Structure of Mg$_n$ and Mg$_n^+$ clusters up to n = 30

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Received 8 December 2010 / Received in final form 31 March 2011
Published online 17 June 2011 – © EDP Sciences, Società Italiana di Fisica, Springer-Verlag 2011

Abstract. We present structure calculations of neutral and singly ionized Mg clusters of up to 30 atoms, as well as Na clusters of up to 10 atoms. The calculations have been performed using density functional theory (DFT) within the local (spin-)density approximation, ion cores are described by pseudopotentials. We have utilized a new algorithm for solving the Kohn-Sham equations that is formulated entirely in coordinate space and, thus, permits straightforward control of the spatial resolution. Our numerical method is particularly suitable for modern parallel computer architectures; we have thus been able to combine an unrestricted simulated annealing procedure with electronic structure calculations of high spatial resolution, corresponding to a plane-wave cutoff of 954 eV for Mg. We report the geometric structures of the resulting ground-state configurations and a few low-lying isomers. The energetics and HOMO-LUMO gaps of the ground-state configurations are carefully examined and related to their stability properties. No evidence for a non-metal to metal transition in neutral and positively charged Mg clusters is found in the regime of ion numbers examined here.

1 Introduction

The properties of nanometer-sized clusters of atoms are significantly different from those of the isolated chemical species as well as the bulk material, and generally exhibit a strongly non-monotonous size-dependent behavior [1]. Clusters are the ultimate nanostructures, where a fundamental understanding of their properties can be achieved one atom and one electron at a time. They thus open a unique window to study the emergence of the properties of macroscopic matter from its microscopic constituents, and have become an active field in basic research. Nanostructured materials also hold, due to low dimensionality and unique composition, the promise of technological applications reaching as far as clean and sustainable energy, reactions, and catalysis [2,3].

The transition from microscopic to macroscopic behavior is particularly obvious for clusters of atoms that are bound by covalent bonds at small atom numbers, but are metals in bulk quantities. These must, at some point, undergo a transition to metallic behavior.

The history of the examination of these clusters is long; we take a fresh view for a number of reasons: one is that we present here the first large-scale application of limeres [4], a new open source density functional theory (DFT) package specifically designed for cluster calculations. The method is formulated entirely in real space. It thus avoids any basis set bias and is particularly suited for modern parallel computing environments [5–7]. Due to its efficiency, the method allows to find ground state configurations and low-lying isomers of fairly large clusters by unrestricted minimization of the total energy in the whole configuration space, using Langevin-Monte-Carlo and/or steepest descent annealing procedures. It thus also eliminates a possible bias due to the choice of a certain symmetry or starting configuration that is present in more restricted minimization schemes. Our second objective is to prepare for studying the influence of a quantum fluid matrix on the formation and structure of metallic clusters in the near future.

The main thrust of this paper is to present a detailed and systematic characterization of neutral and singly ionized magnesium clusters of up to 30 atoms. We also discuss some sample calculations for smaller sodium clusters, mostly for the purpose of studying electron localization. All calculations have been performed in the framework of spin-density functional theory (SDFT), using the Perdew-Wang exchange-correlation functional [8] and local [9,10] as well as norm-conserving non-local pseudopotentials [11] to treat the core electrons. In addition to the spatial structures of the ground state configurations and low-lying isomers, we also report binding energies, ionization energies and fragmentation energies as well as the HOMO-LUMO gap for all clusters. Details of the computational method are given in Section 2.
We have chosen to study mostly Mg$_n$ and Mg$_n^+$ clusters for a number of reasons: the simpler analog, Na$_n$ clusters, has been studied extensively, see, for example, reference [12] for a recent review as well as references to earlier work. Although there are still some open issues [13], Na$_n$ clusters are reasonably well described by a simple jellium model, in particular energetic quantities like magic numbers are well reproduced. In Mg$_n$ clusters, electrons are more strongly localized and, hence, a jellium model is less appropriate. Comparing Mg$_n$ and Na$_n$ clusters can therefore tell us about the consequences of electron localization.

A striking feature is that Mg$_n$ clusters evolve, with increasing ion number $n$, from molecule-like complexes bound by covalent bonds to a bulk metal where the valence electrons are delocalized. For Mg clusters in helium, this non-metal to metal (NMM) transition has been reported to occur around $n = 20$ with different experimental techniques [14–16]. Thomas et al. [16], for example, have measured photoelectron spectra of mass-selected magnesium cluster anions, which are related to the HOMO-(HOMO-1) gap. Similar results have been reported for Cd clusters [17]. We note, however, that the experimental evidence of NMM transitions is rather indirect. References [18,19] argue that due to the method of measurement, the observed NMM transition may even depend on the formation process. For a review and discussion, see reference [17].

