Calculation of electronic properties of point defects with the quantum embedded cluster approach.

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Overview of the invited talk to be presented at the "Multiscale modeling of nanomaterials" Symposium of the International Conference on Computational and Experimental Engineering and Science 2004 (ICCES'04) at Madeira, Portugal.

In this work, our main aim is to devise a methodological scheme to obtain local electronic and structural properties of point defects within semiconductor materials. To keep focus, we will particularly apply this scheme to defects in chalcopyrites, and take $ZnGeP_2$, one of the simplest ones, as our reference. The importance of this material lies on its non-linear-optical properties, which combined with the appropriate nanostructures can give rise

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to laser properties in the micron wavelengths. To do so, a thorough knowledge of the properties of its defects, both native (vacancies, interstitials, and antisites) and foreign (substitutional or interstitial impurities), is required.

There are two main theoretical approaches to the study of point defects: the supercell and the cluster-in-the-lattice schemes. Both deal with interfacing the local distortion around a defect with the perfect lattice. The supercell method does this by imposing periodic boundary conditions on a large cell containing the defect, and is most appropriate to obtain global properties. The cluster-in-the-lattice technique, on the other hand, deals with the interface by embedding a piece of the crystal containing the defect (the cluster) within a model of the effects of the perfect lattice [1, 2, 3, 4, 5, 6]. In our case, this model is not just a more or less classical potential (as, e.g., in the original Ref. [1]: our model mimics all of the quantum interactions that the lattice imposes into the defect, and is thus a quantum embedding technique. This kind of scheme is better suited to study local properties than supercells. In particular, since it is in fact equivalent to a molecular calculation, it can benefit from the wealth of high-accuracy methods developed by quantum chemists to deal with the electron correlation. This is especially important when spectroscopic properties are involved, which require a much higher level of correlation than current DFT exchange-correlation potentials offer.

A successful embedding model should include several different effects. First, due to the low symmetry of the lattice involved, it should appropriately reproduce the electrostatic potential. It also should take into account the short range repulsion between the atoms in the cluster border and their neighbors within the lattice, that is, the quantum electronic effects. In addition, it should describe correctly the gradual relaxation of the neighboring atoms from the vicinity of the defect into the perfect lattice, both in the electron density and in the nuclear geometry. Since any realistic model must be of a finite nature, we have to address the frontier effects that we are introducing. In fully covalent materials, H-termination of the cluster usually is enough to saturate the valence of the outermost atoms, while in ionic compounds there is a complete charge transfer which does not leave dangling bonds. Semi-ionic compounds like the chalcopyrites suffer from both problems, but we will show how to surmount them by using partial ionic charges.

To model our system, we will use different embedding elements. First, the electronic LCAO description will use all-electron basis sets optimized in perfect crystal calculations. Then, the perfect crystal electrostatic potential will

be modeled by finite sets of point charges. The short-range confining potential will be described by means of crystal adapted pseudopotentials (caPS, see Ref. [7]). These caPS are extracted from perfect lattice independent atom calculations (*a*iPI, see Refs. [8, 9, 10]), and include the point charge long range potential, a short range electronic Coulomb potential, and two non-local contributions, those of exchange and the overlap or Pauli repulsion. Their great advantage is that these contributions can be cast into the effective core potential (ECP) functional form, and thus be used to describe complete atoms as if they were frozen atomic cores.

To combine this embedding elements, we have to devise a multiscale model: the geometric relaxation is clearly dominated by the connectivity, whereas the long range electrostatic potential has contributions from the infinite lattice, and the electron density relaxes under the influence of the two previous elements. Thus, an onion-like model is seen to be the most efficient. Centered at the point defect, it would include a shell of geometric relaxation which we will truncate at the second neighbors. The next, larger shell, would include fixed-geometry atoms still within the LCAO calculation, so as to allow for a buffer region in which the electronic structure can match the alien density of the defect with the density of the perfect lattice. The lattice embedding potential will in turn be split in two regions: a short range one, including the atoms in contact with the LCAO cluster, will include caPS to model the short range quantum interactions. The long range region will be treated at the coarsest level, that of classical electrostatics: it will mimic the local structure of the electrostatic potentials by means of a finite set of point charges at lattice sites [6], and it will also reproduce the exact periodic crystal contributions over the defect by means of a set of far-away point charges fitted to give the exact values of the potential and all of its first and second derivatives at the defect site.

This multiscale model includes 8 far-away charges, 284 local point charges, 42 atoms described as caPS, 41 atoms within the LCAO electronic structure region, with 1052 electrons, while only the 5 innermost atoms (the defect and its nearest neighbors) are included in the geometry optimization.

To test for the convergence of all the embedding contributions, we have calibrated our model with so-called self-embedding calculations, in which we take a piece of the perfect crystal and describe it with our model. The model is correct in as much as it reproduces the properties of the perfect crystal, in particular its electron density distribution, the atomic geometry, and the energy. The above model succeeds to do so even for the low-symmetry P-site

in $ZnGeP_2$, and thus it will be used in the present work.

Using experimental evidences, we found that the interesting defects to compute will mainly be V_{Zn}^-, V_P^+/V_P, S_P^+/S_P, and Se_P^+/Se_P. Here, the paramagnetic defects will be the most important, since their EPR signals are easy to detect and give information about the local environment. Thus, the properties that will be calculated will include: (i) the spin densities over the atoms, responsible for the EPR signal; (ii) the ionization potentials, available through photoluminescence experiments; and (iii) the formation energies of the defects, the main terms controlling their stability. Also, local geometries around the defects will be calculated, as those which minimize the energy.

Since all of our properties involve a large cluster, we have to define them in an appropriate way. Thus, the formation energy of the defects will be calculated as the difference in energies of the defect cluster minus the energy of the perfect lattice cluster, so that all energy contributions within the cluster are canceled except for those introduced by the defect, plus or minus the atomic energies of any atoms excluded or included in the defect formation. The ionization potential with respect to the zero interaction level (the removed electron goes to infinity) will be the difference in energy of the cluster with one electron less minus the original cluster describing the defect. If we also compute the IP for the perfect lattice clusters, we can compute the location of the impurity levels within the band gap without falling into orbital pictures, i.e., we will be computing absolute many-electron energy level differences, as opposed to one-electron energy levels. In order to correct the geometries for any systematic error left, we will give atomic displacements instead of positions, and compute them with respect to the self-embedding calculation, instead of with respect to the perfect lattice positions. Finally, we use the Quantum Theory of Atoms in Molecules (QTAM, see Ref. [11]) to compute basis-set independent charge and spin atomic densities, again correcting for any self-embedding residual errors. Thus, all of the properties obtained are in a reasonable agreement with the experiments.

Acknowledgements

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