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Artificial photosynthesis – 4-Aminobenzoic acids effects on charge transfer in a photo catalytic system



Simon Moberg

Uppsala University

Department of Physics
and Astronomy

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Supervisor: Oscar
Grånäs

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Abstract

Artificial photosynthesis is used to harvest solar energy and store it in the form of chemical bonds. The system of interest in this study does this by splitting water into hydrogen and oxygen gas through a plasmon assisted process, collective oscillations from free electron gas. This is a renewable way to store energy that could be used as an alternative to fossil based fuel. In this study, a small part of this photo catalytic system is studied, namely the interaction between plasmonically active silver nanoparticles (Ag NPs) transferring photo-excited electrons via a linker molecule, 4-aminobenzoic acid (pABA). The pABA linker molecule transfers charge from the Ag surface to a semiconductor and a catalyst performing the water splitting. The pABA can bind in different ways onto the Ag-surface and the aim of this study is to examine which bond is strongest and which best enables charge transfer. To this purpose three systems were simulated quantum mechanically using a supercomputer. The total free energy of the systems was computed and compared. Out of the three studied binding sites, the hollow-site bond (pABA binding to three silver atoms) was found to have the lowest energy, meaning it's the strongest of the possible bonds. Additionally it was found that the band gap (the energy needed to transfer charge) for the pABA decreased when bound to the Ag-surface. The hollow-site bound pABA also had the smallest band gap, meaning it requires the least energy to transfer a charge and should therefore be the best bond fitted for the photo catalytic system.

Sammanfattning på svenska

Artificiell fotosyntes används för att absorbera solenergi och förvara den i formen av kemiska bindningar. Systemet som används i denna studie gör detta genom att splittra vatten till vätegas och syrgas genom en plasmon assisterad process. Detta är ett förnyelsebart sätt att förvara energi och kan användas som ett alternativ till fossila bränslen. I denna studie studeras en liten del utav detta fotokatalytiska system nämligen interaktionen där plasmonaktiva silvernano-partiklar (Ag NPs) överför foto-exciterade elektroner genom molekyllänken 4-aminobensoesyra (pABA). Molekyllänken pABA överför laddning från silverytan till en halvledare och en katalys som utför splittringen av vattnet. pABA kan binda på olika sätt till en silveryta och denna studie syftar till att undersöka vilken utav bindningarna som är starkast och vilken som effektivast överför laddning. För att göra detta simulerades tre system kvantmekaniskt med hjälp av en superdator, ett system för varje sorts bindning. Den totala fria energin av systemen beräknades och jämfördes. Av de tre undersökta bindningarna hade hollow-site bindningen (pABA som binder till tre silveratomer) längst energi, vilket betyder att det är den starkaste av bindningarna. Utöver detta så visade det sig att bandgapet (energin som krävs för att överföra laddning) minskade för pABA när den var bunden till Ag-ytan. Hollow-site bundet pABA hade även minst bandgap, vilket betyder att den kräver minst energi för att överföra laddning och är därmed den mest effektiva bindningen för det fotokatalytiska systemet.

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1. Introduction

Artificial photosynthesis is a way of collecting the energy of sunlight and storing it in the form of chemical bonds. A possible reaction mechanism utilizes a multi-step process, where sunlight is absorbed by a metallic nano-cluster as plasmons, charge is transferred through a linker molecule, to an efficient electro-catalyst performing e.g. water splitting. The water splitting creates hydrogen and oxygen that can be used as renewable fuel. Combining the two again releases the energy stored while returning the two gases back to water, resulting in an energy storing process completely free of environmentally damaging rest products providing environmental alternative to fossil fuels. Charge transfer processes is often schematically described by energy level diagrams. Where a key concept is the band gaps, potential energy barriers that has to be overcome in order for the excited charge to be transferred. The barriers can be calculated from quantum-mechanics based simulations, and thermodynamic modelling is often used to describe transfer probabilities. Plasmon activated charge transfer, the photo-induced multi-electron excitations creates near-field effects that are essential for photo catalysis. This means that charge transfer can occur at conditions where it is normally highly unlikely, allowing transfer at dim light conditions or high barriers. Plasmon-driven charge transfer is therefore best described using non-equilibrium techniques, like time-dependent density functional theory. This study aims to quantify the energy barriers, needed to quantify the effect of plasmonic activity by comparing charge transfer characteristics for thermodynamics modelling and time-dependent density functional theory.

To be more specific, the focus on this study is on the charge transfer between a silver nano-cluster and a connected *4-Aminobenzoic acid* (pABA) linker molecule. *Proton-coupled electron transfer* (PCET) reactions is essential in artificial photosynthesis. So understanding and optimizing PCET reactions is critical for the design of solar fuel cells and similar devices [1]. To simulate and analyze this reaction properly we need a way to accurately describe it's quantum mechanical properties. Additionally, calculations with multiple atoms arranged in solids and molecules becomes a many-electron problem [2]. The computational complexity of the many-electron problem requires a supercomputer to describe the system. Then the question occurs, what information is needed to optimize the silver-pABA charge transfer part of the process? Our main goal should be to increase the efficiency of the process. The following scientific questions are raised:

1. Is there an optimal structure of the silver-pABA bond that minimizes the total free energy?
2. If so, how large is the energy barrier? Does the band gap change of the bound pABA and how does that affect the charge-transfer from the silver NPs.
3. What is the binding energy for the different possible bonds pABA can form on a silver surface?

2. Background

2.1 Nano-hybrid photocatalytic system

The ability to transform solar light into chemical bonds (artificial photosynthesis) enables storable energy in the form of sun fuel. This product is undeniably coveted and to optimize the means to get the product is a good way to decrease the use of fossil fuels. While there are several photo catalytic systems that can converse light energy into solar fuel, we want to chose a promising one in both efficiency and economic accessibility. For this study the system chosen is well studied and show great promise in terms of both these criteria, namely *silver nano-particles* (Ag NPs) stabilized with betanin linked via a *4-aminobenzoic acid* (pABA) molecule to a *Titanium dioxide* (TiO_2) semiconductor [3-5].

Photo-coupled electron transfer (PCET) reactions are the driving force in many types of solar fuel cells, including this one. PCET reactions is when a electron and a proton transfer in a single step without a stable intermediate [1]. The system of this study is using a PCET catalytic water oxidation that involves the transfer of $4e^-/4H^+$. Using this reaction, water molecules can be split into H_2 and O_2 , which can be used as solar fuel [3].

It is a good choice to have a large band gap semiconductor like TiO_2 (>3 eV) since high energy is needed to break the bonds in the water molecules. While there are plenty of other alternatives TiO_2 is a well studied photo-catalytic material with outstanding physical and chemical properties. Its high band gap and rate of electron-hole recombination limits its efficiency as a catalyst. TiO_2 are also hindered by the need of UV irradiation to be able to separate charge. While there have been efforts to shift their absorption to visible light, this reduced both reaction scope and overall performance. These limitations can fortunately be overcome by the metallization of TiO_2 . Semiconductor sensitization as used in dye-sensitized solar cells, where the sensitizer harvest sunlight to rapidly inject electrons into the TiO_2 conduction band is one solution. Metallic NPs have large optical cross-sections related to the excitation of *localized surface plasmons* (LSP), which makes for good sensitizers. The LSP creates electric fields near the metallic NPs surface that greatly enhances charge transfer. Furthermore gold group metals like silver shows LSP resonances in the visible region. They have high Schottky barriers and can therefore act as electron traps, facilitating electron-hole separation. The excitation of Ag LSP resonances have shown to improve charge transfer in dye-sensitized solar cells, photocurrents and photocatalytic oxidations [4,5].

