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Calculating Charged Defects using CRYSTAL

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Abstract. The methodology for the calculation of charged defects using the CRYSTAL program is discussed. Two example calculations are used to illustrate the methodology: He⁺ ions in a vacuum and two intrinsic charged defects, Cu vacancies and Ga substitution for Cu, in the chalcopyrite CuGaS₂.

1. Introduction

In recent years it has become possible to accurately calculate defect formation energies in crystalline solids using *ab initio* methodologies. While the calculation of uncharged defects is relatively straight-forward, the calculation of charged defects is more complicated [1]. In this paper we outline a methodology for the calculation of charged defect formation energies using the CRYSTAL program. The techniques used are transferable to other *ab initio* programs.

The first example is a very simple system, consisting of a periodic array of He⁺ ions in a vacuum. The second example involves charged defects in the chalcopyrite CuGaS₂. The defects considered are the vacancy formed by the removal of a Cu⁺ ion (V_{Cu}^-) and the substitution of a Cu⁺ ion for a Ga³⁺ ion ($\text{Ga}_{\text{Cu}}^{2+}$). This example has been chosen as it is of current scientific interest, as CuGaS₂ could potentially be used as an absorber layer in highly efficient solar cells.

2. Computational Scheme

All calculations are performed using the CRYSTAL program. This program computes the electronic structure of systems within Hartree-Fock, density functional (DFT) and various hybrid approximations using local Gaussian basis sets for systems periodic in three, two, one and no dimensions.

Our first example, a periodic array of He⁺ ions in a vacuum, is calculated using Hartree-Fock theory and a standard Pople 3-21G basis set. The second example, V_{Cu}^- and $\text{Ga}_{\text{Cu}}^{2+}$ defects in CuGaS₂, is of current scientific interest, consequently, care has been taken to perform calculations that will lead to accurate defect formation energies. A full account of this work can be found elsewhere [2]. The B3LYP hybrid exchange functional [3] is used. This functional has been shown to provide a reliable description of geometric and electronic structure and energetics in a wide range of materials [4, 5]. In particular, hybrid functionals, such as B3LYP, provide a much better prediction of the band gap of semiconductors than local density approximation or generalised gradient approximation DFT functionals. Polarised triple valence Gaussian basis sets were used.

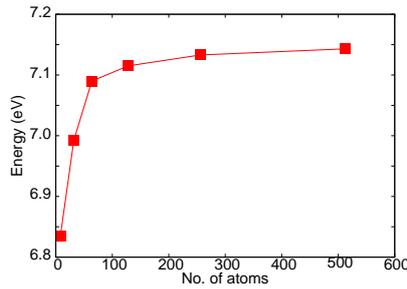


Figure 1. The change in the energy of the uncharged CuGaS₂ system when an electron is removed

3. Defect Formation Energies

The formation energy of a defect, D , of net charge q , in system X is defined as

$$\Delta H_f(D) = E_{\text{tot}}(D) - E_{\text{tot}}(X) + \sum_i n_i \mu_i + q(E_F - E_V) \quad (1)$$

where $E_{\text{tot}}(D)$ and $E_{\text{tot}}(X)$ are the total energies of the system with and without the defect, D . n_i represents the number of atoms of element i that are removed from the system when the defect is formed (a negative value for n_i denotes addition of atoms). μ_i is the chemical potential of element i , it represents the energy of the atoms that are removed (or added) to the system when the defect is formed. The fourth term, $q(E_F - E_V)$, represents the energy change due to the exchange of electrons and holes with the carrier reservoirs. $(E_F - E_V)$ is the Fermi energy relative to the valence band maximum (VBM) of the defect free system.

4. Energy Offset Correction

A consequence of using periodic boundary conditions within electronic structure calculations is that the boundary conditions lead to the conditional convergence of the Coulomb potential. In the case of uncharged systems the potential and total energy converge to well defined values under the conditions described first by Ewald [6]. The total energy of a charged system, however, can only be calculated to within a constant offset [1]. The value of this constant offset depends on the average crystal potential. It can be obtained by calculating the change in the energy of an uncharged system when an electron is removed from it; as the system size is increased the change in energy converges to the value of the offset.

In our first example, He⁺ in a vacuum, the energy offset is equal to zero as the defect free system is simply a vacuum and the total energy of a uniform background charge in the limit of the charge tending to zero (equivalent to the system size tending to infinity) is zero. The change in energy of the CuGaS₂ system before and after the removal of an electron is displayed in figure 1 for increasing supercell size. As the system size tends towards infinity the difference in energy converges to approximately 7.15 eV. The value of $E_{\text{tot}}(D)$ in equation 1 must be corrected by this constant offset multiplied by the net charge of the system.

5. Coulomb Interactions between Defects

The total energy of a periodic system that contains a localised charged defect treated within a finite supercell includes a term due to defect-defect, defect-background and background-background Coulomb interactions. To calculate the energy of an isolated defect this term must be subtracted from $E_{\text{tot}}(D)$. It can be approximated by the multi-pole correction [7]:

$$\Delta E = \frac{q^2 \alpha_M}{2\epsilon_r V^{\frac{1}{3}}} + \frac{2\pi q Q}{3\epsilon_r V} + O(V^{-\frac{5}{3}}), \quad (2)$$

where α_M is the lattice dependant Madelung constant, ϵ_r is the relative dielectric constant, V is the volume of the cell and Q is the quadrupole moment of the defect.

