Project A20
FYS-MENA4111

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Abstract

Quinizarin can function as an organic sensetizer in an upconversion system. In ALD the organic molecule can possibly be deposited in a matrix of lanthanide flouride, to increase the efficiency of the upconversion process in the material. To see how this efficiency can increase and what energy levels can be absorbed by the material, it is wise to investigate the electronic band structure of the molecule. This paper will look in to Quinizarin's own electronic properties, as well as, Quinizarin with lanthanides replacing one a Hydrogen atom, to emulate Quinizarin inside the structure in a simple way.

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Ting å ha i LaTeX:

- abstrakt

  done

- kort introduksjon av materialet

  done

- kort om metode, valg av paramtere (CUTOFF, etc)

  done

- presentasjon av de viktigste resultatene

  done

- diskusjon av hvordan resultatene kan tolkes, f.eks. sammenligne til eksperimenter eller tidligere beregninger i litteraturen

  WIP

- konklusjon/oppsummering
- kilder
- appendix ?

OBS: husk å lagre bilder for rapporten og presentasjonen mens man gjør beregningene

1 Introduction

Photons can be used for many things. However, not all photons are created equal. They come in many different energies, and not all energies are as simple to absorb. A way to increase the efficiency of photon-absorbing materials is by modifying it so that it can absorb photons with a low energy, collect that energy, and re-emit the photon with higher energy. This is known as up-conversion and has many uses. One use is to increase the efficiency of solar panels by allowing it to collect more of the sunlight, where the up-conversion system can be a thin-film on the top of the panel. A different use is to increase the energy to the point where the emitted photon can become ionizing and work as a bacteria or virus killer.

Up-conversion is a phenomenon where incoming photons are re-emitted with a higher energy than they entered with. The photons excite electrons in a material, and by conduction of those electrons they can move to other atoms, where they are further excited. The electron ends up in a high energy state and de-excites releasing all the energy. However, the process can be very inefficient due to narrow energy bands in the material. A form of increasing this efficiency is by adding a material with a wide energy band to allow absorption of photons with more varied energy.

This paper will focus on an organic compound known as Quinizarin. The compound is an organic dye and has a broad energy band. This means it can absorb a broad spectrum of photons energies. The excited electrons from this energy band can move to the actual up-conversion system and hereby increase the efficiency of the up-conversion. The planned up-conversion system will consist of Quinizarin as an organic sensitizer, Nd+3 and Yb+3 as electron migrators (transporting the electrons to the site of de-excitation), and Tm+3

as accumulator and activator (collecting excited electrons and up-converting them, and de-excitation site for said electrons). The system is planned to be inserted into a matrix of YbF3 or possibly YF3.

Since Quinizarin is such an important piece of the system it is wise to know how it interacts with the other materials. This study will therefore investigate how Quinizarin's electronic band structure changes when the Hydrogen in the alcohol group is replaced with different atoms. In this case: Yb, Nd, Tm and Y. See figure (1 for an illustration).

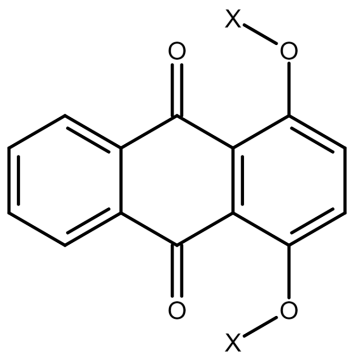

Figure 1: Molecular structure of Quinizarin with H in -OH replaced with atom X. X can be H, Y, Yb, Nd or Tm. Structure drawn with online illustrator from Chem-Space.

2 Method

The supercomputer Saga contains many different POSCAR-files for a wide range of structures. Unfortunately for us, Quinizarin was not included. Therefore we had to make our own POSCAR-file. This was done by drawing the structure in an organic compound structure program we found on the internet: MolView. This site lets the user draw organic structures with many varying features, and it also lets the user export the data as a `.mol`-file. A `.mol`-file has a similar structure with a POSCAR-file, which let us easily make the POSCAR-file for Quinizarin.

The coordinates of the atoms in the `.mol`-file were put in a POSCAR file with Direct coordinates. We added a unit cell and, and opened it in VESTA. In order to make the plane-waves more stable for the calculations, we inserted a vacuum distance in each direction of 12 Å.

To differentiate the two Hydrogen-atoms in the alcohol-groups from the other Hydrogen-atoms, we had to find their positions somehow. This was done in the program GeoGebra, by plotting each atom with their positions in 3D. We found that the Hydrogen-atoms were number 25 and 26 in POSCAR. In hindsight, we discovered that this would be easier to do in VESTA.

In this project we will compare the basic Quinizarin with Quinizarin with both Yttrium (Y) and Ytterbium (Yb) substituted in the Hydrogen-positions described in the subsection above. Therefore we had to make in total three POSCAR-files for the three structures. This was done by opening POSCAR in Emacs and changing the two last atoms given in the file to the substitution-atoms. After that we ran in to issues with relaxing the structure, and so went to the ICSD database to find a decent distance between the new atoms and oxygen. We used approximately 2.3 Å in distance, and that worked well for relaxing the structure.

2.1 Convergence

Testing for convergence of energy and k-point is important to determine if the variables in INCAR or KPOINTS are good enough to be used for further calculations, mostly to ensure decent and applicable results. If the error is less than $1 \cdot 10^{-3}$ the calculation can be considered converged.

The testing of convergence is done by performing VASP calculations with different values of either energy-cutoff (ENCUT) or k-point density. For this project the energy convergence testing was done for ENCUT between 300 and 900 eV, with 50 eV steps. The k-point convergence testing was done for k-point density between 1.0 and 6.0, with 1.0 difference. For the aforementioned test the value for ENCUT was decided from the energy convergence test.

2.2 Relax

A relaxing calculation is performed to minimize the max force of the material. This is done by moving the atoms to find the optimal atom positions for the structure.

We performed the relaxation calculation once for each structure.

2.3 Static

A static calculation is a calculation in which atoms are held at their original positions. These are often used for obtaining a converged energy, as calculations that relax the structure are less safe to use for this.

In this project we have performed static calculations both before and after performing ionic relaxation. The static calculations that were performed before relaxation were to see how the energies changed between before and after relaxation.

2.4 DOS

A plot of density of states shows the at what levels the energy bands, or orbitals, exists and how broad they are. A band with a high density of states allows for more electrons to occupy it, whereas a band with a low density of states allows for fewer. The density of states is generally plotted against the energy, and peaks in the plot show how many electrons are allowed to exist at a specific energy. An energy gap is shown by two peaks separated by a void. The size of the void (span in energy) is the height of the energy gap.

For obtaining a plot of density of states we ran the script dosplot.py for the values generated by the post-relaxation static calculations. This ensured that the values were converged and safe to use. dosplot.py reads the DOSCAR-file and plots the values in an easy-to-read format.

2.5 Bang gap

The density of states plots show where the band gap is located, but it does not give the numerical value. VASP has the command `bandgap` specifically for this, hence we used this to find the numerical value of the band gap for the structures.

2.6 Charge density

The charge density of a structure shows how the charge is distributed around the atoms in that structure. A plot of the charge density therefore shows how many electrons the different atoms attract. To plot the

charge density the file CHGCAR, after a completed VASP calculation, is copied over to VESTA, and then visualized.

3 Results

3.1 Convergence of energy

The energy convergence tests were run as described in Section 2.1. After the runs were completed we looked at vaspout from each of the runs. The total energy per atom, or TOTEN/atom, was plotted against the cutoff energy and this is shown in Figure (2).

Figure (3) shows the difference in energy from one value to the next. This means, the value of ENCUT=300 is the difference in total energy going a cutoff energy of 300 eV to 350 eV.

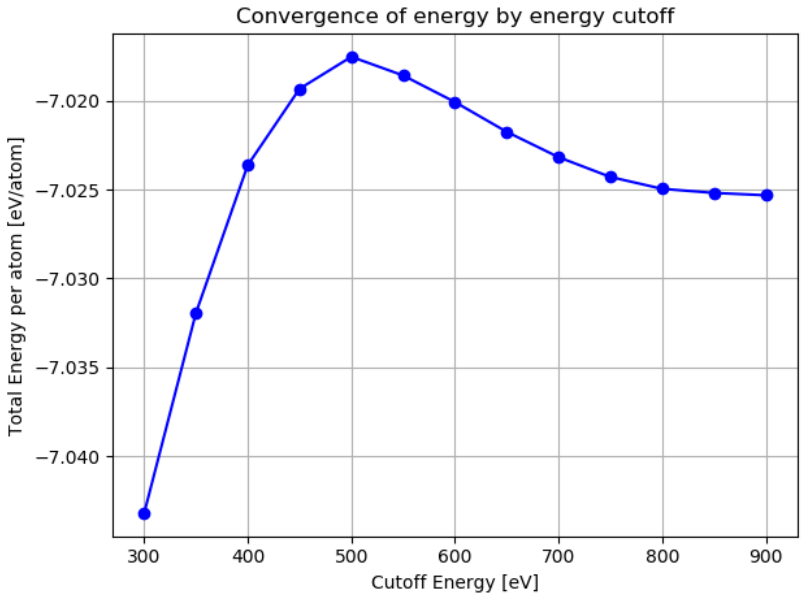

Figure 2: Plot of energy convergence for Quinizarin, with ENCUT ranging from 300 eV to 900 eV.

