DFT investigations of the donor-acceptor couple CuPc/C$_{60}$

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Degree Project C in Physics
June 23, 2016
Abstract

The donor-acceptor couple CuPc/C$_{60}$ has been the subject of recent studies in organic solar cells due to its combined abilities in light absorption (CuPc) and charge transport (C$_{60}$). By better understanding the electronic and geometric nature of the system it is possible to shed light on how the molecules act under different conditions. In this study the geometric properties for three different configurations have been studied by means of Density Functional Theory (DFT). By comparing the molecular structure of pristine CuPc with the structure of CuPc in the presence of C$_{60}$, a slight elongation of the bonds is observed when the fullerene is present. This is especially true for the Cu-N bonds. By further including van der Waals interactions, no change in bond lengths is observed. This, in turn, suggests that, most likely, the interaction between the two molecules is relatively weak and the C$_{60}$ will not have a major influence on the electronic structure of CuPc. The N1s X-ray Photoelectron Spectroscopy (XPS) and Near Edge X-ray Absorption Fine Structure (NEXAFS) calculations confirm these conclusions, as only very small changes in peak positions are observed when comparing pristine CuPc with CuPc/C$_{60}$.

Sammanfattning

Tack vare sina egenskaper inom absorption och laddningsöverföring har CuPc och fullerenen C$_{60}$ varit föremål för omfattande studier bland forskare inom organiska solceller. Genom att få större förståelse för den geometriska såväl som den elektroniska konfigurationen inom och mellan paret kan man förutse hur dessa kommer att bete sig i olika sammansättningar. I denna studie har de geometriska förutsättningarna studerats där olika konfigurationer beräknats genom täthetsfunktionalteori (DFT). Genom att mäta bindningslängderna mellan koppar, kol och de olika typer av kväve i CuPc i de olika systemen, kan det inses att bindningarna förlängs då C$_{60}$ läggs till. Då van der Waals-interaktioner inkluderades observerades ingen större förändring i bindningslängderna i jämförelse med fallet utan van der Waals-interaktioner. Detta tyder på att växelverkan mellan de två molekylerna är relativt svag och att C$_{60}$-fullerenen ej har någon större påverkan på elektronkonfigurationen i CuPc. Beräkningarna av N1s X-ray Photoelectron Spectroscopy (XPS) och Near Edge X-ray Absorption Fine Structure (NEXAFS) stödjer denna slutsats då endast små skiftningar i topparna observerades vid jämförelse mellan rent CuPc och CuPc/C$_{60}$. 
Contents

1 Introduction 3

2 Theory 3
  2.1 Molecular structure and solar cells 3
  2.2 Introduction to Density Functional Theory 4

3 Computational Details 6
  3.1 Geometry Optimization 6
  3.2 XPS and NEXAFS calculations 6

4 Results 8
  4.1 Bond lengths, energies and optimized configurations 8
  4.2 N1s XPS and NEXAFS spectra 10

Abbreviations

HOMO Highest Occupied Molecular Orbital
LUMO Lowest Unoccupied Molecular Orbital
NEXAFS Near Edge Absorption Fine Structure
PV Photovoltaic devices
XPS X-ray Photoelectron Spectroscopy
1 Introduction

The signing of the Paris Agreement at the COP 21 in 2015 showed the world that humanity faces an incredibly difficult task in battling with the rising temperature of the Earth. Approximately 337 billion metric tonnes of carbon have been released into the atmosphere from fossil production since 1751, whereas half of these occurred since the middle of 1970s [1]. This realization has lead to an increasing demand for alternative energy resources where sun power is amongst the fastest growing industries [2]. In this study a type of photovoltaic devices has been investigated. In contrast to solar thermal energy, where the energy from the sun is extracted to steam and thereafter converted to electrical power, Photovoltaic (PV) devices convert solar energy directly to electrical energy.

As organic solar cells have advantages such as flexibility and low production costs, they have been the focus of many research studies since the beginning of the 21st century [3][4]. In this study the active components of one type of PV have been studied, namely the donor-acceptor couple CuPc (Copper(II) Phthalocyanine) and C\textsubscript{60} (also called Buckminsterfullerene). These two molecules are of interest because of their light absorption properties (CuPc), high charge transport capabilities (C\textsubscript{60}) and stability (CuPc and C\textsubscript{60}) [5]. The questions that this report tries to answer are the following: What structural changes take place when this donor and acceptor couple are put together? How does the presence of the C\textsubscript{60} affect the electronic structure of CuPc, in particular when it comes to the N1s core levels (XPS) and the N1s projected unoccupied levels (NEXAFS)? What role do the van der Waals interactions play in the structural and electronic properties of the couple? In order to answer these questions, several configurations of the CuPc/C\textsubscript{60} have been analyzed by means of Density Functional Theory (DFT). The structures have been relaxed both with and without van der Waals corrections to the total energy. For these separate configurations, N1s XPS and NEXAFS spectra have been calculated and compared to pristine CuPc results and experimental measurements from the literature.

