Uwe Gerstmann, *Influence of lattice relaxations on excitation energies and hyperfine parameters of paramagnetic defect states*.
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Abstract

In this work, *ab initio* calculations of deep defects in semiconductors using the LMTO-ASA Green's function method are presented. Conserving the so-called *Atomic Spheres Approximation* (ASA), the formalism was extended to predict local lattice relaxations around a defect — a treatment which was so far expected to be impossible. In the first part of this work, isolated vacancies in SiC and diamond are discussed as reference problems: Minimizing the total energy, the *extended* LMTO-ASA approach is shown to be able to predict Jahn-Teller distortions. In addition, the extension of the method leads to an improvement of the calculated hyperfine interactions of paramagnetic defect states. Previously observed discrepancies between theory and experiment for the interactions at the nearest neighbor ligands nearly vanish for the relaxed structures. The variation of the calculated ligand hyperfine parameters can qualitatively be explained and easily understood within a simple hybridization model.
As a consequence, in diamond, additional hyperfine splittings observed in the experiments and usually assigned to the next nearest neighbor atoms must be unambigously reassigned to the fifth shell of ligands instead.
In the second part of this work, excitation energies and hyperfine parameters of (also excited) defect states of color centers in diamond (various nitrogen-vacancy complexes) are calculated using the *extended* LMTO-ASA method in the framework of the local spin-density approximation (LSDA) of density functional theory (DFT). Using the relaxed geometries, hyperfine interactions of excited states are obtained in the same agreement with the experiments as for ground states, and the excitation mechanism of the neutral vacancy in diamond can be quantitatively explained.
Some defect states cannot be described by one LSDA-configuration only. In these cases, configuration interactions (CI) which are beyond LSDA, have to be taken into account. Thus, the calculation of correct total energies is not possible. Nevertheless, using *one* LSDA-configuration the calculated hyperfine parameters are already in nice aggreement with experiment if this configuration describes at least the correct many-particle symmetry of the defect state.
This is also shown for the negative vacancy in silicon, which has been thoroughly investigated in the past. Since it turns out to be necessary to take into account the lattice relaxation of a larger environment of the vacancy, a combined approach is used: The relaxed structure is obtained using an established supercell approach. Then, using the *extended* LMTO-ASA method the hyperfine parameters are calculated for this structure. As a result of this work, efficient methods are available to investigate the *influence of lattice relaxations on excitation energies and hyperfine parameters of paramagnetic defect states*.

Keywords

density functional theory, excited states, LMTO-ASA-method, Green's functions, defects, lattice relaxation, hyperfine interaction, diamond, SiC, silicon