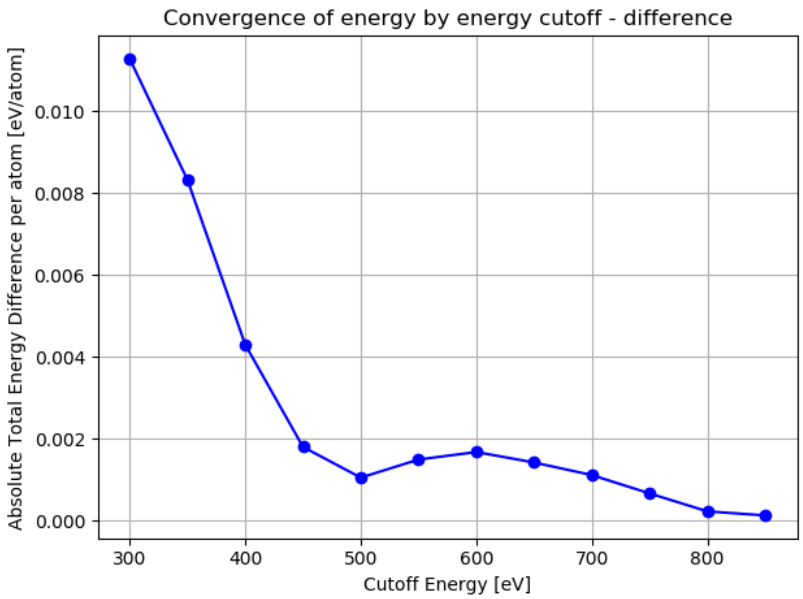

Figure 3: Plot of the difference in energy convergence for Quinizarin, given by ENCUT.

3.2 Convergence of k-points

For the convergence of k-points the span of values were used as described in Section 2.1. Figure (4) shows how the total energy changes as k-density increases. Like with energy, the difference has also been plotted, and this is shown in Figure (5).

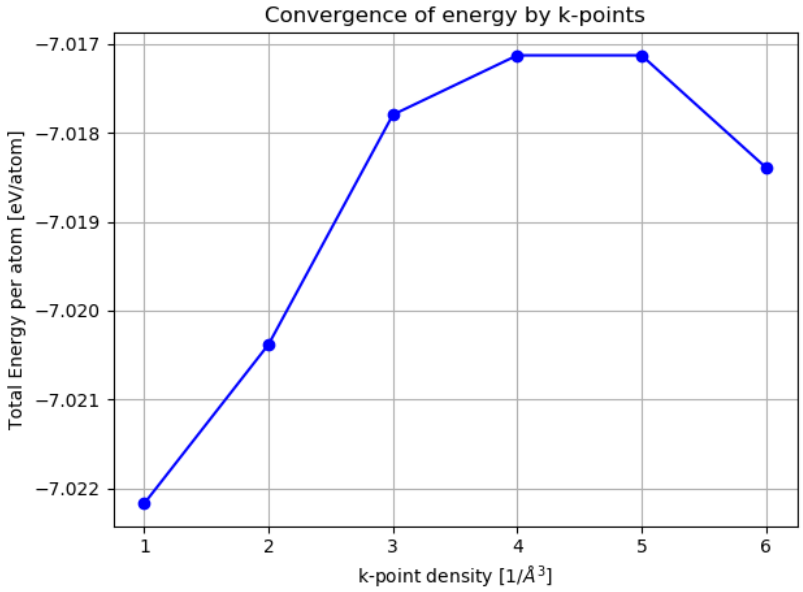

Figure 4: Plot of energy convergence for Quinizarin, with k-point density ranging from 1 to 6.

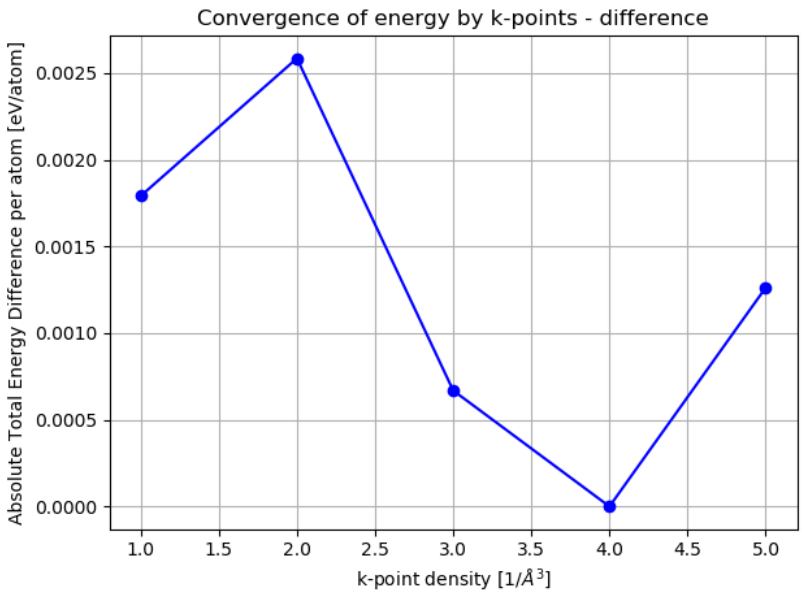

Figure 5: Plot of the difference in energy convergence for Quinizarin, given by k-point density.

3.3 Quinizarin

3.3.1 Relaxing the structure

The initial static calculation of Quinizarin gave a CONTCAR as shown in Figure (6).

After relaxing the structure and performing a new static calculation, CONTCAR looked as shown in Figure (7). We do not show CONTCAR from the actual ionic relaxation as it is identical to the post-relaxation static calculation.

Table (1) shows how the distance between Hydrogen and Oxygen changes from before and after relax.

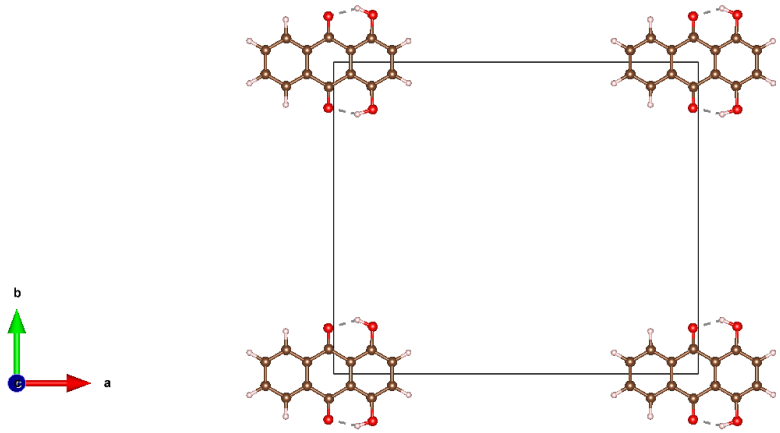

Figure 6: Structure of Quinizarin for static VASP calculation.

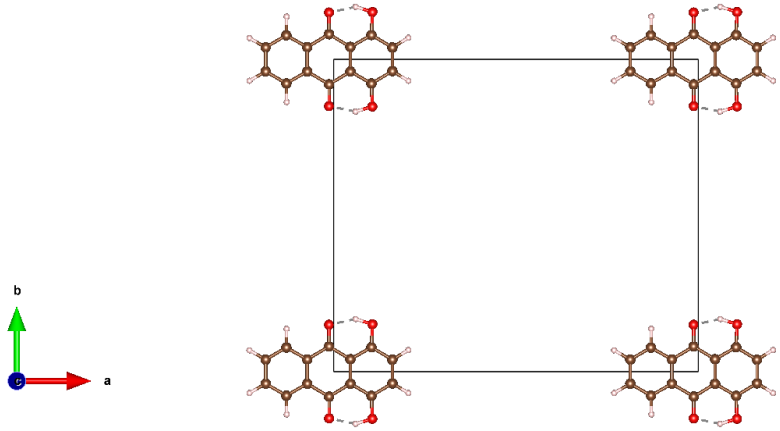

Figure 7: Structure of Quinizarin for static VASP calculation after relaxed calculation.

Table 1: Hydrogen-Oxygen distances. 2x-bonded Oxygen is the central Oxygen atom, which is has a double bond to carbon. 1x-bonded Oxygen is part of the alcohol-group. The values marked with * were not located in OUTCAR, and so were fetched from VESTA.

Calculation	Distance to 2x-bonded Oxygen [Å]	Distance to 1x-bonded Oxygen [Å]
Before relax lower Hydrogen	1.73*	0.93
Before relax upper Hydrogen	1.76*	0.97
After relax lower Hydrogen	1.57*	1.03
After relax upper Hydrogen	1.59*	1.02

3.3.2 Total and relative energies

As can be seen in Table (2), there was a difference in total energies. This turned out to be -0.015 eV in relative energy difference. The data is taken from static calculations of Quinizarin, before and after a relax VASP calculation.

Table 2: Total energy per atom for Quinizarin with static calculations.

Calculation	Total energy per atom [eV/atom]
Before relax	-7.019
After relax	-7.034

3.3.3 Total and local density of states

In Figure (8) we can see the total density of states of the Quinizarin molecule. Figure (9) shows the local density of states for the Hydrogen atom in the lower alcohol group, whereas Figure (10) shows the local density of states for the Hydrogen atom in the upper alcohol group. It is important to note that these figures are zoomed in around the Fermi-level. To see the full pictures, see Figure (32), Figure (33) and Figure (34) in Appendix.

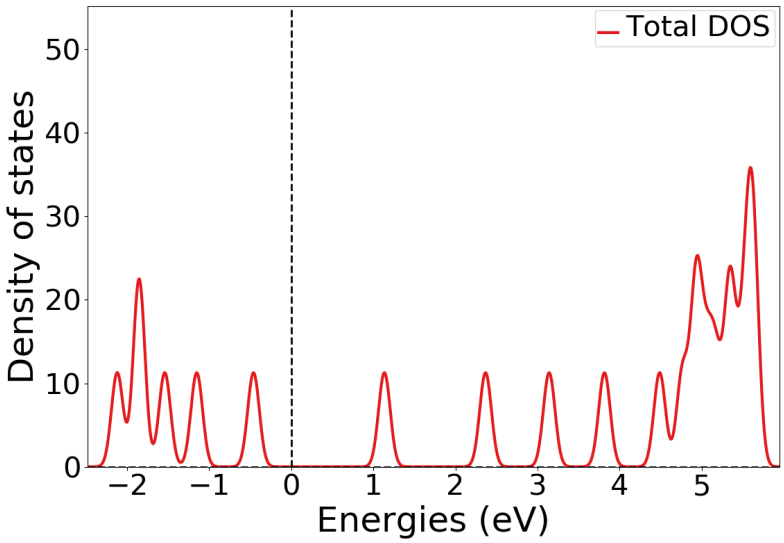

Figure 8: Plot of total DOS for Quinizarin, zoomed in for energies around the fermi level (set to 0 eV).

