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A Systematic Search for the Global Minimum Structures of Cs, Sn and Au Clusters and Corresponding Electronic Properties

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Abstract

Clusters of atoms or molecules form the building blocks of nanoscience and are regarded as a new type of material, as they constitute a bridge between microscopic and macroscopic forms of matter. The experimental and quantum theoretical study of structures, chemical and physical properties and reactivities of nanoclusters represents an innovative and very active field of research, which has resulted in a wide range of applications.

Independent of the model used to describe the bonding in these clusters, one of the prime objectives is to find the geometrical arrangement of the atoms or molecules, for a given cluster size, which corresponds to the lowest energy on the potential energy hypersurface, the global minimum. In order to find such an arrangement, a density functional theory based genetic algorithm code, which is rooted in the Darwinian evolution concept of the survival of the fittest, is developed and utilized to systematically search for the global minimum isomers of homo-nuclear clusters consisting of up to twenty atoms of cesium, tin, gold and of nine atoms of copper. The performance of this algorithm is excellent as numerous energetically lower-lying cluster isomers (compared to those reported in the literature) are found. Extensive valence basis sets together with energy-consistent scalar-relativistic pseudopotentials are employed to optimize the geometry of these clusters and to calculate their electronic properties accurately at the density functional level of theory. Moreover, in collaboration with the Technische Universität Darmstadt, the mean static polarizability of tin clusters are measured by a beam deflection method. The qualitative agreement between measured and calculated dipole moments and static electric dipole polarizabilities of tin clusters up to twenty atoms is satisfactory, thus confirming the accuracy of the theoretical models used in this work. Furthermore, the performance of density functional theory in the field of metallophilicity is investigated for dimeric and trimeric [X-M-PH_3] compounds (X = Cl, Br, I; M = Cu, Ag, Au) and it is found that the metallophilicity decreases down the group 11 elements of the periodic table of elements.

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