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Modeling charged defects inside density functional theory band gaps

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ABSTRACT

Density functional theory (DFT) has emerged as an important tool to probe microscopic behavior in materials. The fundamental band gap defines the energy scale for charge transition energy levels of point defects in ionic and covalent materials. The eigenvalue gap between occupied and unoccupied states in conventional DFT, the Kohn–Sham gap, is often half or less of the experimental band gap, seemingly precluding quantitative studies of charged defects. Applying explicit and rigorous control of charge boundary conditions in supercells, we find that calculations of defect energy levels derived from total energy differences give accurate predictions of charge transition energy levels in Si and GaAs, unhampered by a band gap problem. The GaAs system provides a good theoretical laboratory for investigating band gap effects in defect level calculations: depending on the functional and pseudopotential, the Kohn–Sham gap can be as large as 1.1 eV or as small as 0.1 eV. We find that the effective defect band gap, the computed range in defect levels, is mostly insensitive to the Kohn–Sham gap, demonstrating it is often possible to use conventional DFT for quantitative studies of defect chemistry governing interesting materials behavior in semiconductors and oxides despite a band gap problem.

1. Introduction

Atomic point defects and dopants play important roles in determining materials behavior. Defect chemistry and electronic properties are fundamental to understanding radiation effects and process modeling in semiconductor electronics, active centers in scintillating materials for radiation detectors, or the evolving defect chemistry in nuclear fuels or degradation of nuclear waste. Experimental information of microscopic processes that govern behavior are often incomplete or ambiguous, and atomistic modeling is the best or only means to identify and characterize important atomic-scale processes. Quantum mechanical electronic structure calculations using density functional theory (DFT) [1,2] have emerged as an important tool to probe the microcscopic properties of materials and to quantify the chemistry and electronic properties of point defects. The local density approximation (LDA) [3] and the generalized gradient approximation (GGA) such as the Perdew–Burke–Ernzerhof (PBE) functional [4] are mainstays of density functional investigations. The broad success that these “semilocal” formulations of DFT have enjoyed for structural total energy calculations over several decades is in stark contrast with their generally inadequate description of the fundamental band gap in semiconductors and insulators: the eigenvalue gap derived from the Kohn–Sham (KS) equations of DFT between occupied valence band (VB) states and unoccupied conduction band (CB) states underestimates the experimental gap [5]. This is widely recognized as the “band gap problem” in DFT.

The band gap defines the energy scale for charge transition energy levels, or “defect levels”, of defects, and the band gap problem seemingly precludes quantitative predictions of defect levels using semilocal DFT. Defects take different charge states depending upon the position of the Fermi level within the band gap, and the formation energies of defects with net charge are dependent upon accurate representation of charge transitions. Elucidation of any evolving defect chemistry depends on these defect formation energies; reaction energies are just differences of formation energies. The search for an improved description of the band gap has driven the development of more sophisticated functionals. For instance, the broad success of hybrid methods, that combine conventional semilocal DFT exchange with an admixture of explicit Hartree–Fock exchange, to more accurately reproduce the band gaps of a broad sampling of materials [6] has fueled increasing use of these methods, despite their much greater computational demands.

Soon after the innovation of Kohn–Sham (KS) theory [2], the foundation for density functional calculations, Sham and Kohn warned against interpreting the eigenvectors and eigenstates of the Kohn–Sham equations in terms of excitations [7], noting that

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these were mathematical constructions rather than description of single-particle states. These cautions have obvious relevance to the band gap problem and consequently to the computation of defect properties, but are often overlooked in practice and not closely investigated. In this paper, we explore the relationship between the KS gap and defect level computations, using DFT calculations of silicon and gallium arsenide defects to demonstrate that the shortcomings of the KS band gap are not necessarily transferred to shortcomings in defect level calculations. The silicon system is a good proving ground for the methods. Copious experimental data [8] provide quantitative tests of the accuracy of computational approaches for defect levels.

Gallium arsenide, with much less definitive characterization of defects than silicon, is an excellent theoretical laboratory to investigate the relationship of band gaps and defect levels. Nature is not so accommodating as to allow tuning a band gap for a given fixed material, but the GaAs band gap is a much more malleable quantity in theory. The KS gap for GaAs varies over a wide range for different reasonable choices of density functional and well-converged pseudopotentials [9]—pseudopotentials that yield consistent values for lattice constant, elastic properties and formation energies. Comprehensive calculations of intrinsic defects within these alternate theoretical contexts reveals that defect levels computed from total energy calculations using conventional semilocal DFT are not bounded by the KS gap, nor does the range of defect levels in the different contexts exhibit any dependence on the size of KS gap, even for contexts where the KS band gap almost vanishes.