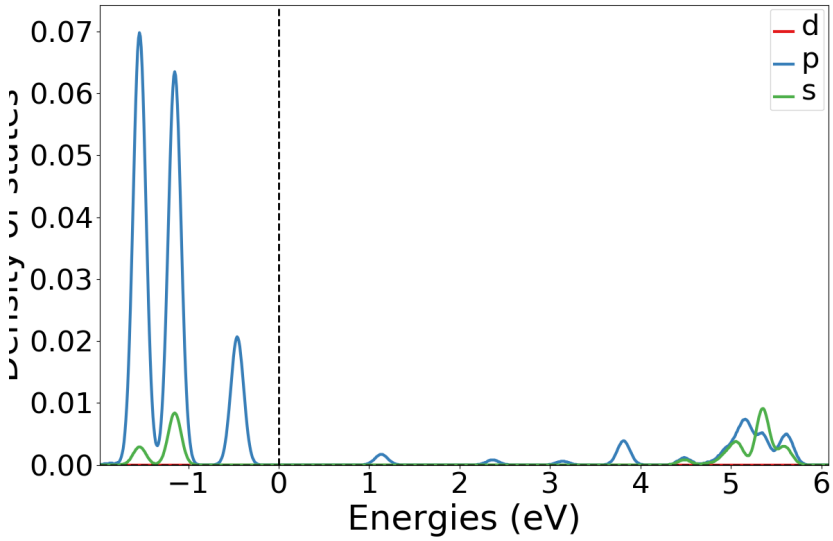

Figure 9: Plot of local DOS for atom number 25(H in alcohol-group) for Quinizarin, zoomed in for energies around the fermi level (set to 0 eV).

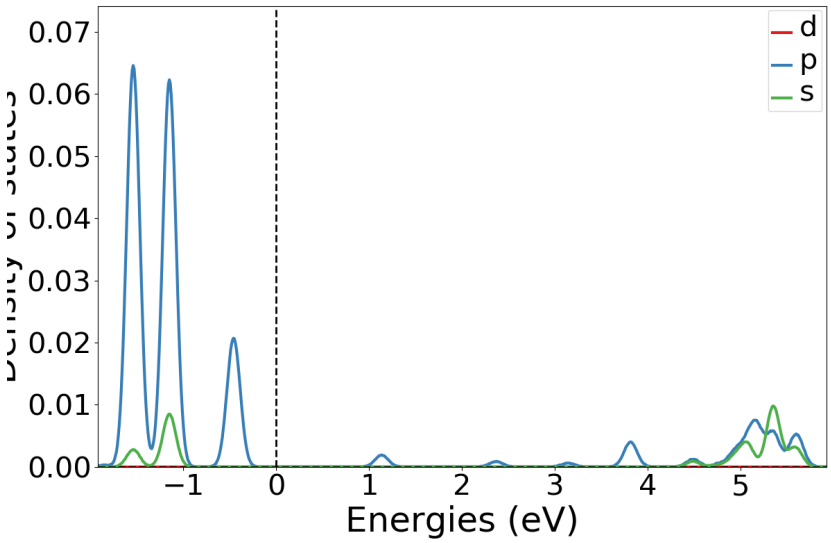

Figure 10: Plot of local DOS for atom number 26(H in alcohol-group) for Quinizarin, zoomed in for energies around the fermi level (set to 0 eV).

3.3.4 Band gap

Table (3) below shows the band gap, the valance band maximum (VBM), and the conduction band minimum (CBM) for Quinizarin, before and after a relax calculation, using static calculations.

Table 3: Band gap, valance band maximum and conduction band minimum for Quinizarin with static calculations.

Calculation	Band gap [eV]	VBM [eV]	CBM [eV]
Before relax	1.773	−5.335	−3.562
After relax	1.594	−5.313	−3.720

3.3.5 Charge density

The charge density before relaxation is shown in Figure (11). The charge density for the static calculation after relaxation can be shown in Figure (12). Figure (13) shows the charge density of a single molecule after having relaxed the structure.

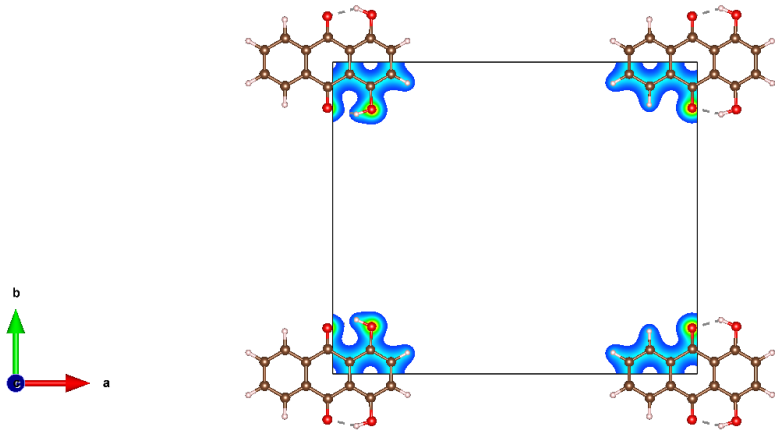

Figure 11: Charge density of Quinizarin for static VASP calculation.

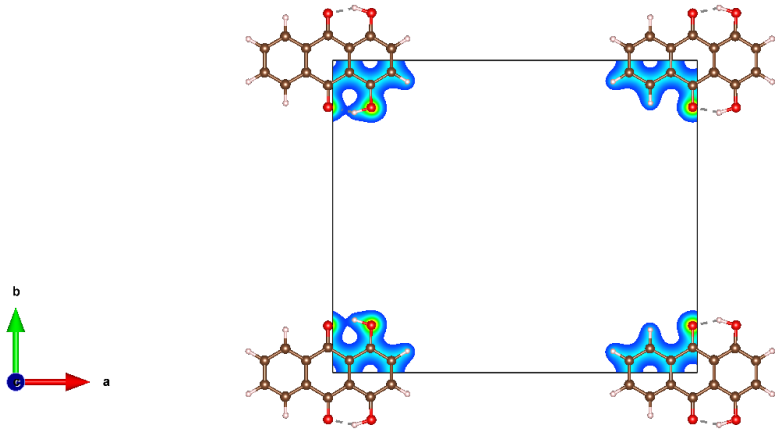

Figure 12: Charge density of Quinizarin for static VASP calculation after relaxed calculation.

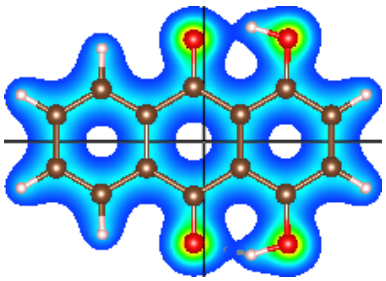

Figure 13: Charge density of a single Quinizarin molecule for static VASP calculation after relaxed calculation.

3.4 Quinizarin with Yttrium

3.4.1 Relaxing the structure

Below we can see the structure of Quinizarin with Yttrium. Figure (14) shows it as it is before relaxing the structure, and Figure (15) shows the structure after having been relaxed.

In Table (4) we can see Yttrium's distance to oxygen, both before and after relaxing the structures.

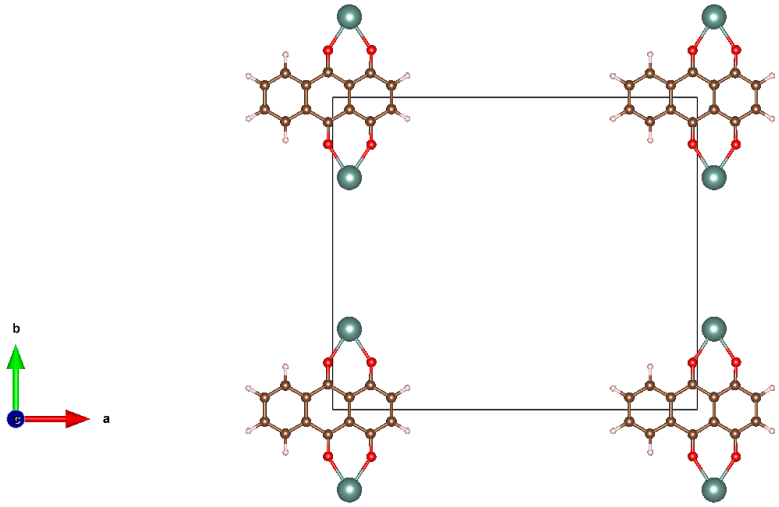

Figure 14: Structure of Quinizarin with Yttrium for static VASP calculation.

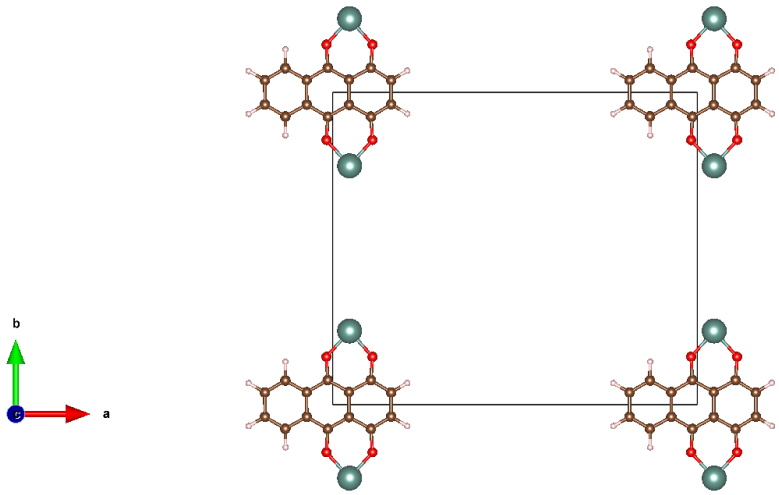

Figure 15: Structure of Quinizarin with Yttrium for static VASP calculation after relaxed calculation.

