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10. Creating Metamaterials at the Nano-scale

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The fact that the founding papers of Density Functional Theory are among the most cited papers ever, testifies for the importance of Quantum Mechanics and its (often) counter intuitive features in characterizing many-particle systems at a nano and sub-nano scale. Density Functional Theory has enabled one to use the computer to predict quantitatively several of the properties of the aforementioned many-particle systems. The prediction of new materials, often exhibiting meta-stability, is one of its distinctive features. In this lecture we will discuss a new class of meta-materials which, being silicon based, exhibit properties which in no way resemble those of its main constituent. In particular, we will discuss the structural and electronic properties of new materials of the form $X@Si_{16}$ (with X=Ti, Zr and Hf) which are predicted to be (meta) stable at room temperature and exhibit a remarkable potential as possible high-T_c superconductors.

10.1 Introduction

A fundamental challenge for nanotechnology is to control fabrication with atomic precision in order to assemble new materials with outstanding properties or functions. Modern theoretical and computational methods are already able to predict the properties of such materials. The importance of this has been recognized with the 1998 Nobel Prize award to Walter Kohn for his development of the Density Functional Theory [1, 2] (DFT) and to John Pople for his development of computational methods in quantum theory. Today, theoretical predictions are competitive with experimental techniques for controlling single

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molecule chemistry given that the required hardware for performing computer simulations is often orders of magnitude cheaper and may be more effective than experiments. The quantitative predictions based on DFT rely on Quantum Mechanics which itself is on the basis of the technological revolution of the XXth century.

Much of what is considered now the information technology revolution has been dependent of an ever increasing miniaturization of devices based on silicon. The number of transistors that can be placed in an integrated circuit, which is a measure of its computing power, has doubled every 20 months since 1971. However, physical limits to miniaturization of devices based on bulk silicon have already been met in the recent 45 nm generation of devices, where a high-k dielectric material like HfO_2 has replaced SiO_2 as a gate insulator [3] for the first time since the beginning of the integrated circuit. The potential "brick wall" facing Moore's Law [4] has motivated an incredible amount of experimental and theoretical work in the search for alternative materials to bulk silicon. Silicon clusters in particular have been under focus, given that nano-structured materials are known to exhibit very different properties from their bulk counterparts. But contrary to fullerene-like carbon clusters, pure silicon clusters have been found to be chemically reactive, precluding the synthesis of cluster assembled materials [5]. Along another route, early experiments by Beck [6, 7] indicated the feasibility of using metal atoms to nucleate several silicon atoms into stable $X@Si_n$ clusters, of which $X@Si_{16}$ was found to be particularly stable. Recent experimental [5, 8–15] and theoretical [16–24] work has confirmed these results for a variety of mixed metal-silicon sandwich [8, 25] and cage [16, 17, 23, 24] clusters, and a special class of clusters with stoichiometry $X@Si_{16}$, with X a metal atom, has been identified [16] as especially stable by means of ab-initio computer simulations. In particular, the stability of $X@Si_{16}$ (X=Ti, Zr, Hf) nano particles has been confirmed experimentally [13], via selective formation of neutral gas phase clusters, using a dual laser vaporisation technique of pure metal and pure silicon targets in an inert helium atmosphere. An additional experimental confirmation of the synthesis of these nano-particles has been reported recently using a mag-