Small Polarons In Cadmium Sulphide

A First Principles Study

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Abstract

A small polaron is a localized state in a material where a charge induces a potential well by perturbing adjacent ions from equilibrium, and getting trapped. A search for small hole polaron states in defect free cadmium sulphide is attempted using iterative density functional theory calculations, with the hybrid functional HSE06.

No small polaron states are found to be stable, the hole state is completely delocalized. When an electron is removed to induce a hole, the system gains more energy by spin-splitting the highest state of cadmium sulphide, to an unoccupied state at higher energy and an occupied state at lower energy, than by deforming the lattice and localizing the hole. Because of the sp$^3$-bonding structure this indicates that small hole polarons are unstable in other sp$^3$-bonded materials, with no defects.

Sammanfattning

Ett litet polaron tillstånd är ett lokalt tillstånd i material där en laddning har rubbat närliggande joner och skapat en potentialminskning, och sedan själv blivit fångad i den. Studien undersöker om små hålpolaron tillstånd finns i kadmiumsuld utan defekter genom att använda iterativa täthetsfunktionalsteoribäckningar, med hybridfunktionalen HSE06.

Inga sådana tillstånd beräknades att vara stabila, håltillståndet var helt delokaliserat. När en elektron tas bort i beräkningen för att inducera ett hål, så tjänar systemet mer på att spin-splitta det högsta tillståndet till ett ockuperat tillstånd vid högre energi och ett ockuperat tillstånd vid lägre energi. På grund av att kadmiumsulfid har sp$^3$-bindningsstruktur så indikerar resultatet att små hålpolaroner är instabila i andra sådana material, då defekter är frånvarande.
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1 Background

1.1 Semiconductors

Semiconductors are the basis of our computer technology and are also found in solar cells and detectors. Understanding semiconductors is important because this opens up for new and improved applications. But what is a semiconductor material?

Materials are divided into three categories depending on their electrical properties: insulators, conductors and semiconductors. Insulators do not conduct electricity, while conductors do. Semiconductors are materials that fall in between. The explanation for these different properties has to do with the band structure of materials.

The electronic states of a single atom are quantized, the electrons only ever occupy discrete states. These states are solutions to Schrödinger’s wave equation for that atom. Materials, however, consist of more than one atom. This has the consequence of there being regions of energy where many states lie close together, allowing electrons to freely change between them and there being regions of energy where there are no states at all. These regions are called bands, and if there are states in a band it is called allowed, otherwise it is called forbidden.

Conductivity in a material is governed by the location of the highest occupied state in the material, the energy of which is called the Fermi energy, \( E_F \). This is shown in figure 1, where the bands are visualized for different materials. If the highest occupied state is next to a forbidden band, then an electron needs enough energy to surpass the forbidden band and enter the next allowed band to move. This energy is usually large, and such materials are insulators, as we can see at the right end of figure 1. If the highest occupied state is in a allowed band, then very little energy is needed to excite an electron to a higher state. These materials are conductors, or metals, and are visualized at the left end of figure 1.

Semiconductors, like insulators, have their highest occupied state next to a forbidden band. The difference is that the energy to the next allowed band, called the band gap, is comparatively small. A consequence of this is that semiconductors can be altered easily to have both conductor and insulator

\(^1\)A more appropriate definition is that \( E_F \) is the energy where the chemical potential of holes equals the chemical potential of electrons. For this study, the given definition is sufficient.
A defect with excess positive charge is called p-type, and one with excess negative charge is called n-type.\[1\]

1.2 Polaron

Consider a charge carrier moving slowly through a material. If the charge were to linger in one place long enough, the surrounding ions would be shifted from equilibrium by Coulomb forces; opposite charged ions would be attracted and vice versa. This would have the consequence of altering the local potential energy, creating a well. This could lead to a bound, localized, self-trapped state, known as a polaron.\[4\] In figure 2 we see an example of a small electron polaron, and the displacement of the surrounding ions.

This idea was first suggested by Landau in 1933\[5\], and has been developed during the 20th century. Polaron's are important to study because of their influence in solar cells and high temperature superconductors.