Table 4: Yttrium-Oxygen distances. 2x-bonded Oxygen is the central Oxygen atom, which is has a double bond to carbon. 1x-bonded Oxygen is part of the alcohol-group.

Calculation	Distance to 2x-bonded Oxygen [Å]	Distance to 1x-bonded Oxygen [Å]
Before relax lower Yttrium	2.32	2.31
Before relax upper Yttrium	2.32	2.32
After relax lower Yttrium	2.02	2.01
After relax upper Yttrium	2.02	2.01

3.4.2 Total and relative energies

Table (5) shows the total energy per atom for Quinizarin with Yttrium, with calculations done by static calculations before and after a relax calculation. The relative energy was -0.109 eV/atom.

Table 5: Total energy per atom for Quinizarin with Yttrium.

Calculation	Total energy per atom [eV/atom]
Before relax	-7.167
After relax	-7.276

3.4.3 Total and local density of states

TDOS and LDOS graphs are shown below. Figure (16) shows the total DOS for Quinizarin with Yttrium, whilst Figure (17) shows the local DOS for the lower Yttrium atom and Figure (**??**) shows the local DOS for the upper Yttrium atom. The full pictures of these plots, see Figure (35), Figure (36) and Figure (37) in Appendix.

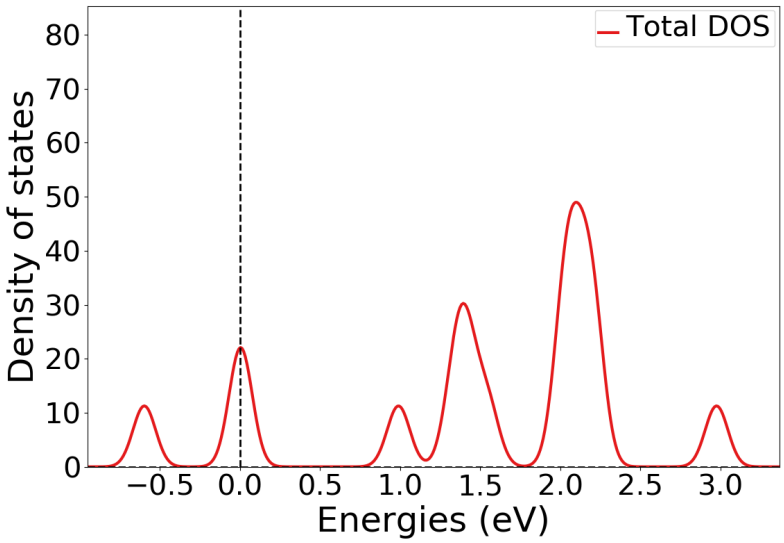

Figure 16: Plot of total DOS for Yttrium, zoomed in for energies around the fermi level (set to 0 eV).

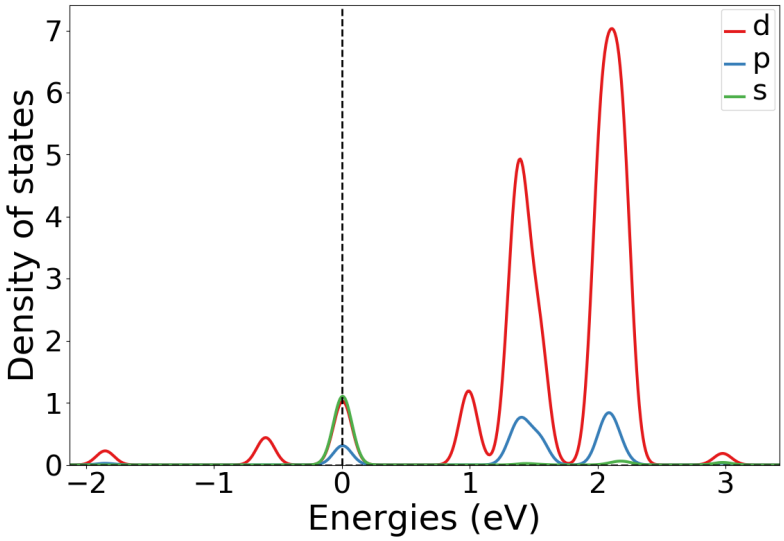

Figure 17: Plot of local DOS of atom number 25(Y in lower alcohol-group) for Quinizarin with Yttrium, zoomed in for energies around the fermi level (set to 0 eV).

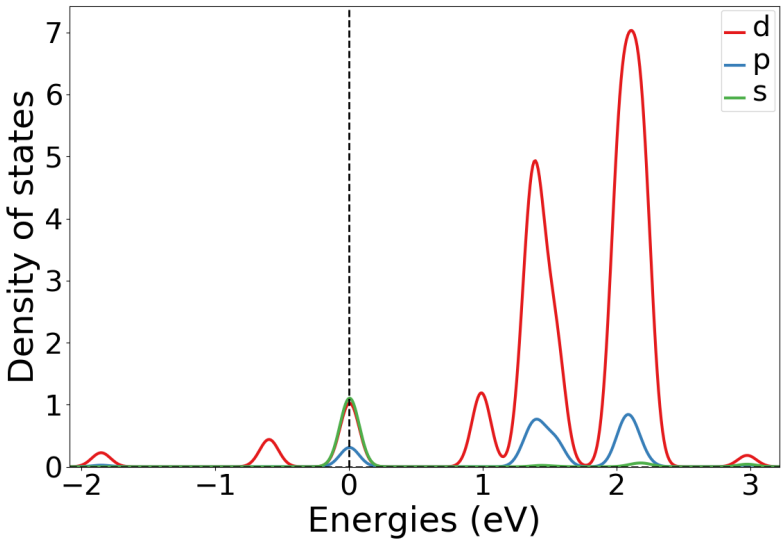

Figure 18: Plot of local DOS of atom number 26(Y in upper alcohol-group) for Quinizarin with Yttrium, zoomed in for energies around the fermi level (set to 0 eV).

3.4.4 Band gap

The table below, Table (6), shows the values of the band gap of Quinizarin with Yttrium. It also shows how the values between before and after relaxing the structure.

Table 6: Band gap, valance band maximum and conduction band minimum for Quinizarin with Yttrium with static calculations.

Calculation	Band gap [eV]	VBM [eV]	CBM [eV]
Before relax	0.042	−3.323	−3.281
After relax	0.029	−2.979	−2.950

3.4.5 Charge density

Figure (19) and Figure (20) show the charge density of Quinizarin with Yttrium, respectively before and after relaxation. Figure (13) shows the charge density of a single molecule of Quinizarin with Yttrium after relaxation.

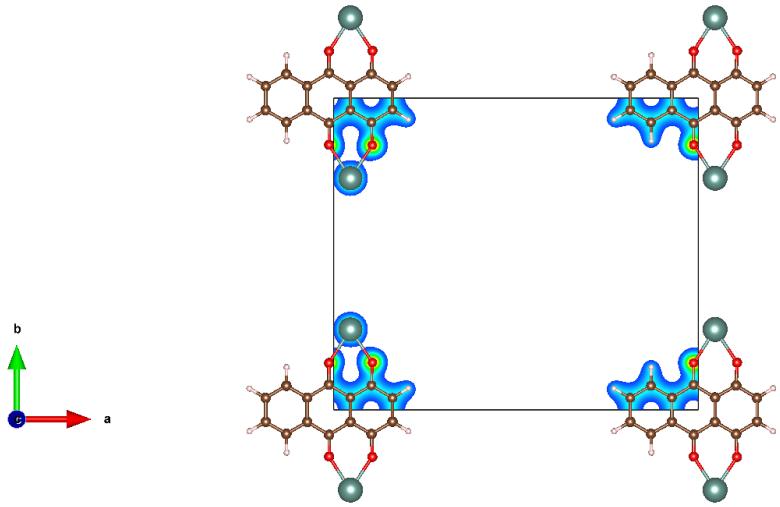

Figure 19: Charge density of Quinizarin with Yttrium for static VASP calculation.

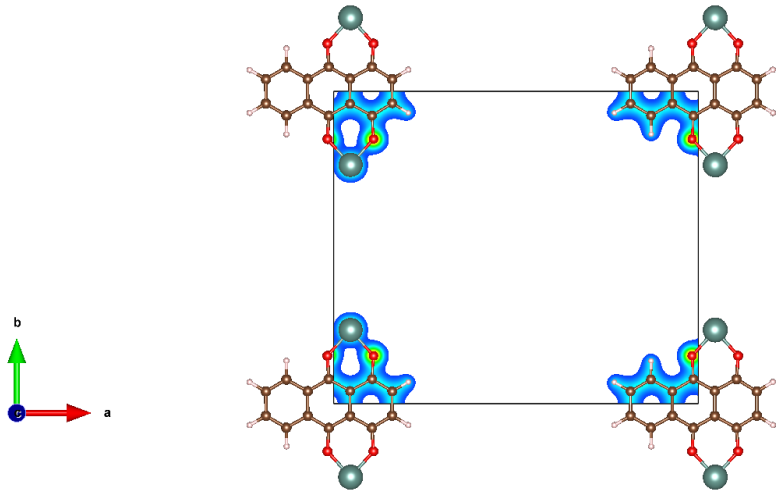

Figure 20: Charge density of Quinizarin with Yttrium for static VASP calculation after relaxed calculation.

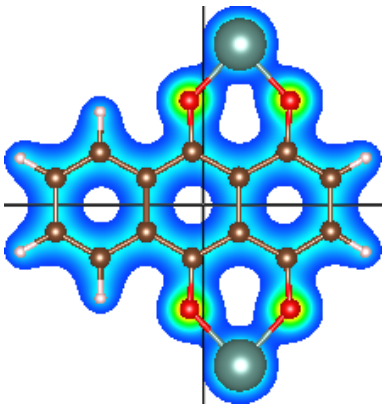

Figure 21: Charge density of a single Quinizarin molecule with Yttrium for static VASP calculation after relaxed calculation.