In this study we will analyze the electron step process that comes before the semiconductor TiO_2 , namely the interaction between the Ag NPs and the pABA linker molecule. The pABA linker is very important for hydrogen production in the system, it has increased the systems efficiency up to 20% [5]. It provides excellent electronic coupling because of its connected p-orbitals, rigidity and planarity [6].

2.2 Crystal structure of Ag

To analyze the system of Ag NPs and pABA the structure is going to be simulated in a program for atomic modeling. To properly represent the materials their structure is needed to be realistically and accurately represented.

An ideal crystal is constructed by the infinite repetition of identical groups of atoms. A group is called the *basis*. The set of mathematical points to which the basis is attached is called the *lattice* [7]. A periodic repetition of the lattice makes up a fundamental concept of describing any crystalline solid called a *Bravais lattice*. The definition of a three-dimensional Bravais lattice follows:

A three-dimensional Bravais lattice consists of all points with position vectors \mathbf{R} on the form

$$\mathbf{R} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3,$$

where $\mathbf{a}_1, \mathbf{a}_2$ and \mathbf{a}_3 are any three vectors not all in the same plane, and n_1, n_2 and n_3 range through all integral values. Thus the point $\sum n_i \mathbf{a}_i$ is reached by moving n_i steps of length a_i in the direction of \mathbf{a}_i for $i = 1, 2$ and 3 [2].

Silver as a crystal lattice is described as a *face-centered cubic* (fcc) Bravais lattice. However, for it to be accurately described as a Bravais lattice one must look at a large crystal and not close to the crystals edges, which is exactly what we'll be doing in this study. The forces acting upon the atoms in the center of a solid are very well distributed and symmetrical. In the case of a silver surface, the structure is large in two dimensions. It must therefore be represented as infinite (much like a Bravais lattice) in these two dimensions and finite in the last dimension. While closer to the edges the forces acting upon these layers don't have the same symmetry as deeply embedded lattice, making the structure more uneven and therefore worse of a fit as a Bravais lattice. This needs to be considered when simulating the silver NPs since the distance \mathbf{a} will vary when moving close to the surface edges. For this reason will be using a program with a relaxation process, that can calculate the forces acting on the atoms and position them accordingly.

3. Method

During the course of the study a number of systems were simulated with a super computer using Quantum ATK and *The Vienna Ab initio Simulation Package* (VASP). Quantum ATK is a platform for atomic scale modeling and simulating of semiconductor materials, nanostructures and molecules. VASP computes an approximate solution of the many-body Schrödinger equation with *density functional theory* (DFT) solving the Roothaan equations. The *Generalized-Gradient approximation* (GGA) was used as the model for relaxation in this study. GGA uses the local constant electron density and the gradient of the electron density to incorporate the effects of inhomogeneities in the considered system. This method should be an improvement from the similar *Local density approximation* (LDA) which only takes the uniform electron gas into consideration [9].

3.1. System set up

While our final product should be a fully relaxed Ag-PABA system, a few steps are required to reach this system. A creation of the Ag fcc bulk structure with fitting input parameters should be the first step. A silver atom was imported from the ATK database and then repeated to create a 2x2x2 small silver bulk. This structure serve as the basis of the fcc Bravais lattice. The starting lattice parameter was 4.0857 Å as automatically constructed by the program. While this is only a small piece of silver nanostructure the periodic properties of the potential energy wave functions combined with the vacuum feature in ATK makes the simulation repeatable. The vacuum zone marks where the wave function repeats and with a good fit the simulated system is therefore not only a 2x2x2 silver structure, but a repeating such in all three dimensions creating a accurate approximation of a perfect crystal [7].

The silver basis set was analyzed with the GGA for different energy cut-off's for the plane-wave basis set. The input parameter ENCUT decides which plane-waves are included in the calculation by cutting of all with a kinetic energy larger than the ENCUT-value in eV [10]. To keep consistency during future calculations the ENCUT-value was varied from 200 eV to 400 eV with steps of 50 eV to find the total energy minimum. The system was fixated during this time since we were only interested in the optimization of the input parameters. The minimum was shown at 300 eV (see *figure 1.*) and was chosen as the ENCUT-parameter for the rest of the simulations. Another important parameter to optimize was the K-POINTS. The k-points creates the k-point grid that is used as reference points for the periodic wave functions. Having more k-points requires a lot more computing time and doesn't necessarily give a better result. To chose an acceptable size for the k-points once more the total energy was plotted now towards k-points from 3x3x3 to 13x13x13 in steps of 2. In *figure 2.* we can see the energy converge as the amount of k-points grow larger. In this study we decided to settle with a 9x9x9 k-pints grid as the convergence starts around there and any larger grid would make the calculations to long. This K-POINTS value should also be held consistent during the remaining simulations with the silver surface involved.

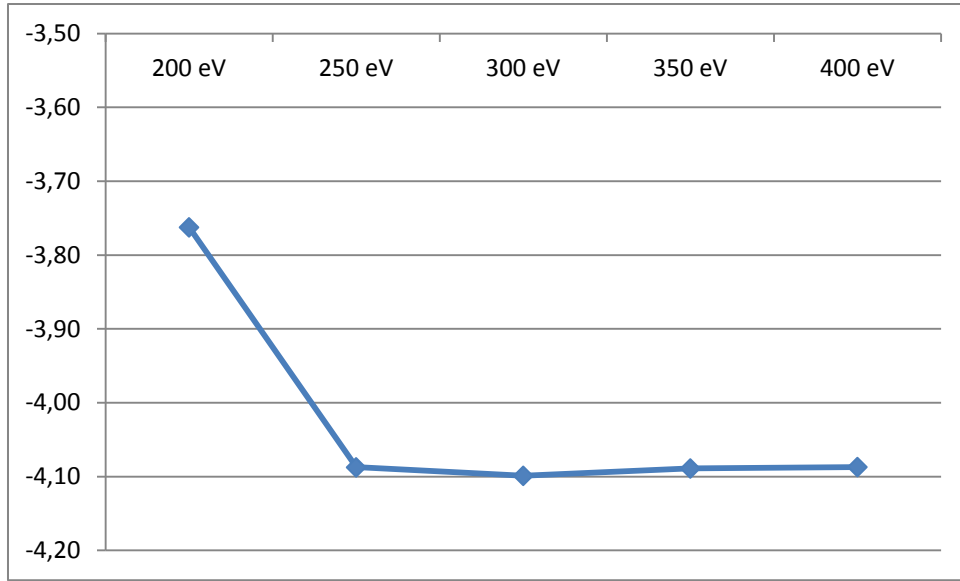


Figure 1. Total energy [eV] of silver basis set as a function of ENCUT-value.