2. Background

In addition to the basic question of the DFT band gap, the more quotidian considerations of computational limitations have impeded theoretical predictions of charged defects and their defect levels. Density functional theory codes for solid state systems are typically constructed to exploit periodic boundary conditions: defects are investigated within the supercell approximation [10], where an isolated defect is represented as an infinite crystal of periodic defects, as schematically depicted in Fig. 1. In the limit of an infinitely large supercell, the supercell calculation approaches the limit of a completely isolated bulk defect, as sufficient bulk-like atoms buffer the interactions between periodic images of the defects. In practice, the computational expense of DFT limits the number of atoms that can be incorporated in these calculations, and the isolation of a defect from its artificial periodic images is imperfect. The simple vacancy in silicon is a classic example illustrating the unphysical artifacts that can result from using smaller supercells: in supercells composed of 64 atoms or less, the lowest energy structure in DFT calculations retains a symmetric tetrahedral configuration rather than the pairing distortion seen in larger supercells [11]. Advances in modern computers and computer codes now routinely enable supercell DFT calculations of several hundred atoms, and these spurious inter-image interactions, at least for neutral defects, are becoming less significant source of errors in DFT simulations of defects.

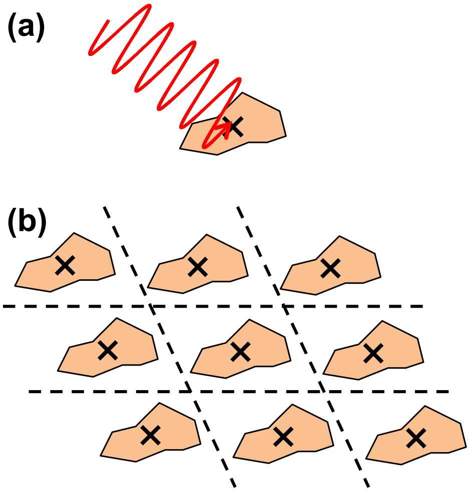

Fig. 1. A schematic depiction of the physics being described and the supercell approximation which is used to model the system in a solid state density functional theory code. (a) A radiation event occurs, causing localized damage such as a point defect. (b) The computational model in density functional theory code approximates this system as a periodic array of damaged regions, in a supercell approximation.

Quantitatively reliable total energy calculations of charged defects, necessary to obtain defect level energies, are more fundamentally hampered by a failure in the supercell approximation: the q/r potentials from periodic images of a defect with charge q corrupt the potential in the local vicinity of the defect, causing the electrostatic potential for a periodic array of net charge to diverge to infinity. This divergence is not mitigated by increasing the supercell size. Reconstructing a viable energy expression for charged defects and charge transitions in the presence of this divergence is a theoretical challenge that has spawned many competing approaches [12–17]. These all adopt the prevalent approximation that neutralizes the net charge in a supercell by adding a flat background charge, or jellium, and discarding the problematic $G = 0$ (net charge) term in the Fourier expansion in solving for the potential [18]. Makov and Payne carefully analyzed the errors in the electrostatic potential and energy within a supercell calculation and fashioned a polynomial expansion in $1/L$, L being a characteristic supercell length, that accurately extrapolates energies for charged atoms and molecules [12]. This analytic approach to fixing the electrostatic energies proved less effective for periodic systems. Methods that replaced the physically-based parameters of the Makov–Payne expansion with an empirical fit, to a series of supercells of increasing size [13] and varying shape [14], have found better success in calculations of bulk defects. Methods that align the electrostatic potential at a point in a defected supercell with the same point in an undefected crystal supercell have also been proposed perhaps culminating in an approach that also incorporates image charge corrections [15] and an approach that explicitly discriminates between long range and short range screening [16], and an approach that carefully distinguishes between polarization and potential alignment while further adding consideration of defect hybridization [17] While these various jellium-based approaches have found greater acceptance, they still exhibit significant uncertainties, attributed to a band gap problem and to the challenge of correctly referencing to a band edge. A particularly careful and useful analysis of the physical and numerical uncertainties in extrapolation methods to compute defect levels can be found in Ref. [19].

An alternative approach to jellium to eliminate the divergence in the electrostatic potential reformulates the solution of the Poisson Equation in the supercell. The local moment countercharge (LMCC) method [20] divides the total supercell density into two pieces: a model charge density that contains the net charge, and a remainder supercell density that, now being net neutral, causes no divergence in a periodic solution for the electrostatic potential. The net charge density is not ignored, its potential is obtained by treating it as an isolated charge, with a specific solution that asymptotically has a q/r tail that decays to zero far from the charge. This incorporates the full asymptotic charge potential within the supercell self-consistently. The potential from this net local charge is truncated at the supercell boundary, thereby not corrupting the potential in adjacent cells, and explicitly avoiding an unphysical