3.5 Quinizarin with Ytterbium

3.5.1 Relaxing the structure

Quinizarin with Ytterbium before relaxation is shown in Figure (22). After relaxation the structure looked as in Figure (23).

OUTCAR can display the nearest neighbors, which is the atomic distance between the atoms in the structure. In Table (7) below, the Ytterbium and Oxygen distances is shown.

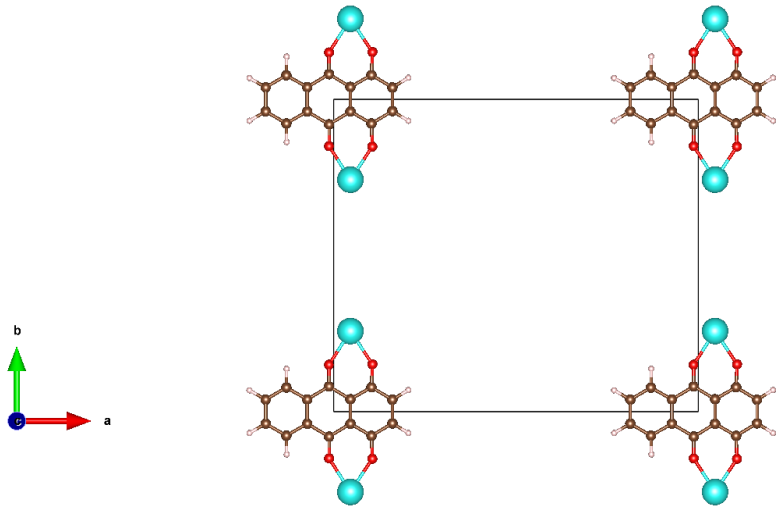

Figure 22: Structure of Quinizarin with Ytterbium for static VASP calculation.

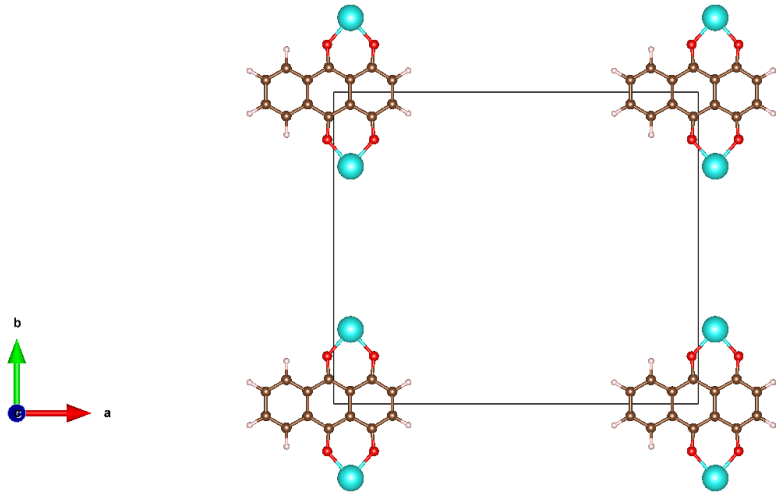

Figure 23: Structure of Quinizarin with Ytterbium for static VASP calculation after relaxed calculation.

Table 7: Ytterbium-Oxygen distances. 2x-bonded Oxygen is the central Oxygen atom, which is has a double bond to carbon. 1x-bonded Oxygen is part of the alcohol-group.

Calculation	Distance to 2x-bonded Oxygen [Å]	Distance to 1x-bonded Oxygen [Å]
Before relax lower Ytterbium	2.32	2.31
Before relax upper Ytterbium	2.32	2.32
After relax lower Ytterbium	2.08	2.07
After relax upper Ytterbium	2.08	2.07

3.5.2 Total and relative energies

See Table (8) for a table comparing the total energies of the static VASP calculations of Quinizarin with Ytterbium. The relative energy was -0.013 eV difference.

Table 8: Total energy per atom for Quinizarin with Ytterbium before and after relaxation.

Calculation	Total energy per atom [eV/atom]
Before relax	-6.869
After relax	-6.882

3.5.3 Total and local density of states

Figure (24) shows the total DOS of Quinizarin with Ytterbium. Figure (25) and Figure (26) respectively show the local DOS of the lower and upper Ytterbium atoms. The f-orbital is cut of due to being so high (around 50). In addition, to see the uncropped figures, see Figure (38), Figure (39) and Figure (40) in Appendix.

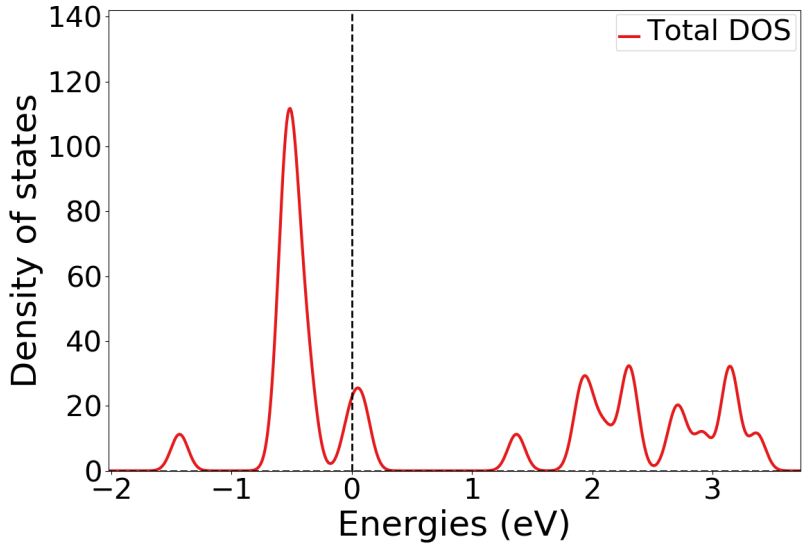

Figure 24: Plot of total DOS for Ytterbium, zoomed in for energies around the fermi level (set to 0 eV).

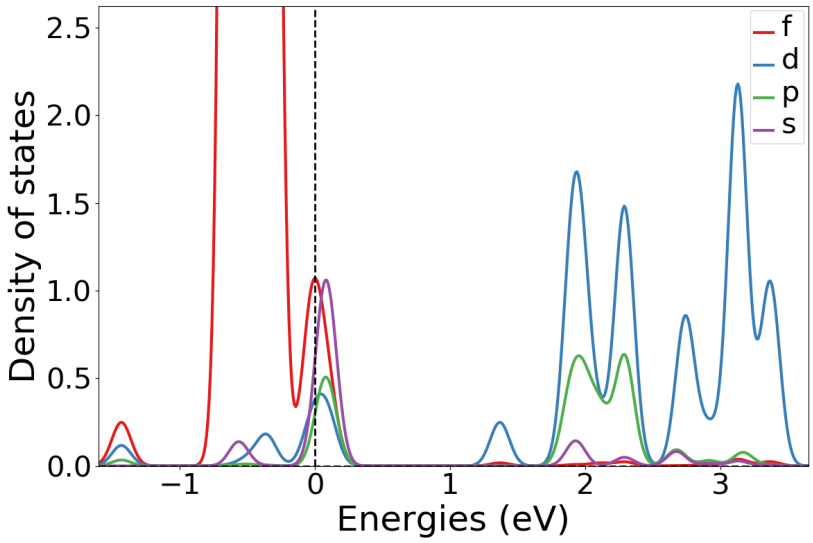

Figure 25: Plot of local DOS of atom number 25(Yb in lower alcohol-group) for Quinizarin with Ytterbium, zoomed in for energies around the fermi level (set to 0 eV).

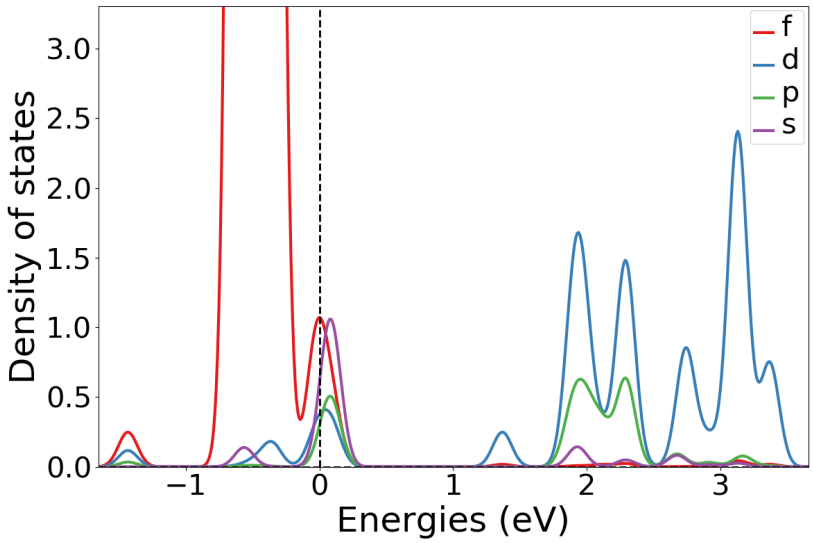

Figure 26: Plot of local DOS of atom number 26(Yb in upper alcohol-group) for Quinizarin with Ytterbium, zoomed in for energies around the fermi level (set to 0 eV).

3.5.4 Band gap

Table (9) shows the band gap of Quinizarin with Ytterbium using static VASP calculations, both before and after relaxing the structure.

Table 9: Band gap, valance band maximum and conduction band minimum for Quinizarin with Ytterbium with static calculations.

Calculation	Band gap [eV]	VBM [eV]	CBM [eV]
Before relax	0.0552	−2.9157	−2.6422
After relax	0.0771	−2.7193	−3.720

3.5.5 Charge density

Figure (27) and Figure (28) show the charge density of Quinizarin with Ytterbium respectively before and after relaxation. Figure (29) show the charge density of a single molecule, also after relaxation.