A polaron state is not in the valence or conduction band, but in between in the band gap. This state is either occupied, if we consider an electron polaron, or unoccupied, if we consider a hole polaron. The polaron state affects the materials conductive properties. If we have a hole polaron, a valence electron might be excited to it, which means we will measure other excitation energies. There are two types of polarons, large and small. Large polarons extend over several lattice constants while small polarons only shift
the closest ions in the lattice. Large polarons are formed by electron-phonon interaction, while small polarons only depend on the Coulomb force and can therefore form at $T = 0$ K.

1.3 Density Functional Theory

In 1964 Kohn and Hohenberg proved that the total energy of a system was the unique functional of the electron density, and that if this total-energy functional was minimized, the corresponding electron density would exactly be the ground state electron density. The energy functional can be written as

$$E[n(r)] = 2\sum_i \left(-\frac{\hbar^2}{2m}\right) \nabla^2 \psi_i d^3r + \int V_{\text{ion}}(r)n(r)d^3r + \frac{e^2}{2} \int \frac{n(r)n(r')}{|r-r'|} d^3r d^3r' + E_{\text{XC}}[n(r)] + E_{\text{ion}}(\{R_{\text{ion}}\}).$$

This functional is called the Kohn-Sham total-energy functional. In the sum, $i$ goes over the doubly occupied states, hence the factor of two. The
first term corresponds to the kinetic energy of the electrons. $V_{\text{ion}}$ is the potential from the lattice of ions, and the second term is the corresponding electron-ion interaction. The third term is the Coulomb interaction between electrons and the fourth term is the exchange-correlation functional. The exchange interaction comes from the fact that electrons are fermions and follow Pauli’s exclusion principle. This principle states that two electrons cannot occupy the same exact state, and has the effect that electrons with parallel spin are more separated in space, and therefore their electrostatic repulsion is weaker, giving rise to a system energy gain. The correlation energy comes electrons with opposite spins also being spatially separated, which reduces the Coulomb energy while increasing the kinetic energy of the electrons. The $E_{\text{ion}}$ term is the electrostatic energy of the ions in the lattice as determined by their lattice positions $R_{\text{ion}}$.

A year later, in 1965, Kohn and Sham showed that the many electron problem could formally be replaced by many, single electron equations in effective potentials. The effective potential corresponds to all of the other electrons, as well as the ionic potential. To determine the set of wave functions $\psi_i(r)$ that minimize the total energy functional, equation 1 we need to solve the Kohn-Sham equations:

$$
\left[ -\frac{\hbar^2}{2m} \nabla^2 + V_{\text{ion}}(r) + V_H(r) + V_{\text{XC}}(r) \right] \psi_i(r) = \epsilon_i \psi_i(r),
$$

(2)

Where $V_H(r)$ is the Hartree potential of the electrons, given by equation 3.

$$
V_H(r) = e^2 \int \frac{n(r')}{|r - r'|} d^3r'
$$

(3)

The exchange correlation potential is given by the functional derivative.

$$
V_{\text{XC}}(r) = \frac{\delta E_{\text{XC}}[n(r)]}{\delta n(r)}.
$$

(4)

This is known as density functional theory, or DFT, and Kohn was awarded the Nobel prize in chemistry, in 1998, for his involvement in its development.

### 1.4 Iterative Density Functional Calculations

In order to perform a DFT calculation you use an iterative process described in figure 3. First we construct a trial electron density. Using this density we
calculate the Hartree potential \( V_H(r) \) and the exchange correlation potential \( V_{XC}(r) \). Then we solve the Kohn-Sham equations, equation 2, numerically. With our new wave functions we get a new electron density

\[ n'(r) = 2 \sum_i |\psi_i(r)|^2. \] (5)

We compare this new electron density with our original one, to see whether it has converged or not. If it has, we are done, otherwise we create a new electron density by some combination of \( n'(r) \) and \( n(r) \) and try again.[7, 11]

When doing iterative DFT calculations certain approximations are made. In the Born-Oppenheimer approximation the movements of the ions in the lattice are considered so slow compared to the electronic movements that they can be regarded as frozen, thus separating the ionic and electronic degrees of freedom. You could therefore construct a potential once and reuse it for several electronic iterations, saving computation power. We also use the single-electron approximation, where we create an effective potential based on all the other electrons, instead of solving the many electron problem.