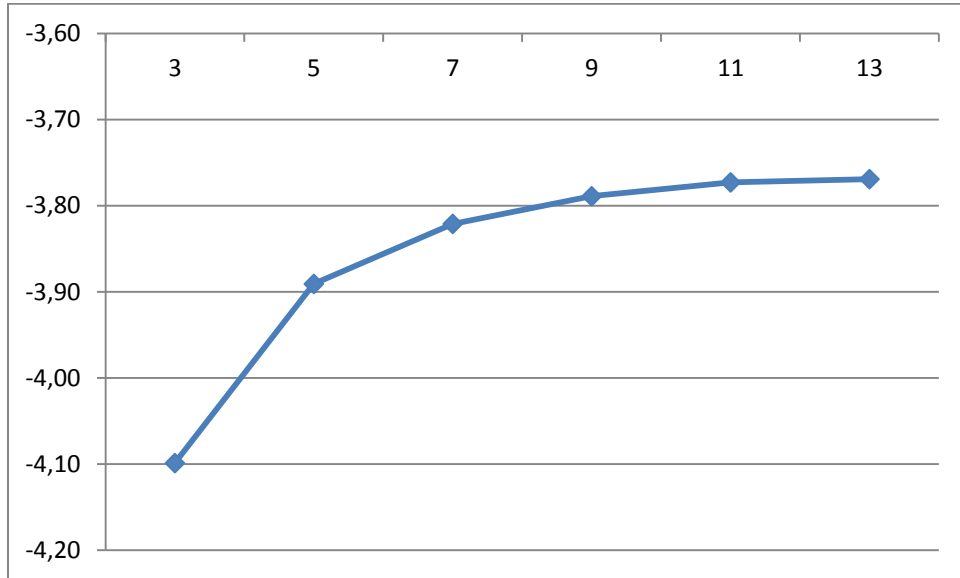


Figure 2. Total energy [eV] of silver basis set as a function of k-points grid.

Next step was to run a relaxation of the silver basis set. The relaxation process uses a step sequence where many-particle forces are calculated and the atoms are moved a small distance towards the force resultant in between each step. The GGA was set such that the relaxation process would run until the total free energy change and the band structure energy change between two steps are both less than 10^{-4} eV. The relaxed basis set was repeated to create a bigger silver NP surface (*see figure 3.*). To simulate a surface a couple of precautions has to be taken. The structures wave functions must be repeated in only two of the three directions, otherwise we are simulating the center of a crystal structure. To solve this the vacuum was extended with 13 Å in the surface direction to minimize the periodic properties of the simulation in this dimension. But then another problem occurs. Since the vacuum box have repeatable properties the bottom layers in the C-direction (*blue axis in figure 3.*) of the silver bulk will also experience a vacuum below. This means at this point the simulation would correspond to a three

atoms thick silver surface. We want to represent the surface of a solid and not just a thin layer. The solution used was to fixate the position of the two bottom layers of the silver bulk. This keeps the infrastructure of the silver NPs intact while also allowing the outer layer to move during the relaxation. The silver surface was relaxed and the total free energy of the system calculated using VASPs GGA.

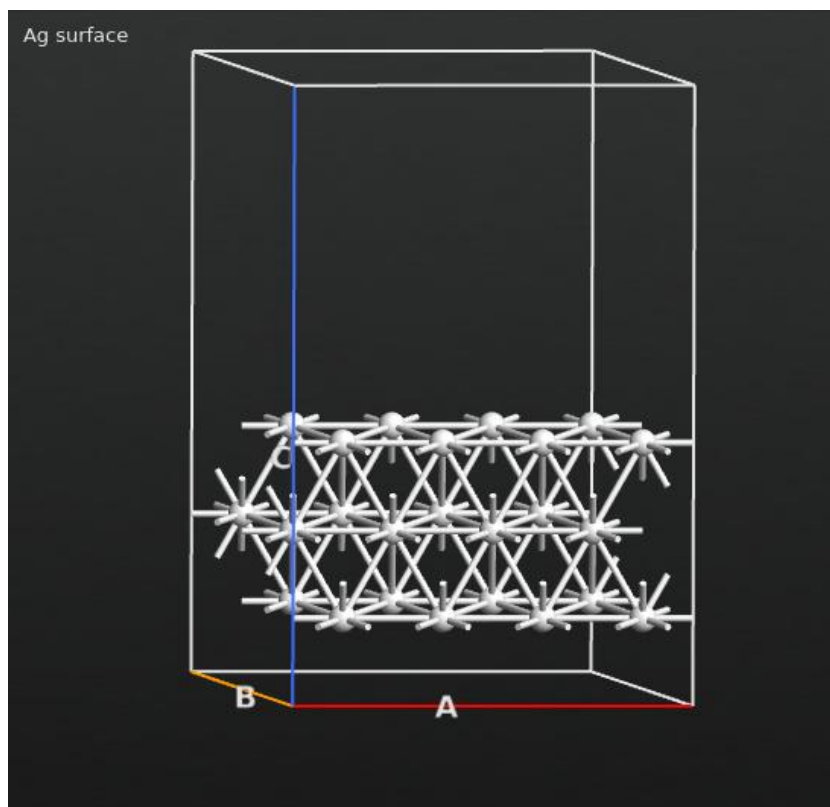


Figure 3. Silver surface with vacuum box.

As for the pABA molecule the periodic charge interaction is not desired. We do need take it through the relaxation process to retrieve the total free energy. To keep it from self interacting a bigger vacuum box is constructed (*see figure 4.*). The same input parameters are used for the pABA as was used for the silver, this is necessary to keep consistency going into the combined simulations with pABA bound on the silver surface. One exception is the KPOINT that was set to 1x1x1. This is because no periodic behaviors will be seen from the pABA molecule. The pABA molecule is then taken through the same process as described above.