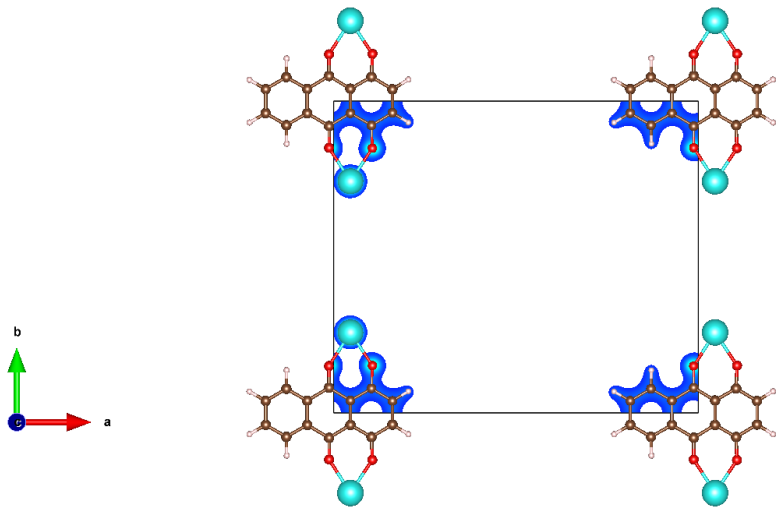

Figure 27: Charge density of Quinizarin with Ytterbium for static VASP calculation.

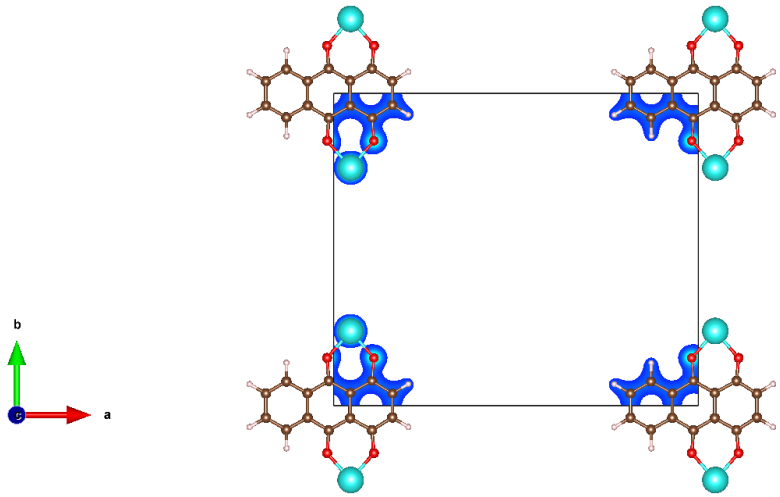

Figure 28: Charge density of Quinizarin with Ytterbium for static VASP calculation after relaxed calculation.

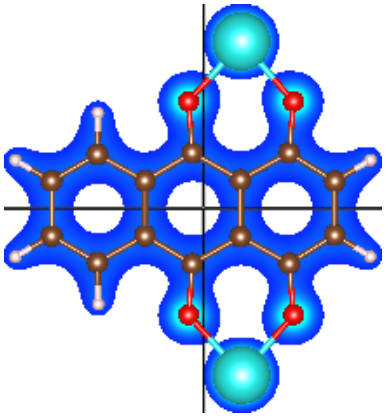

Figure 29: Charge density of a single Quinizarin molecule with Ytterbium for static VASP calculation after relaxed calculation.

3.6 Quinizarin with Neodymium and Thulium

We made an attempt to relax the structure with Neodymium and Thulium. This was abandoned, but below, in Figure (30) one can see how one of the attempts at relaxation went. Figure (31) shows CONTCAR from a different relaxation attempt. It is worth noting that the unit cells are the same size, but the images were saved with different sizes.

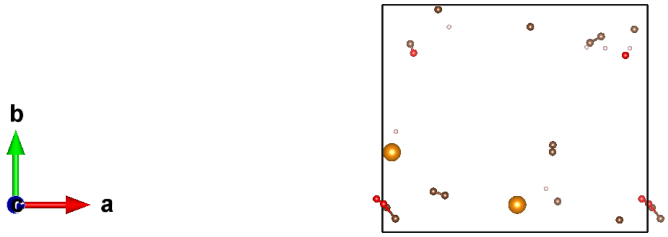

Figure 30: Structure of Quinizarin with Neodymium after relax calculation.

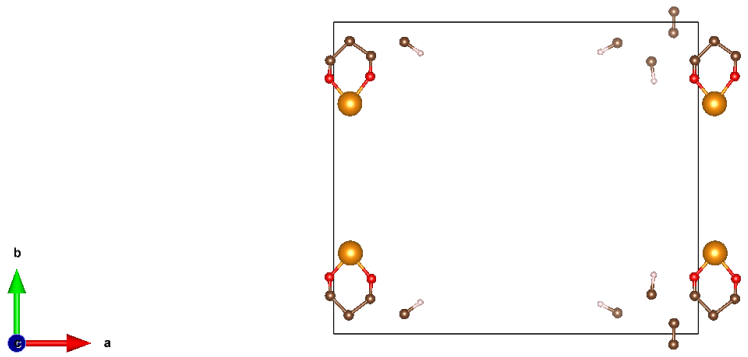

Figure 31: Structure of Quinizarin with Neodymium after a different relax calculation.

4 Discussion

4.1 Convergence of energy

Figure (2) shows that the values change quite rapidly and reach a peak around cutoff 500 eV which then lowers and stabilizes near cutoff 800 eV. However, the values differ by a very small amount, which can indicate that one needs a smaller cuttoff energy than 800. Figure (3) also indicates this.

From Section 2.1 we learned that if the difference in energy is less than 0.003 eV the calculation can be considered converged. The figure shows that ENCUT=450 is below 0.002 eV in difference from ENCUT=500. This shows that ENCUT=450 is safe enough to use. This can seem weird due to it being before a peak and the stabilized total energy is lower, but the values are quite small, and overall should not impact the results in a meaningful way.

4.2 Convergence of k-points

There were fewer data points than with the energy convergence, so it is not as easy to find a pattern as it was with the convergence of energy. For Figure (4) one can see the energy increases to a peak around 4.0 and 5.0 in k-density, which then decreases at k-density 6.0. Due to the lack of a good pattern we quickly moved on to Figure (5) which showed even less of a converging pattern. However, already at k-density 1.0 we could see the difference was less than 0.003 eV. Since the difference increased again with 2.0, we wondered if we could use 3.0, but after a few test-calculations with both 1.0 and 3.0 we found the difference was negligible and so we chose to use 1.0.

4.3 Quinizarin

Figure (6) and Figure (7) compares how the Quinizarin structure differs from before and after a relaxing computation. By examining the figures, there are virtually no difference to be seen. However, Table (1)

shows that there actually are a difference. Before relax, the Hydrogen-atoms are at a distance of about 1.75 Å to the double-bonded Oxygen-atoms and at about 0.95 Å to the single-bonded Oxygen-atoms. After relax, the distance has shrunk substantially to the double-bonded Oxygen-atoms to about 1.58 Å. On the contrary has the distances to the single-bonded Oxygen-atoms increased to about 1.03 Å, therefore the change is not as large as for the double-bonded distance. These changes implies a shift of the placement of the Hydrogen-atoms, where they now are closer to the double-bonded Oxygen-atoms than the single-bonded. This shift is explained by that Quinizarin has a resonance structure. A resonance structure implies that an atom has the possibility to shift placement in the structure. In this case for Quinizarin, this means that the Hydrogen-atoms can shift between the double-bonded Oxygen and the single-bonded Oxygen in the alcohol group. Such a shift has another implication, namely that the bond between the Oxygen-atoms and the Carbon-atoms change. For instance if the Hydrogen-atom has a shift further to the left, therefore shorter distance to the double-bonded Oxygen, will the Oxygen-bond to the Carbon have to change to a single-bond to maintain that Oxygen only can share to bonds. The Oxygen in the, now former, alcohol group then has a dangling bond, and forms a double-bond with the Carbon. For this to happen the activation energy has to be enough to break both the single-bond and the double-bond. We do not know the activation energy for Quinizarin, and could not examine when this change in structure forms in this project. However, this is interesting to study for another project.

Table (2) shows the total energies before and after the relax computation. The total energy after relax is less than before, which is in accordance to that a relaxing computation should make the structure more stable, implying a smaller total energy. The relative energy difference is -0.015 eV.

The total density of states shows that there are no half-filled bands, as the fermi level is not inside a band / an orbital. This indicates a lack of unpaired electrons and could tell us that it is diamagnetic. Figure (8) also shows that further up there are a lot of orbitals connected which means a broad band that can absorb a lot of different photon energies. This is important for a sensitizer to be able to absort many wavelengths so this is good.

In Figure (8) we see a band gap from approximately -0.25 eV to 1 eV (scaled to the fermi level). Looking in EIGENVAL we can see a fully occupied band at -5.31 eV to a completely empty band at -3.72 eV. This corresponds to a band gap of 1.59 eV, which is not completely in agreement with the figure of DOS, but also not that far off. A band gap of 1.59 eV is a semiconductor. This size of band gap means it is quite unlikely for an incoming photon to be re-emitted as phonon vibrations. It will more likely be re-emitted as a photon or, in an up-conversion, be led into the system it self. This is good, and indicates that Quinizarin will not quench any incoming photons.

As for the change in the structure before and after relaxation, the charge density has also not changed much. Figure (11) and Figure (12) displays the charge density for before relax and after relax, respectively. Table (1) shows that the Hydrogen-atoms move some, but this is not possible to see in the charge density figures either.