The size range where the NMM transition has been proposed is easily accessible by DFT calculations. We will contribute to the discussion here by studying the development of HOMO-LUMO gaps as a function of cluster size, and by looking at the degree of localization of the electronic density.

Another objective of our work is to prepare for the study of metallic clusters in quantum fluid matrices. Techniques to agglomerate atoms and small molecules in a quantum fluid matrix – specifically, in superfluid $^4$He – have opened a new and versatile way to study the structural, electronic and spectroscopic properties of nanoparticles. The helium droplets can be viewed as ultracold nanoscopic reactors, which isolate single molecules, clusters, or even single reactive encounters at very low temperatures [20]. Clusters of well-defined composition can be formed inside the droplets, and their examination in the millikelvin regime has already given important clues on magnetism and superconductivity on the nanometer scale [21].

There is increasing evidence that the presence of a helium matrix can indeed change the geometric arrangement and other properties of the metal cluster ions. For example, cluster growth by capturing in $^4$He droplets can lead to different isomers, which are not found with other cluster generation techniques and which may be affected differently by the He environment. Such an effect has been observed for clusters bound by hydrogen bridges: cyclic water hexamers were found in helium droplets, but not in vacuum [22]. There is also evidence that the feedback of the surrounding quantum fluid on the much more strongly bound carbon nanotubes is non-negligible; Kim et al. [23] point out that this is basically dictated by Newton’s third law. An unambiguous interpretation of such experiments requires understanding the influence of the $^4$He surrounding the cluster. Also, metallic clusters that are difficult to generate in vacuum can be formed in a fluid matrix [24]. Liquid helium provides an ideal medium for such “nanoreactors” because it is transparent in the entire spectral range from the far IR to vacuum UV, and high spectroscopic resolution, comparable to the gas phase, can be achieved.

Our paper is organized as follows: in Section 2 we give a brief discussion of the computational methods used. The core of our DFT package is a diffusion algorithm for solving Schrödinger-like equations; a more extensive analysis of the method, including convergence tests, a comparison with the implicitly restarted Lanczos method and an assessment of its performance on parallel computing architectures, has been given in reference [7]. A separate program package for solving the Schrödinger equation for the bound states in an arbitrary local potential is also available [25]. Section 3 turns to the results of our calculations. We briefly study Na$_n$ and Na$_n^+$ clusters and determine their structure and energetics. A somewhat unexpected feature is that local pseudopotentials predict a distorted ground state configuration of Na$_4$. We then turn to our discussion of Mg$_n$ and Mg$_n^+$ clusters. We present results for the ground state configuration, energetics, and stability of these systems and examine the appearance and origin of “magic numbers”. The concluding Section 4 gives a brief summary of our findings.

## 2 Computational methods

### 2.1 Spin-density functional theory

Spin-density functional theory [8] maps the solution of the interacting many-electron problem onto that of a non-interacting auxiliary system, which is described by the Kohn-Sham equations,

$$\left[\frac{\hbar^2}{2m} \nabla^2 + V_{KS}[(\rho\sigma)](\mathbf{r})\right] \psi_{\sigma}^j(\mathbf{r}) = \epsilon_{\sigma}^j \psi_{\sigma}^j(\mathbf{r}), \quad (1)$$

$$\rho(\mathbf{r}) = \sum_{\sigma} \sum_j n_{\sigma}^j |\psi_{\sigma}^j(\mathbf{r})|^2 \equiv \sum_{\sigma} \rho_{\sigma}(\mathbf{r}). \quad (2)$$

These are non-linear Schrödinger equations for a set of single-particle wave functions $\psi_{\sigma}^j(\mathbf{r})$ in an effective potential $V_{KS}[(\rho\sigma)](\mathbf{r})$, where $\sigma$ denotes the spin index and $n_{\sigma}^j$ is the occupation number of the state $j, \sigma$. The effective potential

$$V_{KS}^\sigma[(\rho\sigma)](\mathbf{r}) = V_{\text{ext}}(\mathbf{r}, \{\mathbf{R}_i\}) + V_C[\rho](\mathbf{r}) + V_{SC}[(\rho\sigma)](\mathbf{r}) \quad (3)$$

consists of the external potential $V_{\text{ext}}(\mathbf{r}, \{\mathbf{R}_i\})$ describing the interaction of the valence electrons with the ion cores located at the positions $\{\mathbf{R}_i\}$, the Coulomb term

$$V_C[\rho](\mathbf{r}) = \int \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \rho(\mathbf{r}') \, d^3\mathbf{r}', \quad (4)$$