2 Theory

2.1 Molecular structure and solar cells

Atoms consist of an electron cloud surrounding a positively charged nucleus. These electrons are ordered in orbitals depending on the energy of the electron and covalent bonds can be formed between two atoms due to orbital overlapping. In conductors, the valence wave functions are spread across multiple atoms and therefore the electron cloud can be seen as homogeneous across the material. This also explains why conductors are good at transferring energy since an electron in the conduction band moves freely within the material. In semiconductors, however, there is an energy gap between the valence band and the conduction band. In order for electrons to be transferred into the conduction band, they have to receive at least the energy corresponding to the band gap. Molecular systems work in a similar way where the valence band is replaced by the Highest Occupied Molecular Orbital (HOMO) and the conduction band by the Lowest Unoccupied Molecular Orbital (LUMO). When an electron gets a sufficient amount of energy, it can jump from the HOMO (or below) to LUMO (or above). If an appropriate electron acceptor is combined with the molecule undergoing this excitation process, the excited electron can be harvested and transported through the material. This is how organic solar cells work. Solar power has since it first appeared in the 1970s come to grow into a viable energy source in the society. Whereas today’s solar panels usually are placed on roof tops or in big solar parks, the increasing interest in fossil-free energies has pushed the research into exploring new ways of harvesting this green energy [6]. Production of the commonly used silicon based solar cells uses a significant
amount of energy which lengthens the energy payback time up to several years while organic cells have low manufacturing costs and a payback time of about one year [7].

An organic solar cell consists of three main components. An electron donor which has an absorption range contained in the solar spectrum, an acceptor which allows to extract excited electrons and, finally electrodes to lead the current further for usage. During conversion from solar energy to electric energy, a photon with sufficient energy excites an electron to the LUMO or above leaving a positively charged hole. Since an electron tends to occupy the lowest energy state available together with the Coulomb attraction from the hole, de-excitation is usually the next step. By adding an acceptor which has a LUMO with a slightly lower energy than the LUMO of the donor, the electron can be directed to the acceptor and de-connected from the hole. The highly energetic electron can be then transported to an electrode and gives rise to an electric current.

**Figure 1:** Simplified version of a CuPc/C₆₀ solar cell with HOMO and LUMO of the two molecules. After excitation, an electron transfer occurs between donor(CuPc) and acceptor(C₆₀) and, thereafter another electron transfer from the C₆₀ to an electrode.

### 2.2 Introduction to Density Functional Theory

DFT has been used for calculating the properties of the system. Some of the basics of this method will be described in the following.

Solving the Schrödinger equation for the hydrogen atom is relatively easy given the fact that it contains only one electron. When adding another hydrogen atom, the problem becomes trickier. Assuming that the electrons do not interact with each other directly, the wave function can be written as the product of the individual orbitals [8].

\[
\Psi(r_1, r_2) = \psi_H(r_1)\psi_H(r_2)
\] (1)
This would mean that adding multiple single-electron atoms should give
\[\Psi(r_1, r_2, ..., r_N) = \phi_1(r_1)\phi_2(r_2) \cdots \phi_N(r_N)\] (2)
known as a Hartree Product from the Hartree-Fock theory. This, however does not fulfill the
antisymmetry principle and a Slater determinant should be considered instead:
\[\Psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(x_1) & \chi_2(x_1) & \cdots & \chi_N(x_1) \\ \chi_1(x_2) & \chi_2(x_2) & \cdots & \chi_N(x_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(x_N) & \chi_2(x_N) & \cdots & \chi_N(x_N) \end{vmatrix}\] (3)
where \(\chi(x)\) is a spin orbital consisting the space-spin coordinates \(x = \{r, \omega\}\).

