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# Transition levels of acceptor impurities in ZnO crystals by DFT-LCAO calculations

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**Abstract.** Large scale *ab-initio* calculations are carried out to study the charge state transition levels of nitrogen and phosphorus impurity defects in zinc oxide crystals using the DFT-LCAO approximation as implemented into the CRYSTAL computer code. It is shown that at a high concentration of defects (close location of defects) their formation energy is underestimated due to a significant delocalization of the charge within the supercell. After inclusion the energy offset correction and defect-defective interaction, the formation energy is improved, in a comparison with that calculated in a large supercell. The optical transition levels obtained by a direct calculation confirm the experimental observation: nitrogen and phosphorus impurities are deep acceptor centers with large formation energy in a charged state and, therefore, cannot serve as the effective source of hole charge. The obtained results are in good agreement with the previous theoretical work, in which other calculation methods were used, and are capable of qualitatively describing the energy characteristics of the charged defects.

## 1. Introduction

In recent years, it became possible to accurately calculate the formation energy of defects in crystalline solids using *ab-initio* methodologies. Although the calculation of neutral defects is relatively straight-forward, the calculation of charged defects is more complicated [1]. In this paper, we present the results of calculations of formation energy of charged defects and their optical transition levels in zinc oxide (ZnO) crystals. A complete description of the proposed method for energy corrections can be found in [2].

Our calculations are performed for ZnO doped with single charged nitrogen (N) and phosphorus (P) atoms. A study of these two acceptor impurities is important for production of an effective *p*-type semiconductors so that such a material can potentially be used in optoelectronics, for example, as a *p*-electrode in LED.



## 2. Theoretical background

### 2.1 Computational details

All calculations are performed using the CRYSTAL computer program [3]. This program calculates the atomic and electronic structure of the crystalline systems using Hartree-Fock methods, density functional theory (DFT), and various hybrid approximations in combination with the atomic basis set of Gaussian-type functions for periodic (3D, 2D, 1D) systems.

To describe the atomic orbitals of the ZnO crystal atoms and absorbed impurity, the following all-electronic basis sets of Gaussian-type functions were chosen: 8-411d1G for the O atom [4] and 86-411d31G for the Zn atom [4], 7-311G [5] for the N atom and TZVP [6] for P atom. To achieve high accuracy of self-consistency for the Coulomb overlap, Coulomb penetration, exchange overlap, first exchange pseudo overlap, and the second exchange pseudo overlap integrals, we have chosen sufficiently convergence tolerances  $10^{-7}$ ,  $10^{-7}$ ,  $10^{-7}$ ,  $10^{-7}$ ,  $10^{-14}$ , respectively. The effective atomic charges were calculated using the Mulliken population analysis [7]. The supercells of different sizes, 32, 72, 108, 192, 300, and 400 atoms were used. To analyze purely electrostatic effects, these calculations were performed without geometry optimization.

The hybrid exchange-correlation functional PBE0 [8] was used. As shown earlier, this functional provides a reliable description of the atomic, electronic structure and the total energy in a wide range of materials [9, 10]. In particular, hybrid functionals, such as PBE0, provide a much better prediction of the semiconductor bandgaps than LDA or GGA approximation.

The formation energy of a defect  $D$  with a charge  $q$  in a system  $X$  is defined as:

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

where  $E_{tot}(D)$  and  $E_{tot}(X)$  are the total energies of the system with and without a defect,  $n_i$  represents the number of atoms of the element  $i$  that are removed from the system when a defect is formed (a negative value for  $n_i$  means the addition of atoms),  $\mu_i$  is the chemical potential of element  $i$ , it is the energy of atoms that are removed (or added) into the system when a defect is formed. The study is performed for dopant rich condition, using molecular  $N_2$  and  $P_4$  as dopant sources. The fourth term  $q(E_F - E_V)$  is a change in the electron energy due to the exchange of electrons and holes with the carrier reservoirs.  $E_F - E_V$  is the Fermi energy relative to the maximum of the valence band of a defect-free system.

