THEORY OF MAGNETIC IMPURITIES IN OXIDES. COMPLEX PROBLEM, PRAGMATIC SOLUTION

Gianfranco Pacchioni
Dipartimento di Scienza dei Materiali, Università Milano Bicocca, 20125 Milano
e-mail: gianfranco.pacchioni@unimib.it

Dopants in insulating and semiconducting oxides are of fundamental importance for the design of new materials and often result in the presence of holes or electrons trapped at particular sites with the formation of polarons. The proper identification of these paramagnetic centres is crucial for the understanding of the optical, magnetic, photocatalytic and transport properties of oxides but the proper description of the electron and hole localization represents a challenge for theory. The nature of magnetic impurities can be studied by comparing DFT calculations using hybrid functionals and electron paramagnetic resonance, EPR, measurements. We will provide some historical perspective on the description of holes in the O 2p valence band of SiO2 as a paradigmatic example of interaction between theory and experiment. Then we will discuss N-dopants in TiO2, ZnO, SnO2, ZrO2 and MgO. Here nitrogen can enter as interstitial or can replace an anion in the material leading to isolated magnetic defect centres. Also in this case a comparison with EPR data allows one to assess the accuracy of the DFT calculations. At high N-dopant concentrations the occurrence of a magnetic ordering has been suggested in some of these materials, which implies the existence of magnetic interactions between the isolated defects. While the use of hybrid functionals allows one to properly describe the nature of isolated magnetic defects in oxides, no magnetic ordering is predicted at this level of theory for the dopant concentrations used in experiments. The problems related to the theoretical treatment within DFT of magnetic impurities in insulating and semiconducting oxides are discussed.