4.4 Quinizarin with Yttrium

From relaxing the structure we can see that the atomic distances between the Yttrium and Oxygen atoms decreases. This can both be seen visually in Figure (14) and Figure (15), as well as from the numbers in Table (4). This shows that the initial distances found in ICSD for Ytterbium were not identical for Yttrium. This is good. It was still wise to use 2.32 Å as start distance as the start distance from normal Quinizarin made the molecule explode during ionic relaxation with standard parameters. Another thing to note is how Yttrium is almost in the middle. The initial coordinates also kept Yttrium in the middle, but it is interesting to note how it kept in the middle. It is only 0.01 Å closer to the alcohol-group Oxygen than to the double-bonded Oxygen. This indicates that what used to be double bonds now are single bonds and that both Oxygen's are equally bonded to Yttrium. This is a further step from the resonant structure that was discussed for the normal Quinizarin molecule.

As seen in Table (5) The energy of Quinizarin with Yttrium after ionic relaxation is lower than before ionic relaxation. This proves that the relaxed structure indeed is relaxed, and shows it being more stable. The relative energy was -0.109 eV/atom which shows there was a change, but not a too big one. When it comes to broad-ness in one or more conduction bands this is not as good as normal Quinizarin. There is a band that goes from around 0.5 eV to 1.75 eV, but then there is a gap before a new one pops in around 1.85 eV. Still, the bond is fairly wide, and will likely absorb a fairly wide spectrum.

The plot over total density of states for Quinizarin with Yttrium shows that there is an orbital at the Fermi level. This means that the orbital is half-full which may indicate that Quinizarin has an unpaired electron spin, making the molecule weakly paramagnetic. One thing to note for the local densities of states is that they both look identical. This shows the mirror symmetry of the molecule.

The band gap was reported to be 0.029 eV as shown in Table (6). This is very small and less trustworthy than looking at the density of states. If we observe the density of states there seems to be a bang gap from around 0.25 to 0.75 eV (scaled to Fermi level. Looking in EIGENVAL from the static calculation after relaxation we can see there is a band gap from -3.57 (100% occupied) to -2.98 (58.1% occupied). This is a band gap of 0.59 eV, which corresponds fairly well to the gap found in Figure (16). This band gap would correspond with a semiconductor, and from gut instinct will likely rather emit the energy absorbed as a photon rather as phonon vibrations. This is good as phonon vibrations will lead to quenching, reducing the efficiency of the up-conversion system. This tells us that a if Quinizarin is embedded in a matrix of YF3 it will likely not quench absorbed photons, and work well as a sensitizer.

CHARGE DENSITY

4.5 Quinizarin with Ytterbium

Quinizarin with Ytterbium has similar results when comparing how the structure changes before and after relax as Quinizarin with Yttrium, seen in Section Quinizarin with Yttrium. One similarity is that the Ytterbium-atoms are placed in between of the Oxygen in the alcohol group and the double-bonded Oxygen, this is however mostly for comparison. Another similarity is that after relaxing the structure the Ytterbium moves closer towards the molecule, making the bond length, also called the distance to the double-bonded Oxygen and the single-bonded Oxygen, shorter, while still being maintained in the middle. This can all be seen in Figure (22), Figure (23) and Table (7). In fact, the bond length has approximately the same length as the Quinizarin molecule with Yttrium. However, after relax the bond lengths shrink to both Oxygen-atoms. For both Oxygen-atoms, the distance is cirka 2.32 Å before relax and cirka 2.08 Å after relax. The reasoning behind these changes is therefore the same as for Quinizarin with Yttrium, so the reader is referred to this section.

The total energy of the system changes minimally, but it is more net negative after the relax calculation. Table (8) shows the total energy before and after the relaxation. The relative energy is a -0.013 eV difference. Quinizarin with Ytterbium is therefore more stable after relaxation.

Figure (24) shows the density of states for Quinizarin with Ytterbium. Immediately we see that the fermi level is inside a bond which again can indicate unpaired electrons and the molecule being weakly paramagnetic. After around 1.8 eV there seems to be a very wide band going all the way up to and past 3 eV. A small dip around 2.5 eV, but not a complete gap. This is incredibly good as it means the molecule might absorb photons for the whole spectrum of available light.

There seems to be a band gap from around 0.33 eV to 1.2 eV. In EIGENVAL we see that there is a fully occupied band at -3.05 eV, and the next band is at 2.72 eV and is 67% occupied. This corresponds to

4.6 Quinizarin with Neodymium and Thulium

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We attempted to perform relaxation and evaluation of Quinizarin with Neodymium and Thulim as well. Initially we attempted with the relaxed Hydrogen-system as POSCAR for these atoms, but the distance was way to low. This resulted in an explosion of the molecule a lack of relaxation. We then tried to relax with more electronic steps, but this did not help. This was also the case for Y and Yb initially. After using around 2.3 Å as distance (after looking at various solid structures on ICSD) we managed to get a relaxed structure for Y and Yb. However, this was not the case for Nd and Tm. We then tried to increase the amount of electronic steps, NELM, to 300, without success. We cross-checked some Nd-structures on ICSD, but 2.3 Å seemed reasonable to use. After a final attempt with IBRION=2 and POTIM=0.2 we hoped for a better result. This was not the case, as after 3 hours it still had not converged. We weighed our options of either increasing the maximum time, or to stop trying with Nd and Tm. After a talk with our supervisors we decided to only report for Y and Yb.

4.7 Total comparison

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1. Atom distances
2. Total and Relative energies
3. change in band gap and location of band gap
4. change in DOS
5. compare electronegativity between the atoms

5 Conclusion

MANGLER TEKST

6 References

[1] Ben G. Streetman & Sanjay Kumar Banerjee, 2016, *Solid State Elctronic Devices seventh edition*, Pearson Education

Appendix

A Quinizarin-bilder

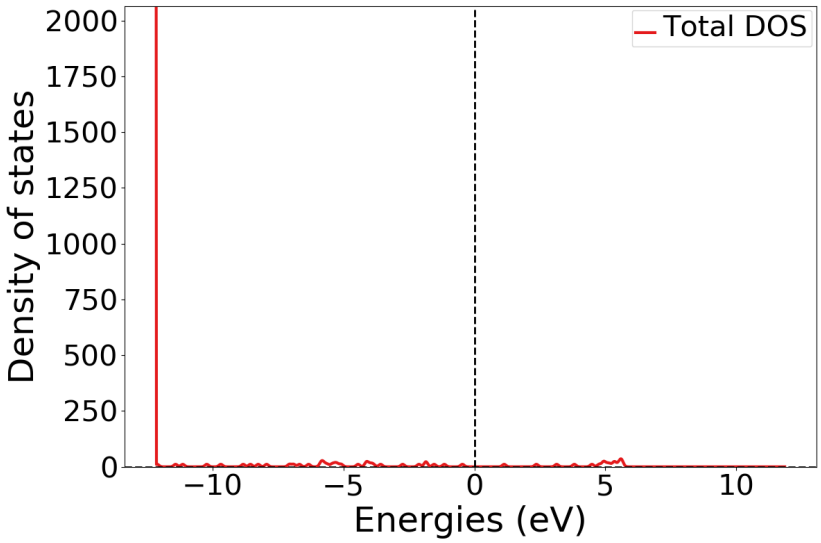

Figure 32: Plot of total DOS for Quinizarin.

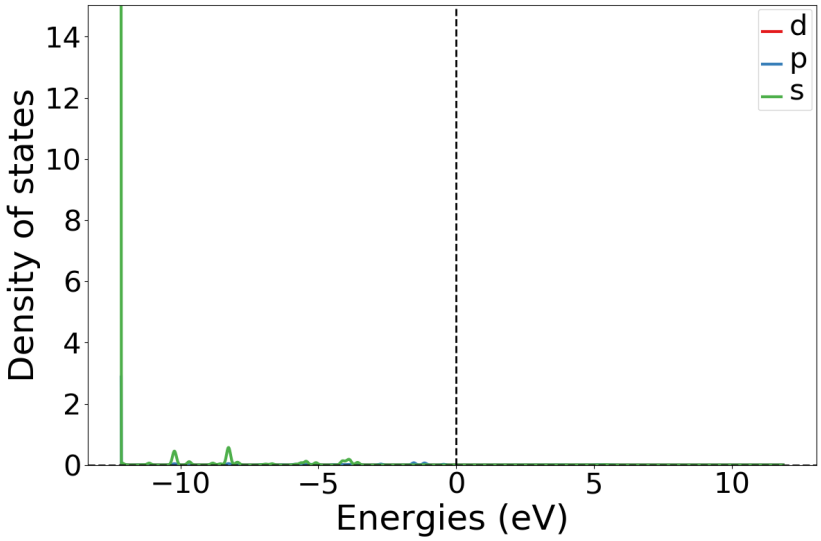

Figure 33: Plot of local DOS for atom number 25(H in alcohol-group) for Quinizarin.

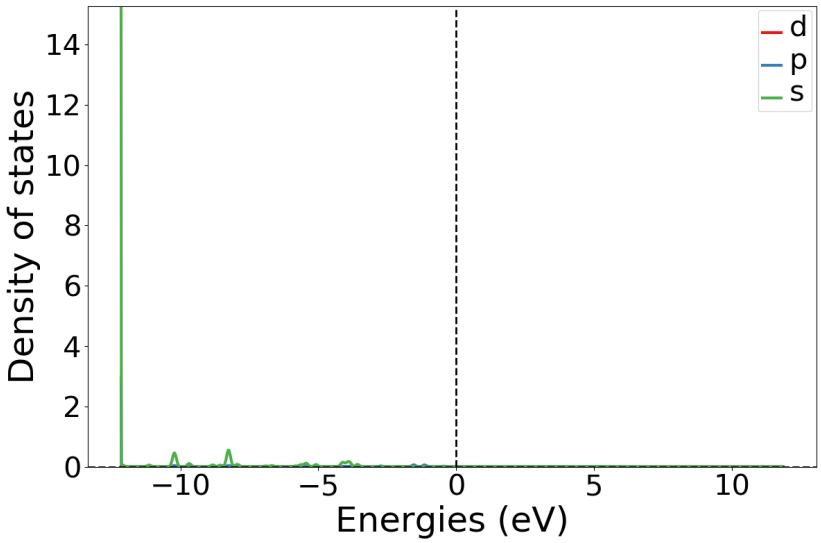

Figure 34: Plot of local DOS for atom number 26(H in alcohol-group) for Quinizarin.