To determine the charge state transition levels for various defects, we used the approximation described by Lany and Zunger [11], based on previous studies by Scherz and Scheffler [12], stating that the transition level is the Fermi energy, at which the formation energy of a charged defect is equal to that of a neutral defect:

$$\begin{aligned} E_{tot}(D, q) - E_{tot}(X) + \sum_i n_i \mu_i + q(\varepsilon(q/q') + E_V) \\ = E_{tot}(D, q') - E_{tot}(X) + \sum_i n_i \mu_i + q'(\varepsilon(q/q') + E_V) \end{aligned}$$

thus

$$\varepsilon(q/q') = \frac{E_{D,q'} - E_{D,q}}{q - q'} - E_V \quad (2)$$

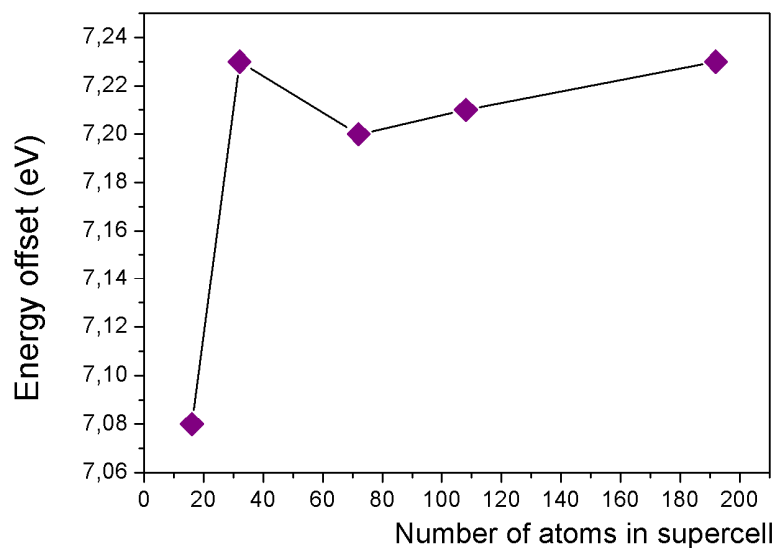
The zero energy reference is set at the top of the valence band,  $E_V=0$ . We have considered cases in which an electronic charge is added to the system, i.e. the state  $q'$  corresponds to a state with an extra electron,  $q+1e$ : this corresponds to a transition from a neutral state to a negatively charged state,  $\varepsilon(0/-1)$ .

However, the problem here is calculation of the total energy of the charged system in eq. 2. The total energy of the charged system has no physical meaning because the interaction must be in balance

with the background charge, that is not taken into account or leveled off in the calculation. This interaction is difficult to calculate in a straight forward way, so we need to find a way to circumvent this problem. Thus, in previous studies of defects in ZnO using the B3LYP functional the difference in total energies was estimated as the difference in single-particle energy eigenvalues [13]. As a next step, Janak theorem was used, according to which the total energy difference associated with vertical transitions is estimated from the shift of the Kohn-Sham eigenvalues after the addition of the electron charge [14]. In this work, we did not apply such schemes but tried to calculate the difference of the total energy in eq. 2 directly. As will be shown below, the usual calculation method gives a good agreement with the results of previous studies.

### 2.2 Energy offset correction

A consequence of using periodic boundary conditions in the calculations of the electronic structure is that the boundary conditions lead to conditional convergence of the Coulomb potential. In the case of neutral systems, the potential and total energy converge to well-defined values under the conditions first described by Ewald [15]. However, the total energy of the charged system can be calculated only up to a certain constant offset [1]. The magnitude of this offset depends on the average potential of the crystal. Offset can be obtained by calculating the change in the total energy of the neutral system when the electron is removed from it. With the increase in the size of the system, the difference converges to a constant value of the offset. The change in the total energy with increasing size of the ZnO supercells before and after the removal of the electron is shown in figure 1. As the size of the system tends to infinity, the energy difference converges to 7.2 eV. The  $E_{tot}(D)$  in eq. 1 includes this offset and must be corrected when calculating the defect formation energy.