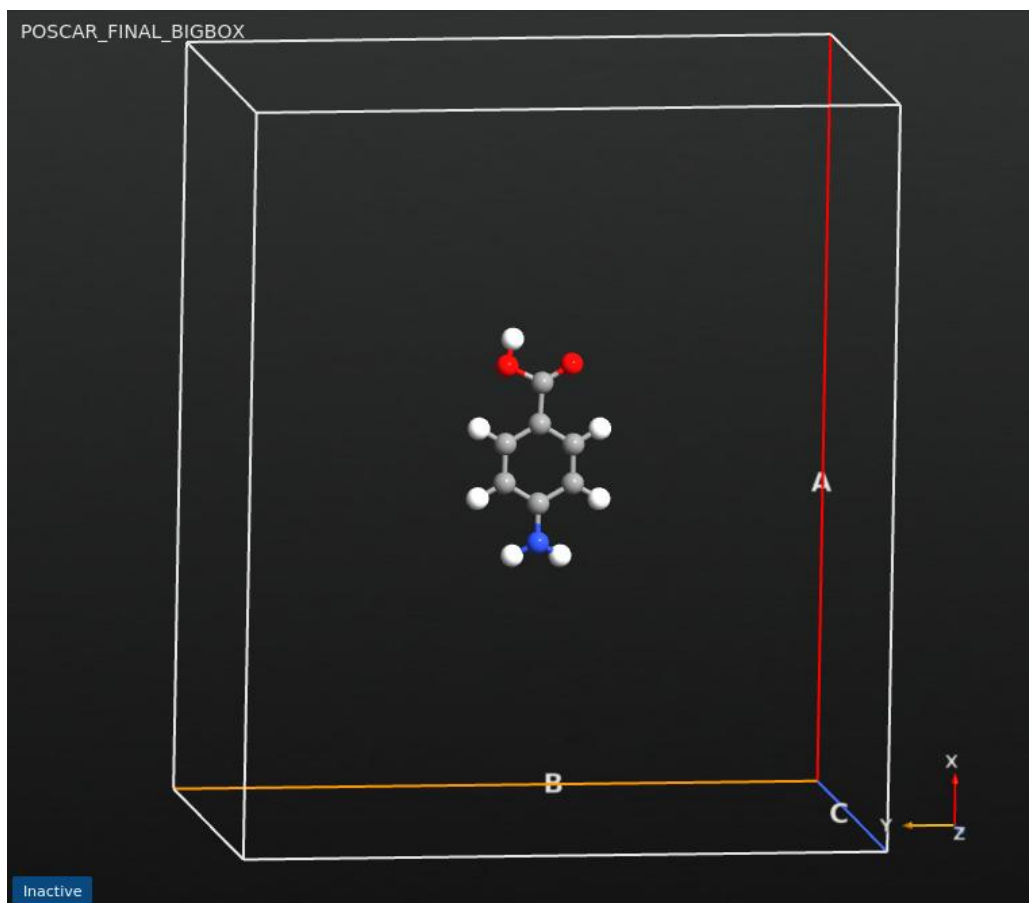


Figure 4. 4-Aminobenzoic (pABA) molecule.

3.2. Collecting data of pABA bound silver NPs system

PABA can be bound in three different ways on the silver surface. It can share a bond with three Ag atoms in a hollow-site, be bound to two in bridge-site or stick to one Ag-atom by binding top-site [11]. To find out which bond have the lowest binding energy, meaning it's the strongest bond, we ran simulations on all three systems. The relaxed pABA molecule was imported and fused with the silver bulk. As with the silver surface the vacuum distance in **C** was set to 13 Å above the pABA to minimize interference. The two hydrogen atoms bound to the nitrogen has to be removed to give space for the Ag-N bond. This will be of importance later as a removal of atoms changes the total free energy and needs to be accounted for. The pABA molecule was placed such that the nitrogen fitted in the three desired geometries, right above an Ag, between two Ag and finally in the middle of three Ag-atoms. The distance above the silver surface (direction **C**) is not as important since the relaxation process will correct this distance as long as the atoms are close enough to form a bond. Once the simulations were finished an unexpected result was observed. All three systems ended up converging into hollow-site bonds. Possible reasons for this will be discussed in the next chapter. Since we're still interested in analyzing all three systems an adaptation had to be done to get relaxed bridge- and top-site systems. To force the nitrogen to stay as said bonds the relaxation freedom had to be restricted in some dimensions to stop them from moving into hollow-site. For the bridge-site bond movement along the **B**-axis was hindered and for top-site both along the **A**- and **B**-axis (*see figure 5. and 6.*). After the relaxation of the three silver-pABA systems their total free energy was collected using VASP.

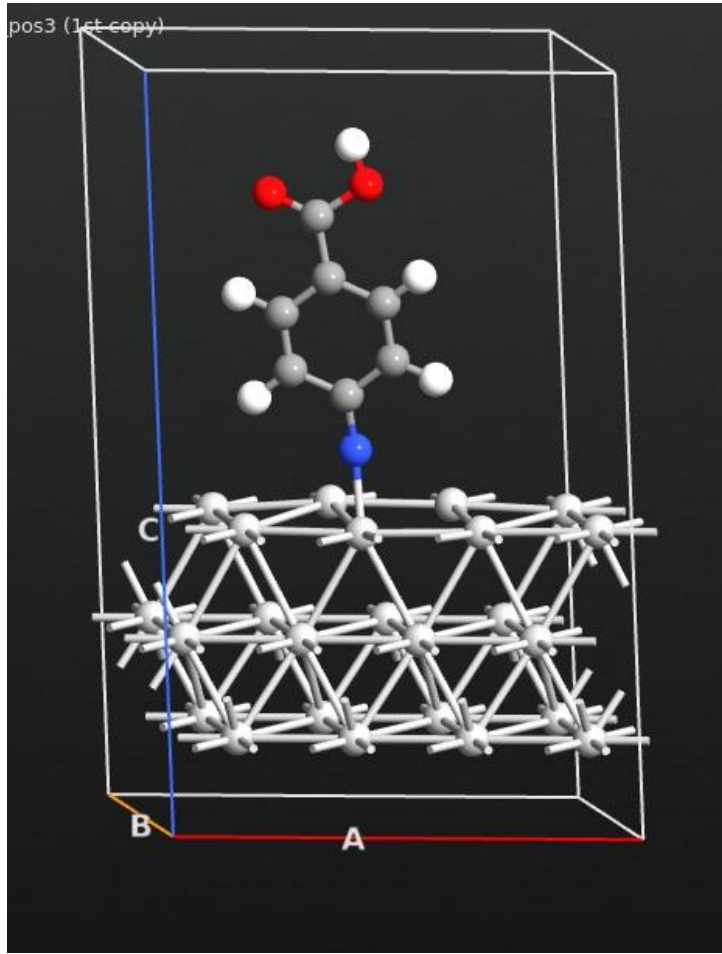


Figure 5. Top-site Ag-pABA system.

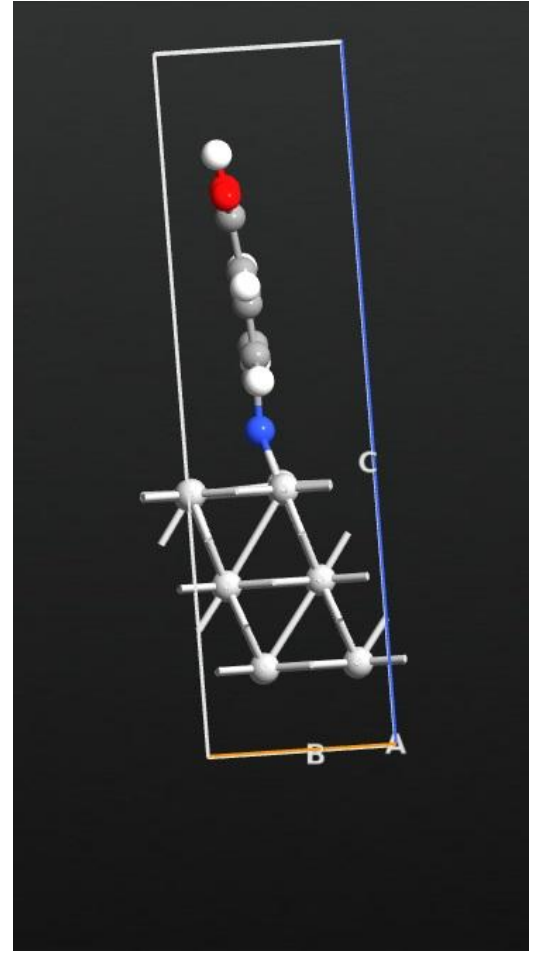


Figure 6. Bridge-site Ag-pABA system.