B Y-bilder

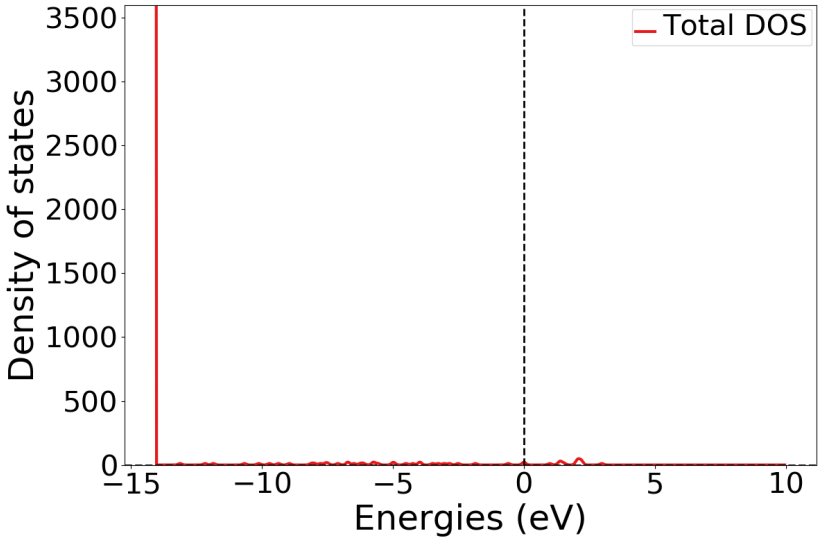

Figure 35: Plot of total DOS for Quinizarin with Yttrium.

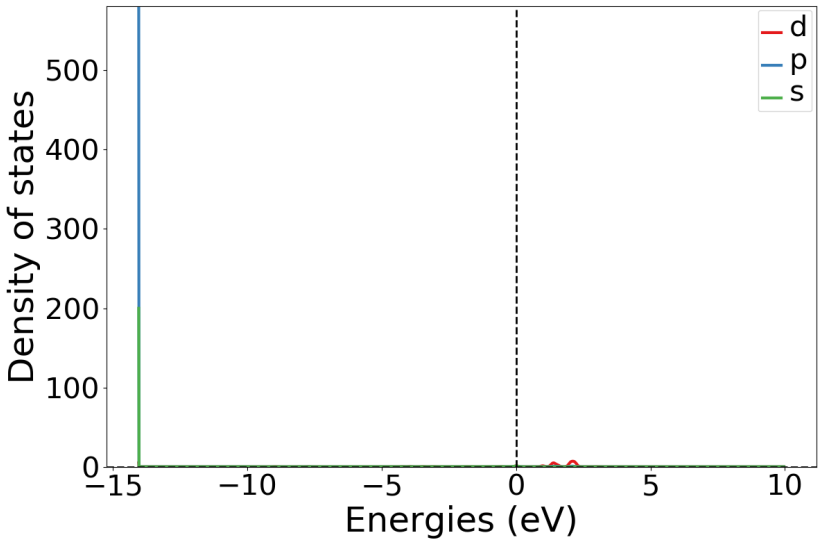

Figure 36: Plot of local DOS of atom number 25(Y in lower alcohol-group) for Quinizarin with Yttrium.

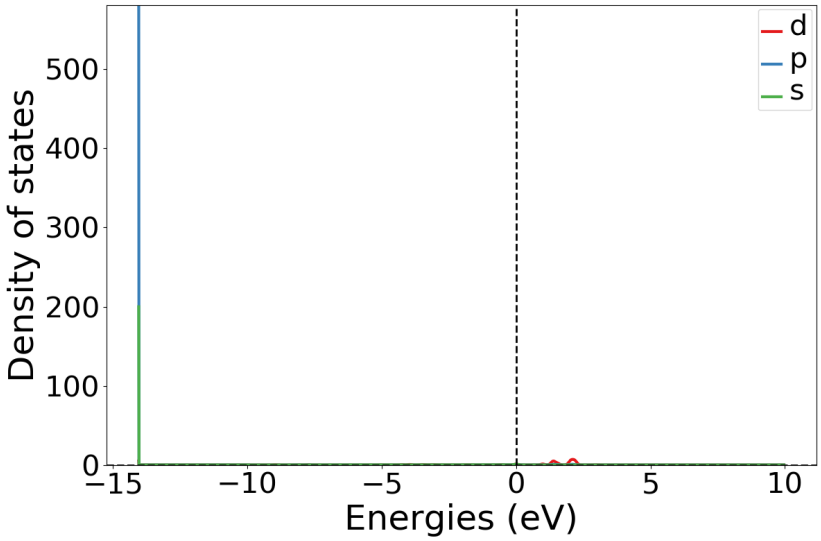

Figure 37: Plot of local DOS of atom number 26(Y in upper alcohol-group) for Quinizarin with Yttrium.

C Yb-bilder

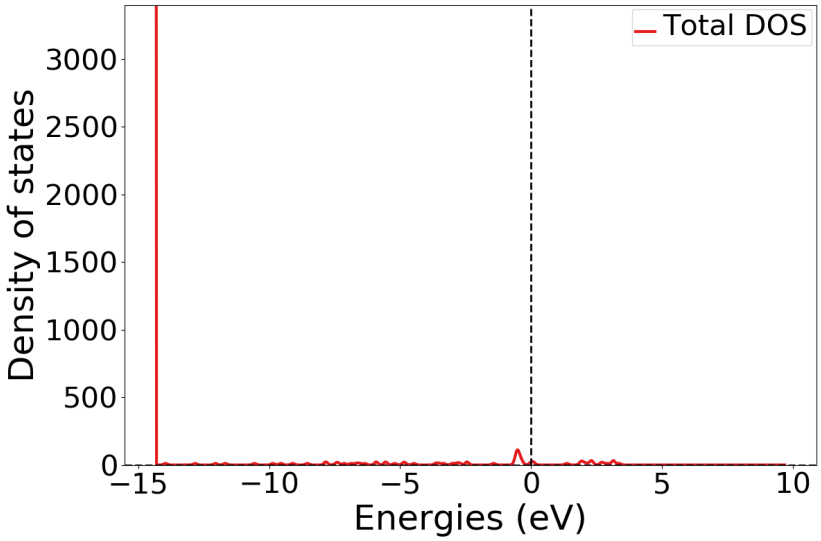

Figure 38: Plot of total DOS for Ytterbium.

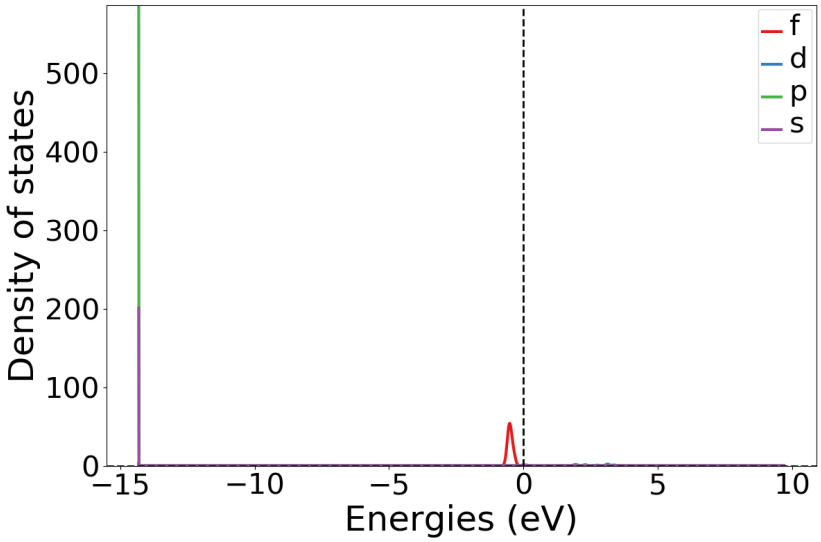

Figure 39: Plot of local DOS of atom number 25(Yb in lower alcohol-group) for Quinizarin with Ytterbium.

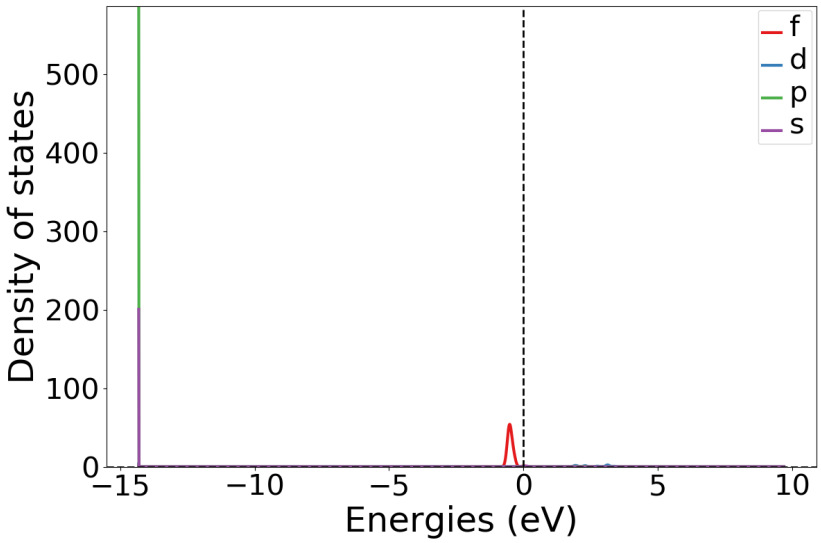

Figure 40: Plot of local DOS of atom number 26(Yb in upper alcohol-group) for Quinizarin with Ytterbium.