**Figure 1.** The change in the energy of a neutral ZnO after one electron was removed.

### 2.3 Coulomb interactions between defects

The total energy of a periodic system that contains a localized charged defect include a defect-defect, defect-background, and background-Coulomb interactions. To calculate the formation energy of an isolated defect, the energy of these interactions must be subtracted from  $E_{tot}(D)$ . All three interactions can be approximated by a multipolar correction of the Makov-Payne [16]:

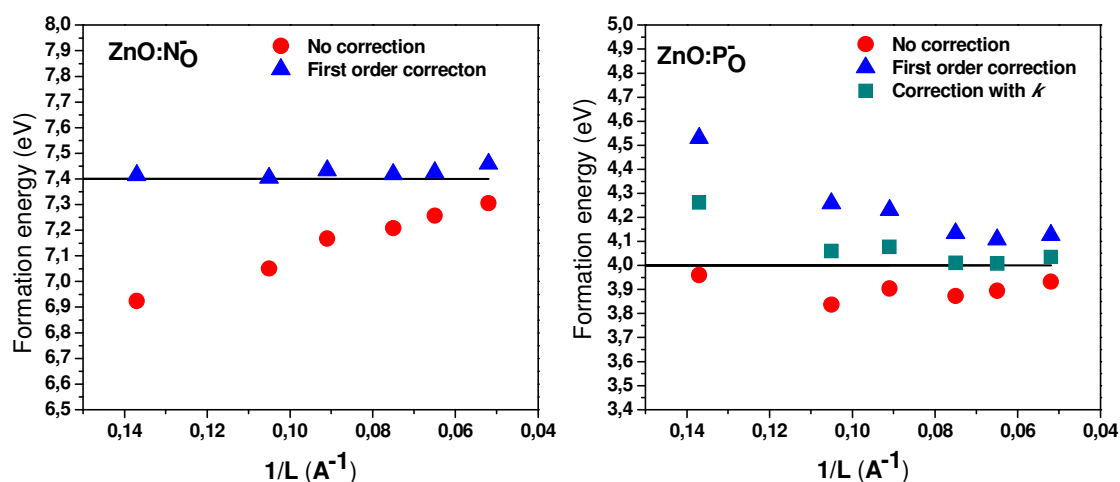
$$\Delta E = \frac{q^2 \alpha_M}{2\epsilon_r V^{1/3}} + \frac{2\pi q Q}{3\epsilon_r V} + O(V^{-5/3}) \quad (3)$$

where  $\alpha_M$  is the Madelung constant depending on the lattice,  $\epsilon_r$  is the relative dielectric constant,  $V$  is the cell volume, and  $Q$  is the quadrupole moment of the defect.

The first term in eq. 3 is the Coulomb defect-defect interaction. It can be trivially calculated using CRYSTAL code, since it is equivalent to the interaction of a periodic system consisting of hydrogen atoms in defect positions multiplied by  $q^2/\epsilon_r$ . The total interaction energy is reported in the standard output of the CRYSTAL calculation. The value of  $\epsilon_r$  in eq. 3 could be obtained from the experimental data or calculated directly using the CRYSTAL. The second term in eq. 2 is related to the interaction between the defects and the background charge of the crystal lattice. The analytical calculation of the second term in eq. 2 is not straight forward, so it is often obtained numerically. However, in many cases this term is rather small and can be neglected. The third term is scaled as  $1/V^{5/3}$  and because of the smallness they can almost always be neglected. In our work the effect of including only the first term in the calculation of the defects energy is investigated.

