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.

Innhold

Ting å gjøre:

- lage en mappe på saga for begge

  done

- skaffe POSCAR, jobfile og INCAR (de andre følger fra disse)

  done

- sjekke at den konvergerer (decent ENCUT og KPOINTS)

  done

  The data shows that we should use 450eV for ENCUT as that is the 1st job with a difference less than 3meV.

  For k-density we see that even the lowest value, 1.0, is within 3 meV (1.0 gives around 1.75 meV), so this can be used. However, the data shows that 3.0 is below 1 meV, with 4.0 being identical in energy to 5.0. This can possibly be discussed in group, but 1.0 should technically be enough for k-density.

- relaxe POSCAR og static etter relax POSCAR

  done

- total og relativ energi (fra static etter relax)

  done

- DOS og LDOS

  done

- romlig elektronstruktur; 3D-plot av ladningstetthet (VESTA)

  done

- bytte ut hydrogen i alkoholgruppen med lantanoidatomer (Yb, Nd, Tm og Y)

  done

- relaxe POSCAR og static etter relax POSCAR

  done

- total og relativ energi (fra static etter relax)

  done

- DOS og LDOS

  done

- romlig elektronstruktur; 3D-plot av ladningstetthet (VESTA)

  done

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

  WIP

- 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

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.

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

2.6 Charge density

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 (**??**).

Figure (**??**) 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.

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 (**??**) 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 (**??**).

3.3 Quinizarin

3.3.1 Relaxing the structure

Show figures before/after relaxing

3.3.2 Total and relative energies

Table of TOTEN for each and TOTEN relative to each other

3.3.3 Total and Local density of states

TDOS and LDOS graphs

3.3.4 Band Gaps

The band gap was X eV"

3.3.5 Charge Density

Show CHGCAR figures

3.4 Quinizarin with Yttrium

3.4.1 Relaxing the structure

Show figures before/after relaxing

3.4.2 Total and relative energies

Table of TOTEN for each and TOTEN relative to each other

3.4.3 Total and Local density of states

TDOS and LDOS graphs

3.4.4 Band Gaps

The band gap was X eV"

3.4.5 Charge Density

Show CHGCAR figures

3.5 Quinizarin with Ytterbium

3.5.1 Relaxing the structure

Show figures before/after relaxing

3.5.2 Total and relative energies

Table of TOTEN for each and TOTEN relative to each other

3.5.3 Total and Local density of states

TDOS and LDOS graphs

3.5.4 Band Gaps

The band gap was X eV"

3.5.5 Charge Density

Show CHGCAR figures

4 Discussion

4.1 Convergence of energy

Figure (**??**) shows that the values change quite rapidly and reach a peak around cutoff 500 eV which then loweres 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 (**??**) 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 (**??**) 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 (**??**) 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.

5 Conclusion

6 References

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

A Appendix 2