In order to determine the total energy and all other properties of interest for a molecular
system, one must solve the Schrödinger equation for that system. If the wave function of
the system is known and, in combination to a proper energy operator, the Hamiltonian, the energy of
the system can be calculated. However, when a system becomes larger than in the simple case
discussed before, the wave function becomes complicated and the Schrödinger equation difficult to
solve. The solution for this kind of problem lies in making approximations and assumptions about
the system. For clarity, we start from the beginning, with the time independent Schrödinger
equation
\[\hat{H}\Psi = E\Psi\] (4)
where \(\hat{H}\) is the hamiltonian, i.e. the sum of potential and kinetic energies of the system,
\[\hat{H} = \hat{V}_{ee}(\vec{r}) + \hat{V}_{eN}(\vec{r}; \vec{R}) + \hat{V}_{NN}(\vec{R}) + \hat{T}_e(\vec{r}) + \hat{T}_N(\vec{R})\] (5)
where \(\hat{V}_{ee}\) is the electron-electron interaction, \(\hat{V}_{eN}\) is the electron-nucleus interaction, and \(\hat{V}_{NN}\) is
the interaction between the nuclei of the system. \(\hat{T}_e\) and \(\hat{T}_N\) represents the kinetic energy of the
electrons and nuclei, respectively.

It is then possible to separate the problem into an electronic and a nuclear part. Since the
nuclei are heavier than the electrons, the movement of the electrons can be separated from
the nuclei giving \(\hat{T}_N(\vec{R}) \approx 0\) and the potential \(\hat{V}_{NN}(\vec{r}; \vec{R})\) a constant. Still having to deal with
solving an equation for a wave function of 3N variables, which is computationally expensive,
Hohenberg and Kohm proposed to use the electron density, \(\rho(x, y, z)\), of the system instead of the
wavefunction \(\Psi\). H-K proved that all information about the system is included in \(\rho\), suggesting
direct correspondence between \(\Psi \leftrightarrow \hat{V}_{ext} \leftrightarrow \rho\). In addition, they formulated a variational principle
for the density. The energy can then be written as a functional of \(\rho\) and the ground state can be
found by minimizing this functional:
\[\hat{E}[\rho] = \hat{V}_{ee}[\rho] + \hat{V}_{ext}[\rho] + \hat{T}_e[\rho]\] (6)
where \(\hat{V}_{ext}\) is the potential created by the nuclei. \(\hat{V}_{ee}\) is the electron-electron interaction and \(\hat{T}_e\)
is the kinetic energy of the electrons. Both of these terms have a known classical and unknown
non-classical part.
Since the electron-electron interaction term and the kinetic energy term from the expression above cannot be computed in terms of the electron density for an interacting electron system, Kohn and Sham proposed to use instead a fictitious non-interacting system with the same density and add all the unknowns in the so-called exchange and correlation functional, as can be seen in Figure 2.

\[ \hat{E} = \hat{V}_{ee}[\rho] + \hat{V}_{ext}[\rho] + \hat{T}_s[\rho] + \hat{V}_{xc}[\rho] \]  

(7)

where \( \hat{V}_{ee} \) now stands for only the classical part of the electron-electron interaction and \( \hat{T}_s \) is the kinetic energy of the non-interacting particles.

3 Computational Details

3.1 Geometry Optimization

For optimization of the different configurations, Gaussian09 [9] has been used. The program uses a local basis set consisting of gaussian shaped functions to describe the atomic orbitals of the system. Linear combinations of the basis functions are then employed to form each molecular orbital. The functional B3LYP [10], which is standard for optimization of organic molecules, has been used and for several configurations, van der Waals (vdW) interactions have been included. The vdW interaction is a weak interaction between molecules, arising due to a non-homogeneous distribution of electrons in the molecules. For maintaining a low computational time, this extra-molecular interaction was added empirically by using pre-calculated dispersion coefficients, \( C_6^{AB} \) [11].

\[ E_{vdw} = - \sum C_6^{AB} \frac{1}{r_6^{AB}} \]  

(8)

\[ E_{TOT} = E_{DFT} + E_{vdw} \]  

(9)

\( E_{DFT} \) gives the energy from conventional DFT and \( E_{vdw} \) adds the correct \(-1/r^6\) dependence. The basis set 6-31G(d,p) was used for the hydrogen, nitrogen and carbon atoms and cc-pVTZ for copper [12][13].

3.2 XPS and NEXAFS calculations

X-ray Photoelectron Spectroscopy (XPS) uses the photoelectric effect originally explained by Einstein in the beginning of the 20th century [14]. The process consist of the emission of an
electron from the material (core levels in our case) due to the absorption of a photon, see Figure 3. This can be described by a simple formula,

\[ K_{hv} = K_e + BE + W \]  \hspace{1cm} (10)

where the kinetic energy of the photon, \( K_{hv} \) is known. Since we may assume no energy loss in the process, the kinetic energy of the electron \( K_e \) can be measured, and thereby the BE (Binding Energy) of the core electron can be calculated. The work function \( W \) is the amount of work that it takes to completely remove the photoelectron from the extended system.