The first term in equation 2 represents the defect-defect Coulomb interaction. It can trivially be calculated using CRYSTAL as it is equivalent to the nuclear-nuclear interaction of a periodic system consisting of hydrogen atoms at the positions of the defects multiplied by q^2/ϵ_r . This nuclear-nuclear interaction energy is reported in the standard output of a CRYSTAL calculation. The value of ϵ_r in equation 2 can either be obtained from experimental results or calculated directly using CRYSTAL [8, 9]. The second term in equation 2 is due to the interaction between the defects and the background charge. The analytical calculation of the second term in equation 2 is not straight forward, hence it is often easier to obtain it numerically. In many cases, however, this term will be small enough to be neglected. The third term scales as $1/V^{5/3}$ and can almost always be neglected. In sections 5.1 and 5.2 the effect of including the first and second order terms in the calculation of defect energies are investigated.

5.1. Example 1: He^+ in a vacuum

The energy of an He^+ ion in a periodic cubic array was calculated for increasing cell size. After accounting for the electrostatic interactions described by equation 2, the energy of the periodic system should equal the energy of the isolated ion. For comparison, the energy of an isolated He^+ was calculated using CRYSTAL with no periodic boundary conditions. The difference in energy between the isolated He^+ ion and the periodic system, before and after accounting for the first order electrostatic interactions, is plotted in figure 2a, second order corrections are also included in figure 2b. A cubic cell of length 2\AA leads to a total energy per He^+ ion that is more than 10 eV smaller than the energy of an isolated He^+ ion if the electrostatic corrections are not taken into account. After subtracting the energy given by the first term in equation 2 the difference in energy between the two systems is reduced to around 1 eV, applying second order corrections reduces the difference in energy to 0.02 eV.

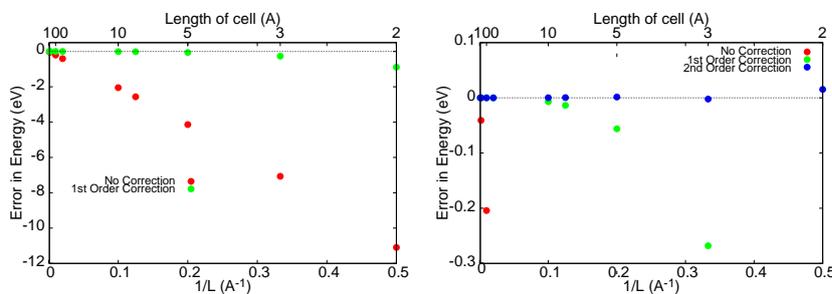


Figure 2. The difference in the calculated energy of an isolated He^+ ion and a periodic system consisting of an He^+ ion in each cell.

5.2. Example 2: V_{Cu}^- and Ga_{Cu}^{2+} defects in $CuGaS_2$

The formation energy of V_{Cu}^- and Ga_{Cu}^{2+} defects as a function of increasing supercell sizes has been calculated. To isolate the purely electrostatic effects these calculations were performed without geometry optimisation. The resultant energies before and after applying first order corrections (the first term in equation 2) are shown in Fig. 3. The straight lines in this figure represent the calculated energies for the largest supercell sizes. The addition of first order terms has led to a better convergence of the formation energies of the Ga_{Cu}^{2+} defect than the V_{Cu}^- defect. Analysis of the results reveals that the convergence of the V_{Cu}^- defect energy can be improved by multiplying the pre-factor of the $1/V^{1/3}$ correction term by 1.8. It is likely that this is because additional factors, such as elastic effects, that also affect the convergence of the formation energy [10, 11]. Geometry relaxation of the defects may also lead to changes in the convergence of the defect energies with respect to supercell size. The convergence of the Ga_{Cu}^{2+} and V_{Cu}^- defect formation energies can not be significantly improved through the addition of a $1/V$ correction term. It is notable that the formation energies calculated for the 8 atom supercell

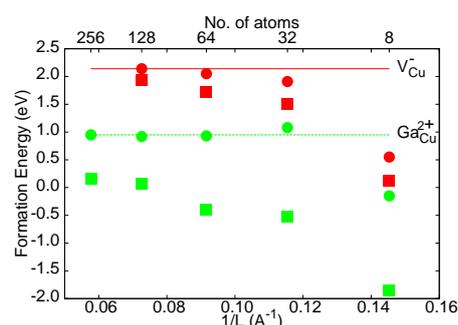


Figure 3. The formation energies of V_{Cu}^- (red) and Ga_{Cu}^{2+} (green) in $CuGaS_2$. The squares denote energies before any corrections are applied and the circles denote energies after first order corrections are applied.

are very poorly estimated, even after first order corrections. It is likely that this is because the defect charge is not fully localised within the supercell.

Ideally, the rate of convergence of a defect formation energy in a fully relaxed system should be analysed for increasing supercell sizes. In most cases, however, it will be computationally expensive to perform such tests. Analysis of our results suggests that the formation energy of a V_{Cu}^- defect in $CuGaS_2$ can be calculated to within an accuracy of 0.2 eV for a 64 atom supercell after including an energy offset correction (section 4) and first order corrections given by equation 2. The formation energy of a Ga_{Cu}^{2+} defect is calculated to an accuracy of around 0.05 eV. Previous studies that have considered a wide range of charged defects show that, after applying first order corrections, a 64 atoms supercell is usually sufficient to obtain charged defect formation energies to within 0.2 to 0.3 eV, and in many cases to within less than 0.1 eV [10].

6. Conclusion

The methodology for the calculation of charged defects has been discussed and illustrated through the use of two example calculations. It is shown that an energy offset correction must be applied to allow a comparison between the energies of charged and uncharged systems. Ideally the convergence of the formation energy of a charged defect should be analysed for increasing system size. It is, however, usually sufficient to perform a single energy calculation on a cell of approximate size $10 \times 10 \times 10 \text{ \AA}^3$ and estimate the energy term due to Coulomb interactions between periodically repeating charged defects to obtain a formation energy of an isolated defect to within about 0.1 eV.

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