Since two hydrogen atoms were removed to form an Ag-N bond these H-atoms have to be simulated to be able to balance the total energy equation:

$$E_{Ag} + E_{pABA} \geq E_{Ag+pABA-2H}^{pos} + E_{Ag+2H}^{pos} - E_{Ag}$$

Where $E_{Ag} + E_{pABA}$ is the total free energy of the isolated Ag-surface and the isolated pABA molecule. $E_{Ag+pABA-2H}^{pos}$ is the position dependent total free energy of any of the pABA bound to Ag-surface systems and E_{Ag+2H}^{pos} is the position dependent total free energy of a Ag-surface with two hydrogen atoms bound to it. Because the Ag-pABA systems are position-dependent the hydrogen atoms should also be simulated on an Ag-surface. To avoid double calculating the Ag-surface this should also be subtracted from the Ag-pABA side of the equation.

The density of states (DOS) for the silver and the pABA were extracted with vaspkit [12] that allows the separation of DOS for each element, or even atom if needed. The data was transferred to Excel and imported in MatLab for plotting.

4. Results and discussion

4.1 Total free energy

As mentioned in the method chapter something unexpected happened while running the relaxation scripts on the three silver-pABA structures, they all ended up forming hollow-site bonds. Considering that for a particle in a conservative force field, the force is directed opposite of the field ($\vec{F} = -\vec{\nabla}U$). In other words the forces pushes the system towards energy minimums (see *figure 7*). This gives an early hint of our results and we should expect the hollow-site to have the lowest total free energy. Even if this strongly suggests that the hollow-site is the strongest, it is still interesting to see the difference between the three possible bonds. This led to the forced fixation of the nitrogen atom in the bridge-respectively top-site systems. As the position is fixed in one respective two dimensions we should be aware this may affect the results. With that in mind, let's take a look at the total free energy of the three Ag-pABA systems. The total energy of the relaxed isolated Ag-surface, pABA molecule and the H₂ systems are also shown in the tables below.

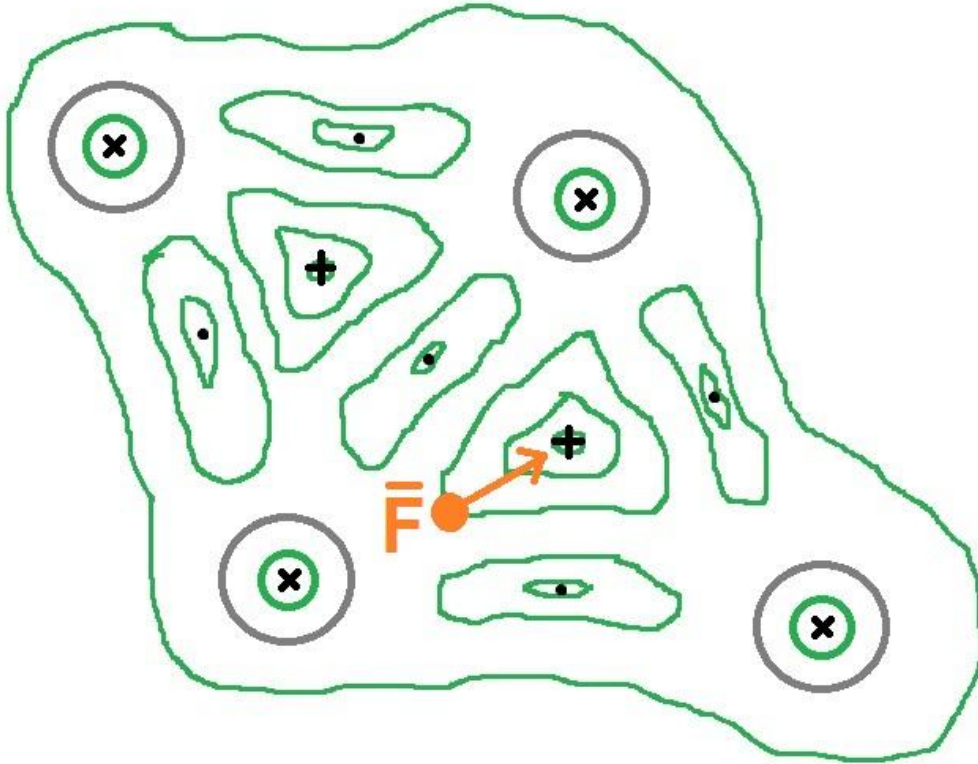


Figure 7. Schematic picture of potential field on Ag-surface. Gray represents Ag atoms, the black plus is hollow-site, x is bridge-site and dots are top-site positions. Green areas represents different field strengths. Forces acting on atoms in the system pushes them towards local energy minimums.

Ag-pABA structure	Total free energy [eV]
E_{Ag+2H}^{pos1} - Hollow-site	-161.3343
E_{Ag+2H}^{pos2} - Bridge-site	-161.0822
E_{Ag+2H}^{pos3} - Top-site	-160.0439

Table 1. The total free energy of simulated Ag-pABA structures.

Individual structure systems	Total free energy [eV]
E_{Ag} - Silver surface	-60.0219
E_{pABA} - pABA	-111.3389
$E_{Ag+2H}^{pos} - E_{Ag}$ - Hydrogen (2H)	-6.4331

Table 2. The total free energy of simulated isolated structures.

With the input parameter EDIFF=1-E4, the precision can be expected to be around 10^{-4} eV for the total free energies [13]. Calculations using GGAs are often accurate for total energy related properties [3] and all these calculations have used the same input-parameters. This consistency combines with the selected vacuum boxes where the height was kept above 13 Å from the repeating Ag-surface should grant a reliable accuracy.

For the Ag-pABA systems we can see in *table 1*. that hollow-site has the lowest total free energy. This means that it has the highest binding energy and is therefore the strongest of the three possible bonds. A lower total free energy also means that this is the bond that is most likely to form. To calculate each bonds binding energy the following inequality was going to be used.

$$E_{Ag} + E_{pABA} \geq E_{Ag+pABA-2H}^{pos} + E_{Ag+2H}^{pos} - E_{Ag} \quad (1)$$

The binding energy could then be found by observing the energy difference of said inequality.

$$E_{Ag} + E_{pABA} = E_{Ag+pABA-2H}^{pos} + E_{Ag+2H}^{pos} - E_{Ag} + E_{Binding}^{pos} \quad (2)$$

Unfortunately for unknown reasons equation (1) did not balance properly. The left-hand side of the equation was found lower than the right-hand side for all three bonds. Hence the binding energy could not be calculated. A number of possible reasons could be behind this. In the simulations the vacuum box was only about 2 Ag atoms wide in the thinnest dimension. This is because adding for example two additional layers would mean another 24 Ag atoms, which would add a whole lot of time to the relaxation process. I did not have that time and as a result the pABA molecule could had been close enough to the vacuum walls to interact with itself. It's not trivial what this effect would do, but it may well be an explanation as the isolated pABA was simulated in a much bigger vacuum box. Another possible explanation could be that using 1x1x1 for the KPOINTS on the isolated pABA molecule effects the total free energy of the system. An effort was made to examine how 9x9x9 KPOINTS would affect the total free energy, but though the it did change slightly, it was still low enough for the problem to remain.