**Figure 3:** A schematic representation of the process during a XPS measurement.

Near Edge X-ray Absorption Fine Structure (NEXAFS) is a widely used experimental technique to investigate the excited states of electrons. Instead of measuring emitted photoelectrons as in XPS, one measures the emission of fluorescent photons due to de-excitation [15]. During a NEXAFS experiment, photons with a continuous set of wavelengths are sent to the sample. Some of them, having specific energies, excite electrons from the core to the unoccupied molecular states, leaving behind a positively charged hole (as depicted in Figure 4).

**Figure 4:** Schematic representation of the process during a NEXAFS measurement.

To simulate these two kinds of experiments, calculations have been performed using StoBe2007 [16], a quantum chemistry software which uses Gaussian type orbitals (GTOs). For energy correlation of vdW interactions the exchange functional by Becke and the functional by Perdew
was used\textsuperscript{[17]}\textsuperscript{[18]}. Having only two molecules in a system, the work function in the XPS calculation has been neglected. The ionization energy, $IE$ of the N1s core levels has been calculated as the energy difference between the ground state, $E_{GS}$ and the ionized state with a core hole, $E_{CH}$.

$$IE = |E_{GS} - E_{CH}|$$

(11)

The IEs calculated for the different types of nitrogen in CuPc have been used to construct the N1s XPS spectrum. In order to better compare to experimental spectra, a gaussian broadening with a constant Full Width Half Maximum (FWHM) of 0.5 eV has been added to the bar graphs. In addition, a shift of 4.4 eV towards lower binding energies has been performed to align the first calculated peak to the first experimental one. This is due to the work function not accounted for in the calculation as mentioned before.

To study the transition of the electron from a $1s$ state, $|1s\rangle$ to the final state, $|f\rangle$, the dipole approximation was used giving a dipole transition probability.

$$I \propto |\langle f | \chi |1s\rangle|^2$$

(12)

where $\chi$ is the dipole transition operator. The intensity $I$ is proportional to the expectation value of the transition to different final states. A half core hole approximation has been considered when calculating the N1s NEXAFS \textsuperscript{[19]}\textsuperscript{[20]}\textsuperscript{[21]}. The bar graphs were broadened using a Gaussian function of 0.4 eV FWHM. The FWHM was increased linearly to 2 eV in the interval $IE - 6eV$ to $IE + 3eV$ and then kept constant for higher photon energies. The individual N1s spectra were shifted such that the eigenvalue of the $1s$ electron is equal to the calculated $IE$. An additional shift of 2.6 eV towards higher energies was performed to match the experimental NEXAFS dataset for CuPc. This shift is due to electrostatic and relativistic effects not included in the calculation \textsuperscript{[21]}.

4 Results

4.1 Bond lengths, energies and optimized configurations

As a first step, the CuPc was optimized without the presence of another molecule. The structure was able to relax and reach an energy minimum. The CuPc showed no bending or twisting during optimization and remained flat and fully symmetric as shown in Figure 5. This was also the case when C$_{60}$ was added in the vicinity of CuPc, but without any vdW interactions included in the calculation.

\textbf{Figure 5:} The CuPc shows no bending when optimized in pristine form.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure5.png}
\caption{The CuPc shows no bending when optimized in pristine form.}
\end{figure}

The structural properties of three different configurations were studied where the C$_{60}$ was rotated or shifted in different ways as can be seen in Figure 6. In a $L_a$ structure, the Cu atom in CuPc
lies directly above a fullerene C at the intersection of a pentagon and two hexagonal faces of the fullerene. In the \( L_b \) structure, the Cu atom sits above the center of a C-C bond between two hexagons. \( L_s \) is a version of \( L_b \) where the CuPc is slightly shifted horizontally by 0.5Å.

\[ \approx 3° \]

**Figure 6:** The three configurations investigated in this study.

When including vdW interactions in the calculations and letting the molecules relax, the CuPc bent around the fullerene as can be seen in Figure 7, with a bending angle of about 3°. This type of bending appeared in all of the structures in Figure 6, when including vdW corrections.

\[ \approx 3° \]

**Figure 7:** When vdW interactions are included, CuPc bends around the \( C_{60} \). The bending angle is 3°.

The bond lengths in CuPc for each configuration investigated are listed in Table 2. The atoms of interest in the CuPc are shown as a figure inset to the table.