To calculate the exact exchange correlation functional \( E_{XC}[n(r)] \) is very computationally intensive, so usually approximations are made. There are several popular approximations with different advantages and disadvantages. A common one is called local density approximation, LDA, with functional

\[ E_{XC}^{LDA}[n(r)] = \int n(r)\epsilon_{XC}(n(r))dr \] (6)

where \( \epsilon_{XC} \) is the exchange-correlation energy for a uniform electron gas with density \( n(r) \). This simple approximation yields surprisingly accurate results. However, this functional and similar ones tend to overdelocalize electrons and underestimate band gaps. To correct for this, one uses hybrid functionals.[12]

A hybrid functional includes some part of the exact exchange-correlation functional, and mixes it with approximations. The hybrid functional used in this project is named HSE06 after Heyd, Scuseria and Ernzerhof, mixes the exact functional for short range exchange interaction and uses approximations for the long range and correlation energies.[13] The development of hybrid functionals, as well as increased computing power, in the last decade has allowed theoretical first principle calculations of localized states, such as polarons, which were previously impossible.
Construct ionic potential, $V_{\text{ion}}$

Construct trial electron density, $n(r)$

Calculate $V_H$ and $V_{XC}$ and form $V_{\text{eff}}$

Solve the Kohn-Sham eq. (2)

Calculate new density, $n'(r)$

Converged?

Yes

Calculate $E[n'(r)]$

No

Update $n(r)$
1.5 Purpose

The purpose of this project is to search for stable, small hole polaron states in the semiconductor cadmium sulphide, using iterative density functional calculation methods. Previous research on polarons in this material have found such localized states at cadmium vacancies, i.e. a small polaron.\[12\] In this project I investigated the possibility of stable, localized hole states without defects. The previous study also found stable small polarons in cadmium selenide and cadmium telluride, but the small polaron state in cadmium sulphide was the most stable. Thus, if stable small polaron states can be calculated without defects in this family of materials, it should be easiest to find in cadmium sulphide.

Cadmium sulphide is an interesting material to study, it is for example used in solar cells and detectors. It is also similar in properties to cadmium telluride which is a very important material in solar cells, because of its almost ideal band gap for sunlight and high efficiency.\[14\]

2 Method

To look for stable states I used DFT calculations, since DFT gives us the ground state electron density. If something is in the ground state, then it is a stable state. I used the Vienna ab initio Simulation Package, VASP to make DFT calculations. VASP uses a plane-wave basis set for their wave functions and potentials, and the projector augmented wave method.\[15\]

I made my calculations using a super cell with 64 cadmium ions and 64 sulphur atoms, with periodic boundary conditions. In figure 4 we see initial lattice positions of the ions in the cell. I used previously converged lattice parameters in my cell. I considered twelve valence electrons for each cadmium, ten d-states and two s-states, and six valence electrons for each sulphur ion, all in the p-state. The rest are considered core electrons and were included in the ionic potential, since they are strongly bound and localized. This gives us a total of 1152 electrons in the cell, but since I searched for hole polarons, I removed one electron to induce an unoccupied state. To compensate for the missing charge I added a constant background charge and to force the system to fully occupy states I required the total magnetic moment to be one. This causes every state to be completely occupied or unoccupied. This simulation is performed at $T = 0 \text{K}$, and with no time
Figure 4: An image showing the initial positions of the ions in my cell. The pink ones are cadmium and the yellow ones are sulphur. There are 64 of each atom, 128 in total.

evolution. I assume the zinc blende structure for cadmium sulphide even though the stable crystal state is wurtzite. I solved the Kohn-Sham equations over a single k-point, $\Gamma$.

3 Results and Discussion

I found no indications of small polaron formation in cadmium sulphide. Calculations designed to find this localized state all relaxed back to the symmetrical lattice, after ionic iterations. In other words, the removal of an electron does not give rise to broken symmetry. These strategies included:

- Moving an ion from equilibrium towards, and away from, the plane of its three closest neighbours, and see if the hole state would localize at this deformation. See figure 9 in the appendix for exact energies of this calculation, for different displacements of the ion in the lattice.

