

Christof Köhler, *Berücksichtigung von Spinpolarisationseffekten in einem dichtefunktionalbasierten Ansatz*.  
PhD Thesis (in german), Department of Physics, Faculty of Science, University of Paderborn, Germany (2003).  
155 pages, 36 figures, 23 tables.

## Abstract

In this work developments of a density-functional based Tight-Binding approach (DFTB) are presented. Starting from the Kohn-Sham approach to spin-density-functional theory (KS-DFT) an approximate, Tight-Binding like total energy expression including charge-density and magnetization-density fluctuations up to second order is obtained. Tests of the description of total energies, geometries and single-particle energies of selected small molecules show good qualitative agreement of the spinpolarized DFTB (SDFTB) results to spin-density-functional data in the local spin-density approximation (LSDA).

The focus of the second part of this work is on a central quantity of KS-DFT, the spin-densities themselves. Isotropic hyperfine coupling constants (hfcc) of protons, carbon and nitrogen in organic molecules are obtained. These are compared to experimental data as well as to theoretical results within the KS-DFT. For the 168 protons considered an accuracy comparable to KS-DFT results is found. For the heavier carbon and nitrogen atoms a somewhat lower accuracy compared to the reference results is apparent which can be attributed to the influence of the core electrons. However, overall a very good qualitative agreement to spin-density-functional results is observed.

Furthermore isotropic hfcc's of paramagnetic defects in bulk-semiconductors have been calculated. Very good qualitative agreement to KS-DFT data within the LSDA can be confirmed for the vacancies in diamond and silicon. Qualitative differences are observed for the carbon and silicon vacancies in 3C-SiC. However, these can be largely attributed to basis set effects and the restricted self-consistency of the SDFTB method. Results for an anti-site vacancy defect complex in 6H-SiC in the unrelaxed and relaxed geometry in two different charge states are again in good qualitative agreement with the LSDA. Therefore, the discrepancies for the vacancies in 3C-SiC can be regarded as isolated cases.

Both, the data for the organic molecules and for the defects in semiconductor bulk show that spin-densities and the exchange couplings of the unpaired electrons to the core molecular orbitals obtained from spinpolarized DFTB are in good agreement to high level KS-DFT data. This opens the door for further applications of the SDFTB method in the field of paramagnetic resonance.

In the third part of this work the results of the first application of a self-consistent DFTB approach to transition-metal clusters are presented. Here, a new approach to search the potential hypersurfaces with inclusion of spinpolarization effects has been developed. New energetically favourable cluster structures have been identified. In addition to geometries and binding energies the magnetic moments of iron clusters have been calculated. After extension of the description of charge transfer effects within the DFTB method very good qualitative agreement to LSDA results is observed for clusters up to Fe<sub>17</sub>.

Building on these results the potential hypersurfaces of clusters from Fe<sub>18</sub> to Fe<sub>32</sub> have been sampled with an accuracy comparable to the LSDA using a genetic algorithm for the first time. The structural evolution has been characterized. The magnetic moments show an overall decrease with two maxima at Fe<sub>25</sub> and Fe<sub>31</sub>. The data for clusters with 2 to 32 atoms confirms that the transition from icosahedral structures to non-icosahedral ones at Fe<sub>13</sub> with its strong effects on the magnetic moments is unique in this size range.

In agreement with LSDA data a non-ferromagnetic spin arrangement has been calculated for the Fe<sub>13</sub> icosahedron with the SDFTB method. This is also the case for the Fe<sub>55</sub> Mackay icosahedron, here a complex non-ferromagnetic spin structure is obtained. While the magnetic moments of the clusters up to Fe<sub>32</sub> are in agreement to experimental data, very small magnetic moments for Fe<sub>54</sub>, Fe<sub>55</sub> and Fe<sub>56</sub> are obtained depending on the spin arrangement which are not in agreement with experimental findings. This makes it clear that further studies with inclusion of a non-collinear approach to the magnetic properties are necessary in future applications of the SDFTB method to clusters in this size range.

## Keywords

Density-Functional Theory, Tight-Binding, electronic paramagnetic resonance, magnetic properties, transition metals, clusters, spinpolarization