### 3. Formation energy of N and P atoms in ZnO

The formation energy of defects was calculated as the function of increasing supercells sizes. To analyze purely electrostatic effects, these calculations were performed without geometry optimization. The resulting energies before and after applying first-order corrections (first term in eq.2) are shown in figures 2a,b. The solid lines in this figure represent the calculated energies for supercells of large size. The addition of first-order terms led to a better convergence of the  $\text{N}_\text{O}^-$  defect formation energy than for the  $\text{P}_\text{O}^-$  defect – the correction leads to underestimate of the formation energy for the  $\text{P}_\text{O}^-$  defect. It is noteworthy that the calculated formation energies for the smallest supercell with 32 atoms are very poorly estimated for both defects, even after first-order corrections. Most likely, this is due to the fact that the defect charge is not completely localized inside the supercell. In addition, the size of impurity atoms that introduced into the crystal has a large influence on the localization of the charge. Indeed, the covalent radius of the nitrogen atom is comparable with the covalent radius of the replaced oxygen atom (for both  $r=0.78$  Å) and for it a linear convergence of the formation energy is observed to the value in a large supercell of the crystal. In the case of P atom ( $r=1.15$  Å), a strong delocalization of the charge is observed, which leads to an underestimate of the defect-defect interaction. Based on our analysis of the formation energy, it follows that the convergence could be significantly improved, if taking into account the impurity atoms size in the evaluation of the defect-defect interaction by multiplying the first correction term in eq. 3 by  $k=1-(r_{\text{imp}}/r_{\text{host}}-1)$ , where  $r_{\text{imp}}$  and  $r_{\text{host}}$  are the covalent radii of the impurity atom and a replaceable lattice atom. The results of formation energy correction are shown in figure 2.

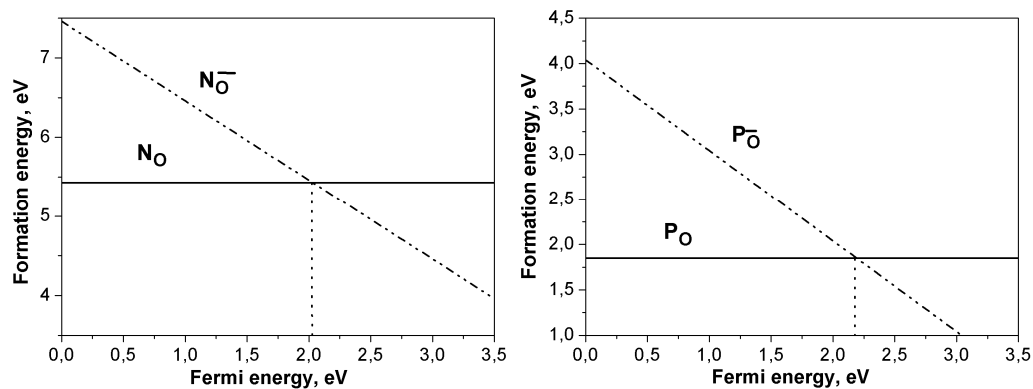


**Figure 2.** The formation energies of (a)  $\text{N}_\text{O}^-$  and (b)  $\text{P}_\text{O}^-$  defects in ZnO crystals.

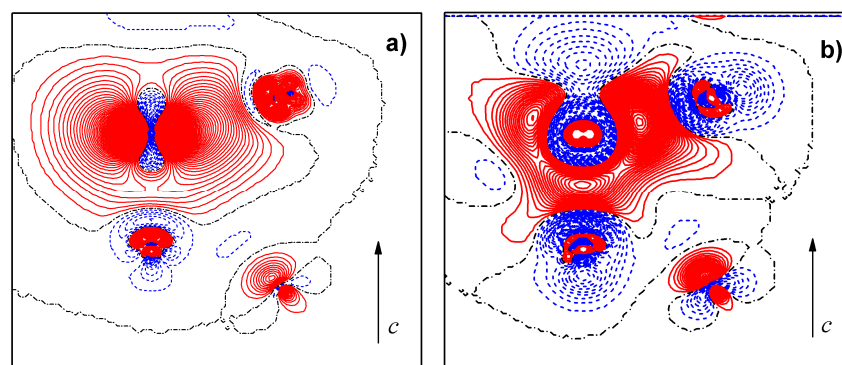
#### 4. Optical transition levels of N and P atoms in ZnO

The formation energy of impurity atoms depending on the Fermi energy under Zn-rich conditions are shown in figure 3. As can be seen, the Fermi energy corresponding to the formation energy at which the charge state transition of the impurity atom from the neutral state to the negative state  $\epsilon(0/-)$  is 2.01 eV and 2.16 eV for the N and P atoms, respectively. These transition energies are in a good agreement with previous studies. For example, in [17] the thermodynamic transition  $\epsilon(0/-)$  for nitrogen was 2.1 eV, whereas in ref.[18] 1.8 eV. In the recent study with the hybrid B3LYP functional [19], the optical transition was 2.16 eV, while the thermodynamic transition was 1.47 eV is obtained.