- Replacing a sulphur ion with a phosphorus ion. The phosphorus ion has one less valence electron, which would correspond to our hole state, but the phosphorus ion is localized. The system then relaxes ionically, and those relaxed positions are used as our new initial position, but
the phosphorus ion is replaced by a sulphur, to see if the hole localizes around the newly replaced sulphur ion.

- Using selective dynamics on the outer atoms of the super cell, so that the inner ones were allowed to relax ionically, but the outer ones were held in place. This symmetry breaking could allow the hole state to localize.

- Basing the initial positions on the successful attempt in the previous study[12], but removing the vacancy, by replacing the missing cadmium ion. Since these positions definitely localize the charge, a similar lattice deformation might localize in the defect free case as well.

When we remove one electron the system splits the highest energy state into two different energy levels, the unoccupied state increases in energy and the occupied one decreases. When the system is not spin-polarized, the highest occupied state is only partially occupied. We can see this by comparing a spin-polarized calculation with a not spin-polarized calculation. If the system is not allowed to spin-polarize, then the induced hole state is partially occupied. (See figure 3 b)) This state also increases in energy because of the occupationally dependent energy functional.

When we allow spin-polarization we see that the occupied part of the partially occupied state decreases in energy and the unoccupied increases in energy, called spin-splitting. Since it is unoccupied, it does not contribute to the total energy of the system. The system decreases in total energy ∼ 80 meV when it is spin-polarized, which corresponds to the decrease in energy of the occupied state. This correspondence can be understood because, to a first approximation, the total energy of the system is equal to the sum of the energy eigenvalues.

This phenomenon is shown in figure 5 based on my the energy eigenvalues of the different calculations which can be found in the appendix, table 3. This schematic view is similar to the density of states for each calculation, an example of which can be seen in figure 6. It is difficult to extract the schematic information from the density of states, because the energy scale is very small. Therefore figure 3 is a way of visualizing this information, and it is not to scale. The density of states graph was calculated from the energy eigenvalues, and smeared using a Gaussian blur, with a standard deviation of 0.1 eV in VASP. The density of states for the other calculations can be found in the appendix.
Figure 5: Schematic of the states in the different calculations. Shading indicates occupation. a) describes the control calculation with all electrons present. b) and c) both have one electron removed but c) is spin-polarized (SP). The partially unoccupied state (dashed line) in b) is then allowed to split into two states in c). The occupied state lowers in energy, while the unoccupied state increases. The decrease in energy of the occupied state corresponds to the decrease of the total energy of the system.
The distance between all atoms also decrease when allowed to respond to the removed electron. Due to a decrease in charge of the electron gas, the lattice has to scale down to a new equilibrium. This is another way the system stabilizes rather than forming a polaron. The energy gains the system can make are shown in figure 7, as well as in the appendix, figure 2. We see that the system gains \( \sim 20 \text{ meV} \) when the lattice is allowed to relax, and \( \sim 80 \text{ meV} \) when the highest state is allowed to split into a high, unoccupied state and a low, occupied state.

A small polaron consists of two parts, the lattice deformation and the charge, in our case a hole, localizing at this lattice deformation. The density of states and energy eigenvalues corresponding to the formation of a small polaron would look the same as the ones I have presented, a localization would also give rise to spin splitting.

The reason I can state that these states are not localized is because of the charge density \( n_{\text{hole}}(r) = |\psi_{\text{hole}}(r)|^2 \) is not localized. In figure 8 we can see clearly that the charge density is delocalized, and that it is equal on every sulphur ion. We can also see the characteristic p-state shape of the charge density. If the hole polaron had formed, then the charge density would be localized on a single sulphur ion. Here the spin-splitting occurs without
Figure 7: A comparison of the energies for different situations, allowing and not allowing spin-polarization and lattice relaxation respectively. Energy is normalized to the lowest energy case, Spin-polarized with relaxed volume. The area of the box corresponds to the volume of the lattice.
Figure 8: The specific charge density of the hole state in the performed calculations is completely delocalized, and the p-state shape of the density is clearly seen on every sulphur ion.

the symmetry breaking as an effect only due to DFT description where the exchange potential is dependent on the occupation numbers.

