

An effective capacitance model for computing the electronic properties of charged defects in crystals

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ABSTRACT

By examining how a defect within a crystalline material responds to small changes in its charge state, the electronic properties of an ionized defect can be modeled by an effective work function and capacitance. Such an approach leads to a correction formula to the total energy of a charged periodic system and allows a comparison between the electronic band structure of the ionized defect to its corresponding neutral one. The correction formula can be related to the potential alignment method and Makov–Payne correction widely adopted in charged periodic systems. The new approach suggests both an alternative interpretation and improvements to the popular Makov–Payne and potential alignment scheme. P-doped Si, which has a shallow donor level, and an isolated vacancy in crystalline Si, which has a deep defect level within the Si energy gap, are chosen as prototypical systems to demonstrate our method.

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1. Introduction

The ability to examine theoretically the ionization of defects and dopants in semiconductors is critical to the understanding and development of many applications. Semiconductors are intentionally doped with impurities which can be thermally ionized to generate charge carriers. Unintentional structural defects and impurities can trap charge carriers, and the ionizations waste energy as heat for both electronics and photovoltaic materials. A detailed understanding of defect ionization can aid in the design and optimization of such devices. Electronic structure simulations of defects in crystalline materials are accomplished by a supercell approach where the defect is periodically repeated to minimize surface effects. Unfortunately, this poses serious problems to the study of charged defects since the Coulomb interaction is long-ranged leading to a divergence in the total energy of a charged periodic system [1]. The divergence is relieved by introducing a neutralizing jellium background into the supercell [2]. However, there is an

artificial dependence of the ionization energy on the supercell size L owing to the jellium background. One popular attempt to remove such an artifact is the Makov–Payne (MP) correction [3–5], which considers the electrostatic multipole interaction between charged periodic unit cells and arrives at a convenient correction formula for the total energy. The total energy can also be corrected by finite-size scaling, where the L dependence is extrapolated to infer the asymptotic value [4,5]. The interaction between the multipoles can be removed by introducing atom-centered Gaussian charges [6] or local moments to counter the multipole moments [7,8] within the unit cell. For aperiodic (such as molecules) or partially periodic systems (such as nanowires and nanofilms), interaction between unit cells can be reduced by restricting the wave functions [9–11] or truncating the electrostatic potential [12–14] along the aperiodic directions. There are specific schemes that address partially periodic systems [15], such as charged nanowires [16,17] and surfaces [18–21].

In the supercell approach adopted in typical plane-wave codes for electronic structure calculations, the self-consistent electrostatic potential is handled by Fourier transform. Since the supercell is periodically repeated throughout the whole space, the constant term corresponding to the vacuum energy level of the Fourier transform is not defined. While the vacuum level is irrelevant for neutral systems as it is cancelled out in the total energy expression [22], the total energy does depend on its value for a

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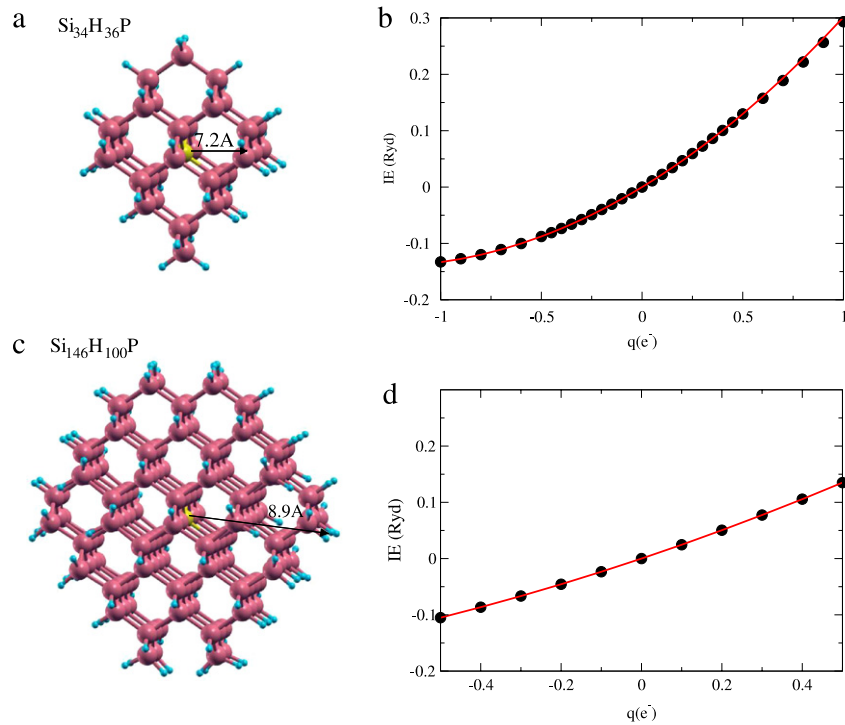