In contrast to previous suggestions that the group V impurities could serve as a source of hole charge bias, this is likely not the case: For both defects, a high formation energy in a negatively charged state is observed, especially for the Fermi energy near the top of the valence band (figure 3). Even if stabilization of these defects was achieved, when their formation energies are smaller than those for neutral defects, the optical levels of the charge state transition will lie far from the top of the valence band, making them, therefore, *very deep acceptors*. This excludes nitrogen and phosphorus impurities from candidates of an effective source of a hole charge.



**Figure 3.** Formation energies of (a) nitrogen and (b) phosphorus defects as the function of the Fermi energy, calculated with the PBE0 functional.



**Figure 4.** The difference electron density maps  $\Delta\rho(r)$  (the total density of the interface minus the sum of the substrate and adsorbate densities) for (a) nitrogen atom and (b) phosphorus atom. Solid (red) and dashed (blue) isolines correspond to positive (excessive) and negative (deficient) electron density, respectively. The increment of isolines is  $0.001e$  in the interval from  $-0.1$  to  $0.1e$ .

It is shown in figure 4 that the positive charge of neutral  $N_0$  is localized along the chemical bond with Zn ion parallel to the  $c$  axis ( $N_{0||}$ ). A similar results were obtained also in ref. [20] for  $N_{0||}$  configuration with the energy lower by 45 meV in a comparison with hole localized along the bond

perpendicular to  $c$  axis ( $N_{O\perp}$ ). This result also is in good agreement with the results of electron paramagnetic resonance (EPR) [17, 21] and demonstrates a high reliability in the description of the electronic properties of defects based on the hybrid functionals. In case of the P atom, the similar picture was observed, which does not agree with results [20], suggesting the opposite picture - a hole charge is distributed perpendicularly to the  $c$  axis. Unfortunately, we could not verify this result. It maybe possible due smallness of supercell (72 atoms) where charge redistribution is considered. On the other hand, in ref. [20] the chemical potential of molecular  $P_4O_{10}$  was used instead of  $P_4$  in our work, which could cause discrepancy in our results.

## 5. Conclusion

In this work, large scale *ab initio* calculations of the transition levels for V group impurity atoms in zinc oxide crystals were performed using a hybrid density functional method. Owing to the introduction of energy offset correction and defect-defect interaction, we were able to accurately calculate the formation energy of negatively charged defects in a small cell, which were then used to calculate the optical transition levels. We also showed that defect-defect interaction is strong dependent on impurity sizes, and thus addition correction is needed for a reliable description of defect formation energy. The optical transition levels were calculated in a direct way, the obtained results are in good agreement with previous works. Impurity centers remain electrically neutral, even at high Fermi energies (ca. 2.0-2.1 eV) within the band gap, which indicates a high binding energy of the hole charge at the impurity center thus impossible for hole bias. In principle, we should consider the formation energies and, consequently, the transition levels, in a completely relaxed supercell, but due high computational cost of such calculations, it suffices to calculate the formation energy of charged defects in a large supercell and estimate the interaction energy between charged defects, to obtain a formation energy of an isolated defect with accuracy about 0.1 eV.

An analysis of obtained results show that impurity defects of nitrogen and phosphorus are deep acceptor centers, with large formation energy in a charged state and thus cannot serve an effective source of a hole charge necessary for  $p$ -doped ZnO.

Modeling of neutral N and P defects showed also high reliability of the method including charge distribution near the defects. It was shown that the hole charge is localized along the  $c$  axis of the ZnO crystal, which agrees with the EPR measurements.

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