Some Considerations on "Isoarithmic" and Isoelectronic Clusters

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We briefly summarize trends in the structural and electronic properties of small clusters of Na, Mg and Si. In particular, the validity of the spherical jellium picture is discussed and the applicability of the concepts used to classify magic and non-magic number clusters in alkali metals is examined for other systems.

Introduction

One of the ultimate goals of the theoretical investigation of small clusters is to provide a simple scheme for the classification of their structural as well as their electronic properties. One of the first steps in this search is the study of general trends, which should lead to the identification of valuable classification parameters. While in the study of solids one usually aims at (and can restrict oneself to) classifying the structural properties of isoelectronic systems [1], in the case of finite-size aggregates we are confronted with two — most of the time — distinct problems, namely the classification of the equilibrium structures of clusters with the same number of atoms (which we define as "isoarithmic") and the classification of the electronic properties of isoelectronic clusters. In either of them, the question arises, "what special characteristics do the magic-number (MN) clusters have?" Clearly, this whole project is quite formidable. A large data base is also required before one can start to build such a general and simple scheme.

In this paper, we shall discuss our findings for a still restricted data base, i.e., some microclusters of Na, Mg, Al and Si, which were obtained with the Car-Parrinello method [2,3].

Clusters with the Same Number of Atoms

In the search for trends in the physical properties of aggregates with the same number of atoms, we have considered the 13-atom clusters of Na, Mg, Al and Si in detail [4]. The low-energy patterns presented indeed no common characteristics, apart from the fact that non-crystalline exotic structures were highly favored over crystalline arrangements. While only pentagonal rings were found for the multitude of quasi-degenerate isomers of Na13, hexagonal rings were also observed in Mg13. The pentagonal motif had indeed been previously identified as a characteristic feature of the structures of sodium microclusters [5]. While for Na, Mg and Si the icosahedron turned out to be highly unstable, for Al13 a slight Jahn-Teller induced
distortion was able to stabilize an icosahedron-like geometry. The reason for this can be understood in terms of the spherical jellium model, for which 40 electrons correspond to an electronic shell closing. In Al$_{13}$ the number of valence electrons is 39 and thus corresponds almost to the shell filling. In fact from experiments the anion Al$_{13}^-$ can be classified as a MN cluster [6]. Si$_{13}$ is also observed to be magic, in the sense that it is particularly unreactive to several molecules [7]. In contrast with previous predictions [8] of an icosahedral structure that could explain this special inertness, we find that it cannot be simply explained in terms of a particularly rigid and compact atomic configuration. The low-energy structures are, however, characterized by a seed unit that is either a trigonal prism or a trigonal antiprism.

This type of trend from Na to Mg to Si also manifests itself in our results for the 10 and 20-atom clusters [5,9,10], i.e., the presence of pentagonal rings in Na, of trigonal prisms as central seeds in Si and the character of Mg, being somehow intermediate between Na and Si. The calculated structures of lowest energy [10] for Mg$_{10}$ and Mg$_{20}$ are illustrated in Fig. 1(a) and (b). Mg$_{10}$ is a tetracapped trigonal prism (TTP) similar to Si$_{10}$, while Mg$_{20}$ can be described as a three-layered structure with two capping atoms. These geometries are confirmed by other independent calculations that also used the Car-Parrinello method [11,12].

Clusters with the Same Number of Valence Electrons

In this section we shall consider isoelectronic clusters with 20 and 40 electrons, which correspond to electronic shell closing in the spherical jellium model and to MN clusters for alkali metals. Among the issues of interest, we have considered the following: Is shell closing true for magic-number clusters of elements other than the alkalis? Can we define some — either structural or electronic — simple parameter that distinguishes magic from non-magic number clusters? Is the angular momentum $l$ also a good quantum number for the classification of one-electron