Fig. 1. Ionization of P-doped Si nanocrystals with the confined boundary condition. (a) The geometry of a $\text{Si}_{34}\text{H}_{36}\text{P}$ nanocrystal. The lightly shaded atom at the center is the P dopant, and the dangling bonds of the Si nanocrystal are passivated by small H atoms. The arrow indicates an approximate radius of the nanocrystal. (b) The data points are the ionization energies IE as a function of charge state q calculated using the confined boundary condition. The curve is a least-square fit using Eq. (1). The same plots are depicted for a $\text{Si}_{146}\text{H}_{100}\text{P}$ nanocrystal in (c) and (d).

charged system. The vacuum level can be specified by aligning the electrostatic potential of a small region of the supercell to a physically meaningful value. A case study on ZnO and GaAs suggests that the MP correction together with potential alignment can lead to well-converged formation energies of charged defects after the finite-size effects unrelated to electrostatic interactions are eliminated [23]. Based on an analysis of the electrostatics in dielectric media, Freysoldt et al. derived a more rigorous correction scheme for the electrostatic interaction between supercells and the correction due to the potential alignment [24].

Here we present an alternative perspective of this charged defect problem. A defect in a crystalline material introduces defect levels within the energy gap of a crystalline semiconducting material. For small variations of its charge state, we regard the defect level as an effective electron reservoir. The addition or extraction of an electron from the defect level can thus be characterized by a work function W and a capacitance C . Upon charging, a potential difference builds up within the material and contributes to the ionization energy of the defect. Due to the long-ranged Coulomb interaction between periodic ionized defects, both W and C depend on the supercell size L , and lead to the size dependence of the ionization energy IE of a defect. By examining the trends of W and C with respect to L , a correction to W and C can be inferred and results in a correction for IE . We shall show that the correction due to W is equivalent to the potential alignment, and the correction formula for C can be related to the MP correction. Our scheme not only provides an alternative description of the popular MP scheme, but also suggests that a charged defect has a finite size, which should not be treated as a point charge in a dielectric medium as in the MP correction formula. The capacitances suggested in our scheme can be utilized to align the electronic band structure of the ionized defect against the neutral system. Our scheme is first validated by comparing the ionization energy of a P-doped Si nanocrystal calculated using a confined boundary condition (*i.e.* no periodicity imposed) with that calculated by the

three dimensional (3D) periodic boundary condition. The scheme is then applied to crystalline Si, where the ionizations of a shallow P substitutional dopant and a deep isolated vacancy are examined.

Our calculations are based on PARSEC [25,26], which is a real-space electronic structure code for density functional calculations (DFT) [27,28]. The local density approximation (LDA) using the Ceperley and Alder exchange–correlation functional [29] parameterized by Perdew and Zunger [30] is employed. Since the ionization energy of P in Si is insensitive to spin polarization (the error is less than 0.02 eV), the calculations are not spin polarized. The ion-core potentials are based on the Troullier–Martins pseudopotentials [31] in the Kleinman–Bylander form [32]. The real space grid is set to be 0.7 a.u., which is sufficient to model the ionization of P and Si. Since the goal is to simulate isolated defects, sufficiently large supercells are employed such that only the Γ point is used for the k -point sampling. Atomic structures are relaxed such that the force on each atom is less than 0.001 Ryd/Bohr.

2. Ionization energy of a P-doped Si nanocrystal

To demonstrate the idea, we evaluate the ionization energies IE of a small hydrogen-passivated P-doped $\text{Si}_{34}\text{H}_{36}\text{P}$ nanocrystal as illustrated in Fig. 1(a). For the confined boundary condition, the system is enclosed by a spherical domain where the wave function is set to be zero at the boundary. $IE(q) = E(q) - E(0)$ is found by the difference in the total energies of the nanocrystal between charge state q and the neutral state. The equation

$$IE(q) = Wq + \frac{q^2}{2C} + \Delta E_{relax} \quad (1)$$

describes the trend as depicted in Fig. 1(b). If a small amount of charges ($|q| < 1$) are added or extracted, then the defect level within the Si energy gap can be regarded as an electron reservoir, and the system is effectively metallic in this small q regime. The energetics of charging a piece of metal can be described by

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