster model approaches in this study. Several cluster models was used and the effect of cluster size on the adsorption geometry was studied. We have found that a cluster with 22 Ag atoms is able to produce reasonable adsorption geometry. We have used this cluster model for the further investigations of the chemical interactions. We have shown that the lack
of the dispersion terms at DFT approaches have strong influence on the adsorption geometry. Resembling the adsorption geometry of PTCDA on the Ag(110) surface, DFT gives a strongly bended adsorption geometry of NTCDA on Ag(110). Also, from the MO projection we have found similar bonding mechanism for PTCDA and NTCDA. However the LUMO of NTCDA is strongly hybridized with the substrate MOs which is not the case for PTCDA. This hybridization is a kind of $\pi-\pi$ interactions and cause chemical interaction between adsorbate and the substrate. Both adsorbates (PTCDA and NTCDA) are strongly adsorbed on the surface and the average distance height for carbon is rather similar. For the Ag$_{32}$ cluster the MP2 C average distance heights are 2.68 Å and 2.60 Å for PTCDA and NTCDA respectively. The larger size of PTCDA induces larger vdW interaction and one expects stronger bonding between the PTCDA and the Ag(110) surface. However due to more properly hybridized MOs for adsorbed NTCDA, this molecule interacts more strongly with Ag(110) surface.

In the comparison between the adsorption geometries of NTCDA and naphthalene we have shown that B3LYP method is only able to investigate the interaction of functional groups with the Ag(110) surface and it is not able to include the interaction of aromatic core.
Chapter 5

Conclusions and outlook

In this thesis we presented the studies of the adsorption geometry of the organic molecules, PTCDA and NTCDA on noble metal surfaces using different ab initio methods. A calculation of the interaction of such organic molecules and metal surfaces is a very important topic since details of these interactions are important for understanding e.g. charge injection at the electrodes of organic semiconductor devices. Presently, most of the calculations reported in the literature are being carried out using DFT, employing a variety of different functionals. In the present thesis such DFT calculations are compared with the results obtained from a different theoretical approach based on wave functions, where dispersion interactions are considered explicitly by using MP2.

The geometry of PTCDA adsorbed on a (110)-oriented silver crystal was optimized on a finite metal cluster used as a rigid substrate. In a comparison between MP2 and DFT, we found pronounced differences: MP2 gives a nearly flat adsorbate, in agreement with the geometries deduced from X-ray standing wave studies on similar substrates, whereas the lack of dispersion interactions in DFT results in a strongly bended geometry. In MP2, the vdW attraction counterbalances the overlap repulsion, resulting in an average height of the PTCDA adsorbate above the topmost substrate layer of 2.68 Å for C atoms, comparing favourably with recent measurements based on X-ray standing wave techniques. The carboxylic oxygens interact more strongly with the substrate than the anhydride groups, so that we predict a height difference of 0.13 Å between both types of oxygen atoms. In the reference geometry obtained from MP2, we have applied the B3LYP functional to a computation of the vibrational properties of the adsorbate and the shift of the core levels, and for both phenomena, the observed trends have been reproduced. This nice agreement with experimental findings underlines the need to include dispersion interactions in the ab initio scheme used for the geometry optimization.

We also used MP2 and DFT calculation to study the adsorption of NTCDA on the metal surface. Smaller size of NTCDA allowed us to investigate the effect of the cluster size on the adsorption geometry. Several cluster models were used and we have found that a cluster with 22 Ag atoms is able to produce reasonable adsorption
geometry. We used this cluster model for the further investigations of the chemical interaction. Contrary to the adsorption energy which strongly depends on the cluster size, adsorption geometry does not depend too much on the cluster size and we can find a reasonable adsorption geometry even with a relatively small cluster. Resemble to PTCDA, DFT and MP2 adsorption geometries of NTCDA have pronounced differences. A small bending was found along the short side of the NTCDA molecule both at DFT and MP2 relaxed geometry. MP2 calculations like the ones presented can serve as a guidance for the parametrization of improved density functional accounting implicitly for long-range correlations required for the vdW interaction.

Due to the limitation of the cluster model which was used in this study we were not able to find the precise values of the adsorption energies. A very interesting topic for further research, inspired by Chapters 3 and 4, would be to use currently developed MP2 slab calculation. These types of calculations had not been developed in the time that this project was started.