4.2 Density of states

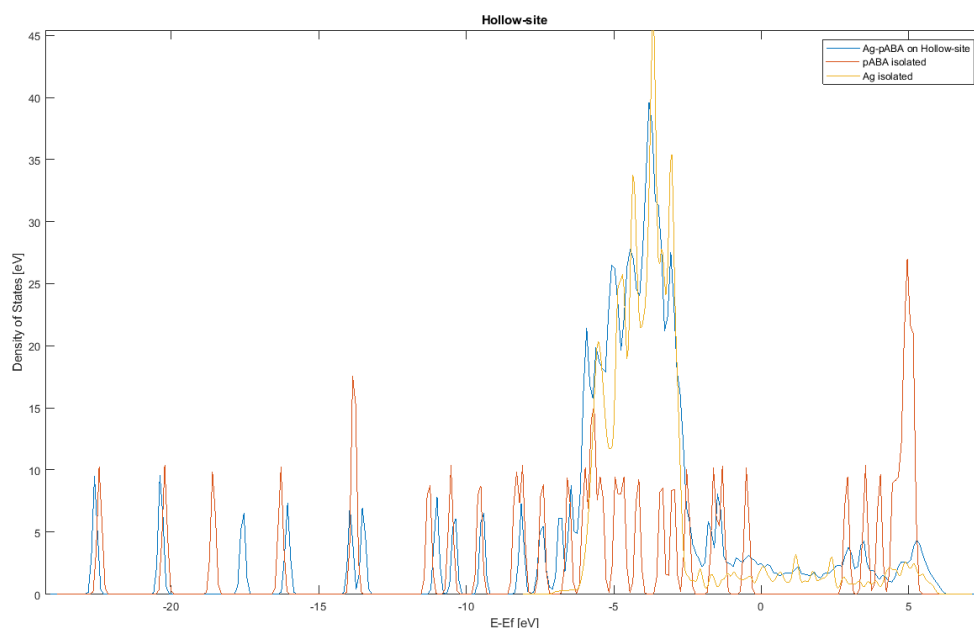


Figure 8. DOS of Hollow-site bound Ag-pABA (blue), isolated pABA (red) and Ag-surface layer (yellow). The isolated pABA gives as expected from a molecule a number of discrete peaks, while the Ag surface shows an continuous number of states through its interval.

With all the systems simulated through this study, a lot of data can be extracted. VASP allows the user to extract data of the density of states down to singular atoms or even electron shells in systems. To make the results as understandable and visible as possible only a few plots have been chosen to be included. The focus will be of the band gaps and around the Fermi level (marked as 0 eV in plots below) since these have the highest relevance for hot-electron transfer. We will see how the interaction between pABA and silver surface affects the available states and the band gap. While looking at the density of states of Ag only the top layer of the silver surface was included. This is because this is the location where the charge transfer will take place. Removing the lower layers from the plots will make changes easier to spot without removing vital information. While GGAs are very accurate in terms of total free energy calculations they tend to strongly underestimate the band gap of molecules [3]. This should be kept in mind when going into the results that follows. In the figures below, the density of states are displayed for isolated pABA and each studied bond of pABA on the silver surface. Only the DOS of the pABA molecule are shown in *figure 9-12*, meaning the states of Ag have been removed.

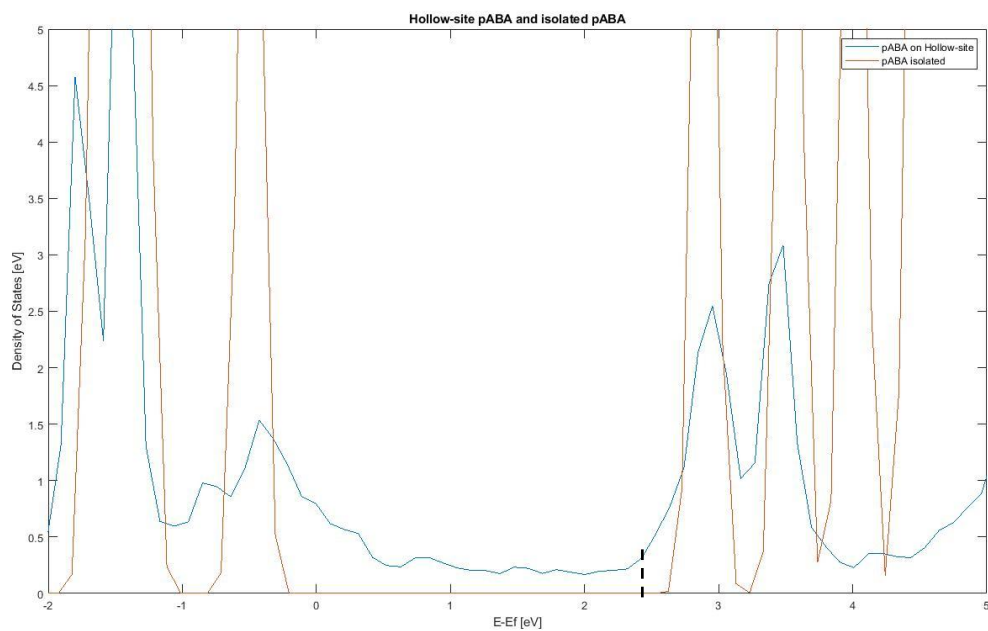


Figure 9. Comparison of DOS of pABA bound hollow-site (blue) on Ag and isolated pABA (red). The DOS of the Ag is not included. The dotted line marks where the conduction band is assumed to start.

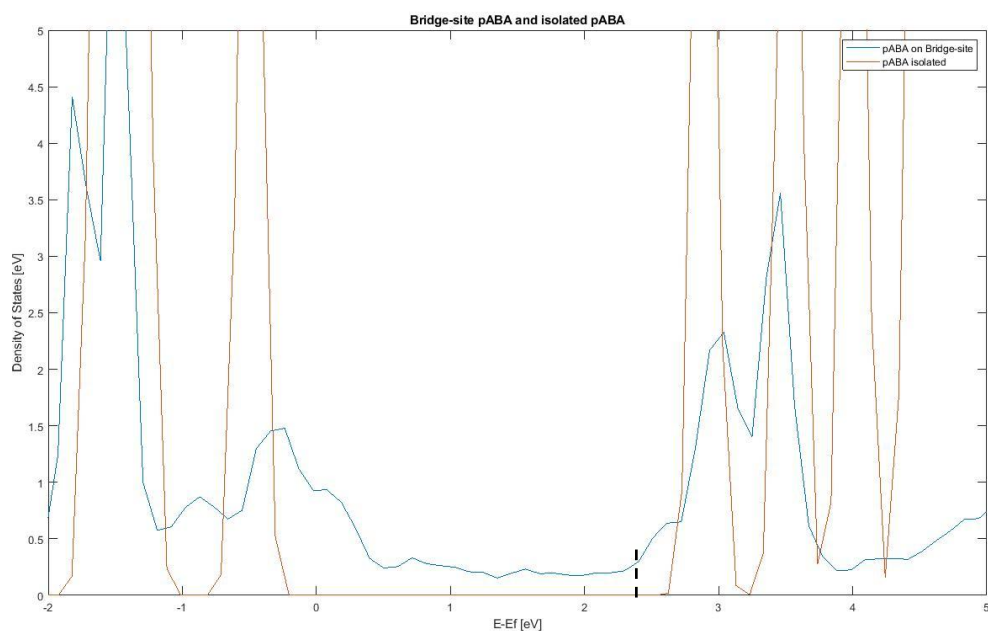


Figure 10. Comparison of DOS of pABA bound bridge-site (blue) on Ag and isolated pABA (red). The DOS of the Ag is not included. The dotted line marks where the conduction band is assumed to start.