The valence electrons from the sulphur ions are primarily in p-states, while the valence electrons from the cadmium are s-states. The valence electrons are in an sp$^3$-hybrid configuration, which corresponds to the tetrahedral structure.

The delocalization of the unoccupied state gives rise to an energy gain for the system. If this state were localized instead it would give the same energy gain to the system, i.e. saturating the bonds, but the system would also lose the energy required to perturb the lattice. Since we see a spontaneous spin-splitting without lattice distortion in this material, we should see it in other materials with sp$^3$-hybrid electron configuration.

We can see this from the fact that the energy of lattice distortion is different in different materials, but spin-splitting should be spontaneous in all of them. Thus small polarons should not be stable in these materials either. This should especially be true for cadmium selenide and cadmium telluride, as the previous study found the energy gained by the hole polaron in these materials even less than in cadmium sulphide.
4 Conclusions

In cadmium sulphide the small polaron state is unstable without defects. Because cadmium sulphide has sp$^3$- hybrid electron states, this should be generalizable to all semiconductors with that electron structure, such as cadmium selenide and cadmium telluride.

5 Outlook

It is worth noting that I can only exclude polarons smaller than the size of my cell from being stable. There may very well be stable large polarons in these materials without defects. A small polaron is however smaller than my cell, so a continued search for small polarons without defects by increasing the size of cell would not yield a stable state. I also performed my calculation at the biggest size that is practical at current supercomputer technology. In the future further, more accurate calculations can be made.

Further studies in this area should confirm my results by performing calculations on other materials. It would also be interesting to compare the energies the system gains in this case, and in the case with defects to confirm that in the defect case the energy gained by localizing the unoccupied state is higher.
References


A Tables and Graphs

In this section the exact results are presented for the curious reader.

<table>
<thead>
<tr>
<th>Band Nr.</th>
<th>Occ. Nr.</th>
<th>Eig. [meV]</th>
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<td>2.00000</td>
<td>42.99</td>
</tr>
<tr>
<td>575</td>
<td>2.00000</td>
<td>42.99</td>
</tr>
<tr>
<td>576</td>
<td>2.00000</td>
<td>43.00</td>
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</table>

Table 1: The total energy and energy eigenvalues of the highest occupied states of the system with no missing electrons. Note that since we have a different amount of electrons, the absolute values cannot be compared to the other results.

<table>
<thead>
<tr>
<th></th>
<th>Volume Relaxed</th>
<th>Volume Fixed</th>
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<tbody>
<tr>
<td>SP</td>
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<td>21.6</td>
</tr>
<tr>
<td>−SP</td>
<td>75.1</td>
<td>99.2</td>
</tr>
</tbody>
</table>

Table 2: The total energy in each system measured in meV, normalized to the total energy of the spin-polarized (SP) calculation with a relaxed volume.
Figure 9: The total energy of +1 charged CdS is plotted as a function of lattice distortion. One sulphur ion was moved towards and away from the plane of three of its neighbours. Here we see the total energy of the system dependent on how far it was moved. Note the small scale on the energy axis.
Table 3: The energy eigenvalues ($\Gamma$) around the highest occupied state for the spin-polarized and not spin-polarized (SP) calculations. The energy is relative to $E_F$.

<table>
<thead>
<tr>
<th>Band Nr.</th>
<th>Occ. Nr.</th>
<th>Eig. [meV]</th>
<th>Occ. Nr.</th>
<th>Eig. [meV]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Volume Relaxed</td>
<td>Volume Fixed</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>First Spin Channel</td>
<td>Second Spin Channel</td>
<td></td>
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<td>1</td>
<td>0.2</td>
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</table>

Figure 10: Density of states of +1 charged CdS volume fixed, SP.
Figure 11: Density of states of +1 charged CdS volume relaxed, \( \neg SP \).

Figure 12: Density of states of +1 charged CdS volume fixed, \( \neg SP \).