In this thesis we just studied the adsorption of molecules on the Ag(110) surface. Similar studies can be done for the adsorption of NTCDA or PTCDA on the other surfaces. Particularly the Ag(111) surface is one of the most interesting surfaces due to the large numbers of experimental results which are available. Of course, performing such MP2 calculations for the adsorption geometry of PTCDA or even NTCDA on the Ag(111) surface is more challenging due to the higher numbers of substrate atoms which are needed to model surfaces but further software or hardware developments may make such studies feasible.
Bibliography


[136] “Obtained with RIMP2 scheme [85] in TURBOMOLE 5.7,”


[140] “the MP2 optimization of PTCDA on Ag$_{32}$ takes 60 days cpu time on an AMD Opteron processor with 2.0 GHz and 8 GB RAM,”


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List of Publications

A. Abbasi and R. Scholz,
Ab initio calculation of the dispersion interaction between a polyaromatic molecule and a noble metal substrate: PTCDA on Ag(110).
http://pubs.acs.org/doi/abs/10.1021/jp902370b

A. Abbasi, E. Nadimi, P. Plänitz, C. Radehaus,
Density functional study of the adsorption of Aspirin on the hydroxylated (001) α-quartz surface.
http://dx.doi.org/10.1016/j.susc.2009.06.004

R. Scholz and A. Abbasi,
Influence of dispersion interactions on the adsorption of PTCDA on Ag(110)

A. Abbasi, M. Schreiber, and R. Scholz,
Influence of dispersion interactions on the adsorption of NTCDA on (110)-oriented noble metals.

Conference Contributions:

A. Abbasi, R. Scholz, and M. Schreiber,
Influence of dispersion interactions on the adsorption of NTCDA on (110)-oriented noble metals.

A. Abbasi and R. Scholz,
PTCDA chemisorbed on Ag(110): Dispersion interactions and charge equilibration.
A. Abbasi, E. Nadimi, P. Plänitz, C. Radehaus,
Density functional study of the adsorption of Aspirin on (001) surface of $\alpha$-quartz surface.

M. Abdel-Hafiez, M. Toader, T.G. Gopakumar, A. Abbasi, and M. Hietschold,
Adsorption Geometry and Molecular Orbital Structure of Fluorinated Cobalt Phthalocyanine (F16CoPc) Layers on HOPG Substrate.

Thermal and photo-induced phase transformations of Silver(I)-2-[2-(2-methoxyethoxy)-ethoxy]acetat.

A. Abbasi, R. Scholz, and M. Schreiber,
Influence of dispersion interactions on the adsorption of NTCDA on (110)-oriented noble metals.

M. Abdel-Hafiez, M. Toader, T. Gopakumar, A. Abbasi, M. Hietschold,
Adsorption Structure of Fluorinated Cobalt Phthalocyanine (F16CoPc) Layers on Crystalline Substrates.
Materials for Advanced Metallization Conference (MAM) Dresden (Germany), March 2 - 5, 2008.

A. Abbasi, R. Scholz, and M. Schreiber,
Quantum chemical calculations of PTCDA and NTCDA adsorbates on Ag(110).

A. Abbasi, R. Scholz,
Organic adsorbates on open metal surfaces: PTCDA and NTCDA adsorbates on Ag(110).
383. WE-Heraeus-Seminar on ”Physics of Highly Ordered Organic Interfaces and Layers”,
A. Abbasi, M. Schreiber, and R. Scholz,
Chemisorption of PTCDA on Ag(110): A quantum chemical study.
A. Abbasi, R. Scholz, and M. Schreiber,
Quantum chemical investigation of the adsorption of PTCDA on Ag(110).
DPG Conference, Berlin March 4 - 9, 2005.

L. Mancera, R. Scholz, A. Abbasi, M. Schreiber, B.A. Paez, G. Gavrila, G. Salvan,
D.R.T. Zahn,
Theoretical Investigation of the Reactivity of Mg Deposited on PTCDA Films.
DPG Conference, Berlin March 4 - 9, 2005.

R. Scholz, A. Abbasi,
Spectroscopic properties of α-PTCDA single crystals and PTCDA molecules adsorbed on metals substrates
International Karlsruhe Nanoscience Workshop

H. Sabzyan, A. Abbasi,
Ab initio study of structure, intramolecular rotation and hydrogen exchange potential energy surfaces, and possibility of diabatic level crossing for 2-hydroxy-4-phenyl-2,4-cyclopentadien-1-one.
Physical Chemistry Conference, Booshehr, Iran 2002.

**Book Chapter:**

T. Khayamian, M. Esteki, A. Abbasi,
Application of wavelet neural networks in multivariate data analysis (Chapter 4).
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