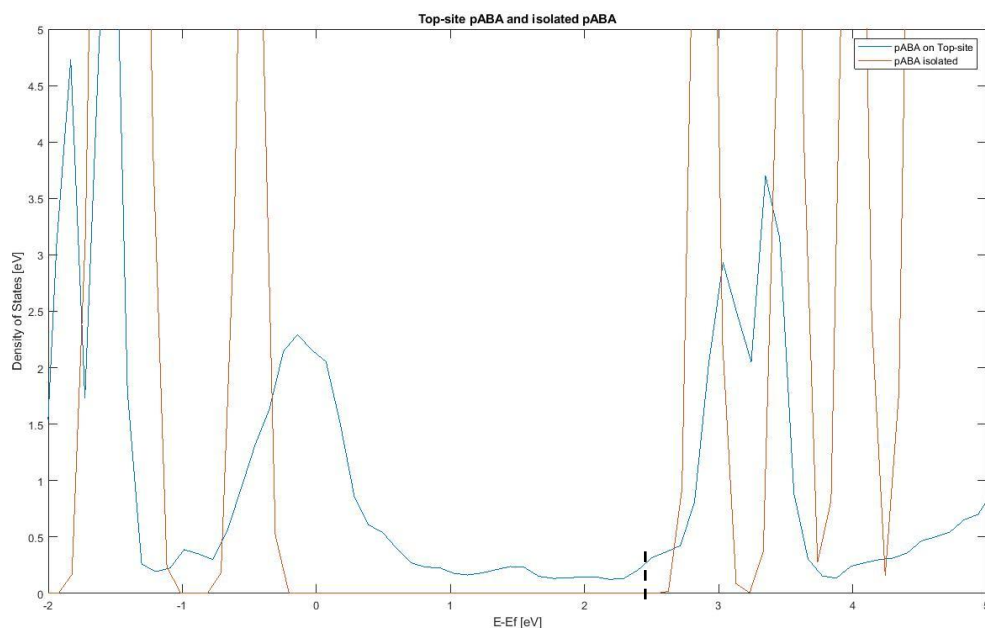


Figure 11. Comparison of DOS of pABA bound top-site (blue) on Ag and isolated pABA (red). The DOS of the Ag is not included. The dotted line marks where the conduction band is assumed to start.

Here we see the density of states for unbound pABA and the three different bound pABA on the silver surface. For the isolated pABA we see the band gap very clearly and measure it to about 2.8 eV. In another study this band gap got measured to be 3.4 eV [14] which is more probable given that our method generally displays band gaps smaller than they actually are. Even if the value of the band gaps in this study can't be accurately measured, we should still be able to compare these to find the better candidate. As can be seen in *figures 9-11* a thinner bridge connects the two peaks of the valence and conduction band of the bound pABAs. This is unexpected for the molecules as we should expect a clean band gap for the bound pABA as well. The explanation is probably that the wave functions from the silver interact with the closest atoms of the pABA which results in showing some of the silver's DOS even when we have removed these atoms from the plots. To further increase the credibility of this we plot the DOS of the closest atom to the Ag-surface (the nitrogen atom) separately in *figure 12* below. There we can see that about 50% of the states of the bridge is from the nitrogen atom close to the Ag-surface. If these states were to really be located on the pABA atom, it would intensify the undesired recombination pathway, which it has been shown not to do [3]. Thereby it would not increase the photocatalytic hydrogen production generated by the system, which it has also been shown to do [5]. The future of the analysis will therefore be on the conditioning that this bridge is falsely represented.

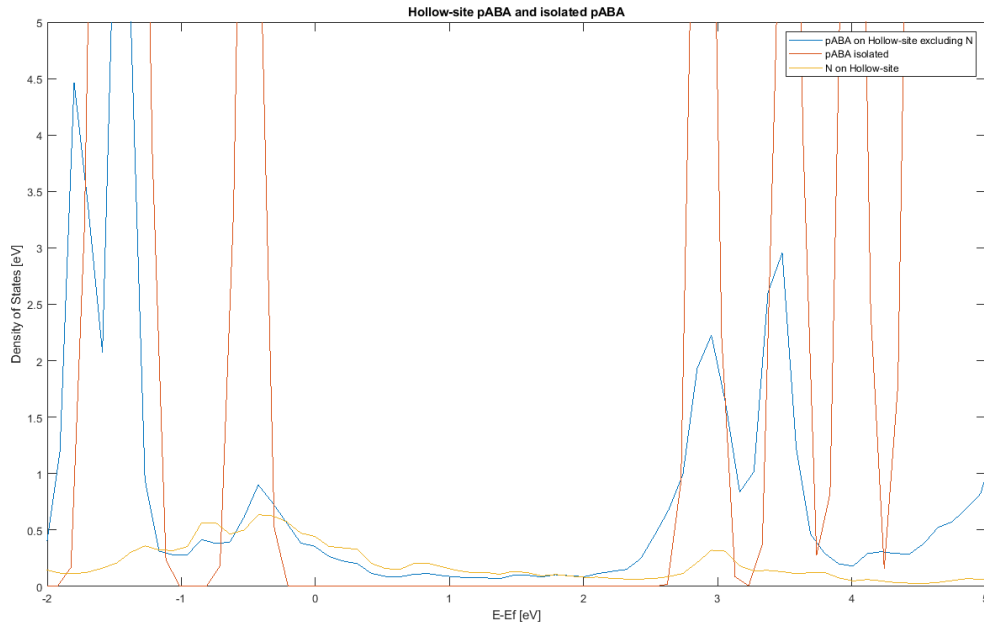


Figure 12. DOS of isolated pABA (red) and pABA bound hollow-site (blue) on Ag excluding the nitrogen shown separately (yellow).

Above the Fermi level two bigger hole clusters can be seen. For the bound pABA the band gap have been reduced in all the three structures. The band gap is slightly moved towards higher energy from hollow-site to bridge-site and again from bridge-site to top-site. This have the consequence of increasing the required energy for the charge to transfer to the higher energy states. The states are naturally occupied up to the Fermi level so when the closest unoccupied states in the conduction band are higher, more energy is needed for the electrons to transfer. The energy from the Fermi level to the conduction band was measured to be about 2.4 eV for the hollow- and bridge-site and 2.5 eV for the top-site bond. The points these values was measured to is marked as a dotted line in *figure 9-11* for reference. Because of the disturbance of the Ag-surface it is not easy to get an exact value, therefore these band gap values should be considered as comparisons towards each other and not the true value of the band gaps of the structures. The electron excitations of Ag through the plasmon resonance can occur between 0 and 3.2 eV above Fermi level [3]. Even if our measured band gaps are displayed as thinner than in reality, they should still be inside this range. The isolated pABA in the other study [14] was shown to be 21% larger than the measured value in this study. If we assume the displayed band gaps are consistently underrepresented our hollow-site band gap would correspond to about 2.8 eV.