When optimizing the \( L_a \) structure without vdW interactions, it relaxed to the \( L_b \) configuration. However, when optimizing the \( L_b \) structure with vdW interactions, it relaxed to the \( L_a \) structure instead. The energies for the \( L_a \) and \( L_b \) structures without vdW were equal. In addition, the energy was equal for \( L_s \) and \( L_a \) with vdW interactions. This would suggest that the \( L_b \) is lower in energy in the case of no vdW interactions, while \( L_a \) is the energy minimum with vdW interactions.
Table 2: Calculated N-Cu and N-C bond lengths in Å.

<table>
<thead>
<tr>
<th>System</th>
<th>vdW</th>
<th>N2-C</th>
<th>N1-C</th>
<th>N1-Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuPc</td>
<td>no</td>
<td>1.32</td>
<td>1.38</td>
<td>1.95</td>
</tr>
<tr>
<td>$L_s$</td>
<td>no</td>
<td>1.32</td>
<td>1.37</td>
<td>1.95</td>
</tr>
<tr>
<td>$L_s$</td>
<td>yes</td>
<td>1.32</td>
<td>1.38</td>
<td>1.97</td>
</tr>
<tr>
<td>$L_a$</td>
<td>yes</td>
<td>1.33</td>
<td>1.37</td>
<td>1.97</td>
</tr>
<tr>
<td>$L_b$</td>
<td>no</td>
<td>1.33</td>
<td>1.37</td>
<td>1.97</td>
</tr>
</tbody>
</table>

The calculated bond lengths in Table 2 correspond well with earlier calculated data [22]. The N1-Cu and N2-C bond lengths are of particular interest in this study. One can see a slight increase in the length of these bonds in presence of the C$_{60}$. Another interesting observation is that the bond lengths of the $L_a$ and $L_b$ structures shows no change whether adding vdW interactions or not. This suggests that the chemical environment of the nitrogens is not affected by vdW interactions within the couple configurations.

4.2 N1s XPS and NEXAFS spectra

In order to further investigate the influence of the fullerene on the electronic structure of CuPc, the N1s XPS and NEXAFS spectra were calculated for pristine CuPc and the structures $L_s$, $L_a$, and $L_b$ with vdW interactions. The XPS results are shown in Figure 8 in comparison to experimental data. The NEXAFS results can be seen in Figure 9 and 10 together with experimental data for pristine CuPc. The N1s XPS spectrum of CuPc matches well with experimental data for the same system. The energy difference between the two different N peaks is very similar to the one reported in earlier studies [23][24]. Adding the same shift for the work function to the couple configuration as for pristine CuPc results in a slight difference from the corresponding experimental data. This is probably due to the fact that the experiment used separate layers of CuPc and, respectively, C$_{60}$, while in this DFT investigation only one molecule of each type has been considered. No major difference is observed when comparing pristine CuPc with the CuPc/C$_{60}$ configuration with or without vdW interactions, in line with the conclusion of the previous section.
Figure 8: N1s XPS of (a) CuPc with experimental data [23] and (b)-(d) CuPc/C_{60} in different configurations N1s states with exp. data [25]. The bars represent the calculated data with DFT while the plots in red and blue are fitted using broadened gaussians to facilitate composition to experiment for easier comparison.

Figure 9 represents the calculated as well as the experimental NEXAFS spectrum for pristine CuPc. The calculated spectrum is in particularly good agreement with the experimental data. The shape of the first peak looks similar and the intensity of the following peaks matches well with the experiment. This shows that the approximation used in the calculation works very well for this type of system.

Figure 9: The NEXAFS spectrum of CuPc at the N1s absorption edge calculated using DFT. The experimental spectrum of CuPc is shown for comparison [26].

When adding the C_{60}, the unoccupied states appear to experience only a very small shift towards lower energies by 0.1 eV. This is a sign that the electronic structure of the CuPc is virtually not affected by the presence of the C_{60}, even when including vdW interactions.
Conclusions

To summarize, in this study I have analyzed and compared the structural and electronical behavior of pristine CuPc and the couple CuPc/C$_{60}$ in different configurations. I have found that no significant geometric change is found when adding the C$_{60}$ except for the bending of the CuPc molecule when including vdW interactions. No changes in N1s XPS and NEXAFS spectra were observed when adding the C$_{60}$ or, by further including vdW interactions. This leads to the conclusion that the electronic structure of the CuPc is not affected by the presence of the buckminsterfullerene. In order to further check the CuPc and C$_{60}$ interaction, the C1s XPS and NEXAFS would be interesting to calculate. Furthermore, the analysis of the bulk system and of the molecules on various substrates would provide more insights into the interactions and would be more realistic in comparison to actual devices. Finally, a theoretical estimation of the open circuit voltage and recombination rates of this type of system is possible by analyzing the HOMO and LUMO wavefunctions and would also be highly relevant.

References


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