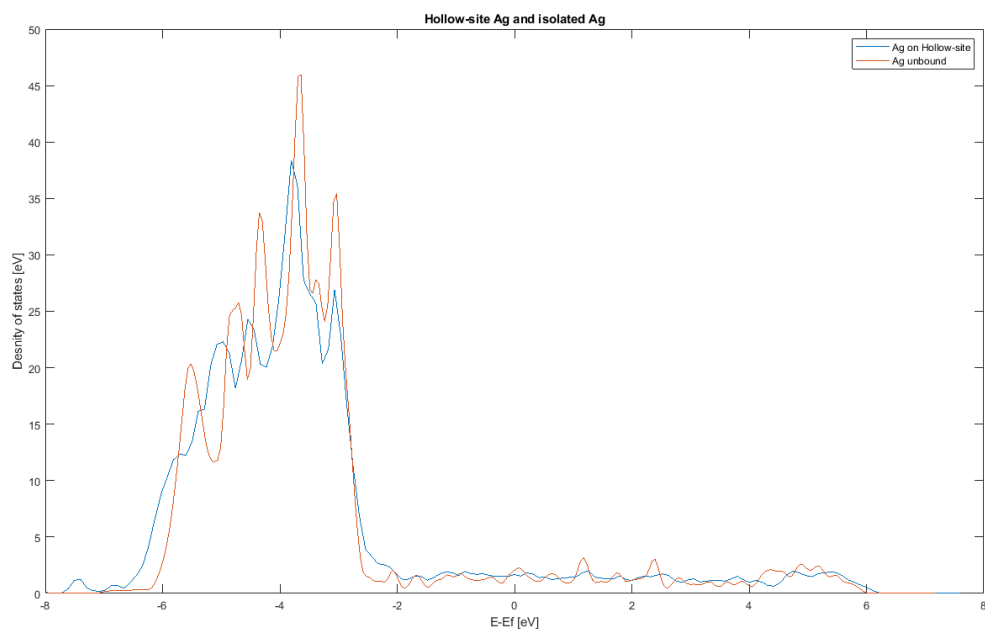


Figure 12. DOS of top layer of Ag bound hollow-site (blue) and isolated top layer of unbound Ag (red). No vital changes can be observed in the DOS of the Ag layer when bound to pABA comparing to the isolated Ag.

5. Recommendation (Outlook)

It was earlier mentioned that GGAs tended to underestimate band gaps of molecules. This study is good for comparison but for more exact calculations of the band gaps further works is needed using a more accurate method for band gap measurements. For the process of calculating the binding energies could be improved by simulating a larger part of the Ag-surface to increase the vacuum boundaries and therefore reducing the pABAs possible self interaction. A next step could also be to further analyze the interaction between Ag NPs, pABA and the titanium oxide semi-conductor. For the interaction between pABA and TiO_2 I advise looking at study [14], still a study observing the three simultaneously could be of interest. One can take a spectroscopy as done in previous named study to check if the optical band gap differs from the simulated results. This would enable further analysis of how Ag-bound pABA effects its band gap. It would also contribute by the ability to compare simulated results to that of reality, which may prove very useful.

6. Conclusions

Three structures of pABA bound to an Ag-surface, hollow- bridge- and top-site was simulated and analyzed using the computer programs VASP and Quantum ATK. By calculating the total free energy of the systems it was shown that the hollow-site was the strongest out of the three bonds. The exact binding energy could not be found. The band gaps of these three structures was also analyzed to compare the pABA linker molecules properties as a charge transfer. The method used was not able to accurately measure exact sizes for these band gaps, but a comparison could still be made between the three. The results shown that the hollow-site had the thinnest band gap and therefore requires the least excitation energy to transfer charge. Further studies needs to be done to further analyze said band gaps.

References

- [1] Hammes-Schiffer S. Theory of Proton-Coupled Electron Transfer in Energy Conversion Processes. *Acc. Chem. Res.* 2009;42(12):1881-9
- [2] Ashcroft NW, Mermin DN. *Solid states physics*. Tokyo: Holt-Saunders, cop; 1976
- [3] Hattori Y, Abdellah M, Rocha I, Pavluik MV, Fernandes DL, Sá J. Light-induced ultra fast proton-coupled electron transfer responsible for H₂ evolution on silver plasmonics. *Materials Today*. 2018;21(6):591
- [4] Devi LG, Reddy KM. Photocatalytic Performance of Silver TiO₂: Role of Electronic Energy Levels. *Applied Surface Science*. 2011;257(15):6821-6828
- [5] Pavliuk MV, Fernandes AB, Abdellah M, Fernandes DL, Machado CO, Rocha I, et al. Nano-hybrid plasmonic photocatalyst for hydrogen production at 20%. *Scientific reports*. 2017;7(8670):1
- [6] Sukegawa J, Schubert C, Zhu X, Tsuji H, Guldi DM, Nakamura E. Electron transfer through rigid organic molecular wires enhanced by electronic and electron-vibration coupling. *Nat. Chem.* 2014; 6(10): 899-905
- [7] Kittel C. *Introduction to Solid State Physics*. 8 Edition. New Caledonia: John Wiley & Sons, Inc; 2005
- [8] Kresse G, Hafner J. VASP, ver. 5.4.4. [computer program]. *Phys. Rev. B* 47, 558;1993. [cited 2019 May 24] Available from <https://www.vasp.at/>
- [9] Banerjee A. *Materials Modelling for Energy Harvesting*. Uppsala: Acta Universitatis Upsaliensis; 2019
- [10] The VASP Manual [Internet]. Boston: GNU Free Documentation License; [revised on 2019 Mar 7; cited 2019 May 13]. Available from https://cms.mpi.univie.ac.at/vasp/vasp/ENCUT_tag.html
- [11] Wu DY, Liu XM, Huang YF, Ren B, Xu X, Tian ZQ. Surface Catalytic Coupling Reaction of p-Mercaptoaniline Linking to Silver Nanostructures Responsible for Abnormal SERS Enhancement: DFT Study. *J. Phys. Chem.* 2009;113(42):18212-22
- [12] Wand V, Xu N. VASPKIT: A Pre- and Post-Processing Program for the VASP Code. [cited 2019 May 24] Available from <http://vaspkit.sourceforge.net>
- [13] The VASP Manual [Internet]. Boston: GNU Free Documentation License; [revised on 2019 Mar 7; cited 2019 May 20]
- [14] Thomas AG, Jackman MJ, Wagstaffe M, Radtke H, Syres K, Adell J, et al. Adsorption of p-Aminobenzoic Acid on the Anatase TiO₂(101) Surface. *Langmuir*. 2014; 30(41): 12306-14