**Ab initio** calculation of neutral and singly charged Mg\(_n\) (\(n \leq 11\)) clusters

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**Abstract**

Under generalized gradient approximation (GGA), geometrical structure, size dependence of stability and electronic properties of neutral Mg\(_n\), singly charged cationic Mg\(_n^+\) and singly charged anionic Mg\(_n^-\) clusters consisting of up to 11 atoms have been studied systematically by ab initio method within the norm-conserving pseudopotentials. In addition to the electronic shell effects, the "closed" geometrical structure can also enhance the stability of the clusters. The enhanced stability for the cationic cluster resulted from the removal of an antibonding electron is larger than that for the anionic cluster by promoting an extra electron to occupy a bonding orbital. The density of states (DOS) shows the increase in interaction between valence and unoccupied states leads to an increase in s–p hybridization.

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1. Introduction

Metal clusters are promising catalysts, building blocks for electronic devices and other functional nanoscale materials due to their pronounced difference in various properties compared to their bulk counterpart [1–5]. The addition or removal of a few electrons produces little change in bulk systems; however, such an addition or removal may have large effects in clusters and produces a large change in geometry, electronic and magnetic behavior. As is well known that, the physical and chemical properties of neutral and singly charged clusters are determined by their geometrical structure, so an understanding of the geometrical configuration and electronic properties of the clusters is fundamental for applications of the clusters. Experimentally, metal clusters have been studied using electronic-spin-resonance (ESR) [6], abundance spectrum [7], photoelectron spectroscopy (PES) [8], Knudsen effusion [9] and X-ray photoelectron spectroscopy (XPS) [10], etc. At the same time, various theoretical approaches have also been used to investigate the clusters, such as embedded-atom-method (EAM) [11], pair-potential theory [12], semiempirical n-body potential theory [13,14], molecular dynamics (MD) method [15,16], pseudopotential local spin density (LSD) approximation [17,18] and the first-principles (FP) [19–22], etc. In all of these theoretical methods, the FP is the most precise one.

Magnesium is an element that exhibits a transition from weak van der Waals bonding in the diatomic molecule to metallic bonding in the bulk. Thus, many experimental techniques [7,8,23] and theoretical simulations [16–20] have been used to investigate the geometrical structure, electronic properties and bonding nature of Mg clusters. From the theoretical point of view, Reuse et al. [17,18] explored structural and electronic properties of neutral and charged magnesium clusters (\(n \leq 7\)) using the LSD approximation. Using the density-functional MD method, Kumar and Car [16] calculated the gap between the highest-occupied molecular orbital and the lowest-unoccupied molecular orbital (HOMO–LUMO gap) for neutral magnesium clusters over the size range from 2 to 11 and the jellium-type magic clusters were observed. Lyalin et al. [20] investigated evolution of the optimized structures and electronic properties of neutral and singly charged cationic magnesium clusters with increase in cluster size. However, there still exists debate over theoretical minimum energy structures even for the smaller clusters. This problem is further compounded by the difficulty of direct experimental
In this paper, we present the \textit{ab initio} calculation within the norm-conserving pseudopotentials for the neutral Mg\textsubscript{n}, singly charged cationic Mg\textsubscript{n}\textsuperscript{+} and singly charged anionic Mg\textsubscript{n}\textsuperscript{−} clusters consisting of up to 11 atoms. Address the issue of the enhanced stability and changing of geometrical structure due to addition or removal of a single electron from a neutral cluster. The remainder of the paper is organized as follows. In Section 2, we describe some details about our \textit{ab initio} calculations. In Section 3, we present the binding energies per atom, the second differences of total energy, the HOMO–LUMO gap, and density of states (DOS) of some Mg clusters with increase size, and compare our results with available experimental and theoretical results. Finally, Section 4, we draw an explicit conclusion about our research.

2. Method

All calculations were performed within the framework of density functional theory (DFT) using a basis set consisting of plane waves, as implemented in the Cambridge Serial Total Energy Package (CASTEP) \cite{24}. The electron–ion interactions were described by means of \textit{ab initio} norm-conserving pseudopotentials \cite{25}, and electron exchange and correlation energies were calculated with the Perdew–Burke–Ernzerhof (PBE) formulation of the generalized gradient approximation (GGA) \cite{26}. The specific simulated strategy is as follows: we adopted periodic boundary conditions and place an \textit{n}-atoms cluster in a cubic box with edge length of 20\text{"}. The size of the cell is large enough so that the interaction between the cluster and its periodic images is negligible. The structure was optimized with the Broyden–Fletcher–Goldfarb–Shanno (BFGS) method \cite{27}. In the ground state, the electron configuration of the Mg atom is 1s\textsuperscript{2}2s\textsuperscript{2}2p\textsuperscript{6}3s\textsuperscript{2}. The Mg 3s\textsuperscript{2} electrons are treated as valence electrons in the pseudopotential construction while the remaining 10 electrons 1s\textsuperscript{2}2s\textsuperscript{2}2p\textsuperscript{6} are treated as the core electrons. The calculations have been carried out at the \textit{Γ} point, as proposed by Monkhorst and Pack \cite{28}. The kinetic energy cutoff (330 eV) of the plane wave basis was used throughout. The energy tolerance was 5.0 \times 10\textsuperscript{−8} eV/atom, the force tolerance was 0.01 eV/\text{"}, and the displacement tolerance was 5.0 \times 10\textsuperscript{−4} \text{"}. The calculated values were obtained at 0K.

For each Mg cluster with \textit{n} atoms Mg\textsubscript{n}, there are various isomer configurations, with increasing the cluster size \textit{n}; the number of the isomer configurations grows dramatically. Considering molecular point group, we constructed possible initial geometrical structures for each \textit{n}-atom cluster, for examples, for dimer Mg\textsubscript{2}, there is only a linear structure in point group notation D\textsubscript{∞h}; for trimer Mg\textsubscript{3}, in addition to a linear structure D\textsubscript{∞h} there is an equilateral triangle D\textsubscript{3h} as well. All possible configurations of each neutral Mg\textsubscript{n}, singly charged cationic Mg\textsubscript{n}\textsuperscript{+} or singly charged anionic Mg\textsubscript{n}\textsuperscript{−} cluster with \textit{n} from 2 to 11 are optimized with the BFGS method.

3. Results and discussions

The lowest-energy configurations are shown in Table 1 together with corresponding point groups, average interatomic

<table>
<thead>
<tr>
<th>\textit{n}</th>
<th>Mg\textsubscript{2}</th>
<th>Mg\textsubscript{2}\textsuperscript{+}</th>
<th>Mg\textsubscript{2}\textsuperscript{−}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Structure</td>
<td>Point group</td>
<td>\langle d \rangle (\text{&quot;})</td>
<td>E\textsubscript{b} (eV)</td>
</tr>
<tr>
<td>2</td>
<td>D\textsubscript{∞h}</td>
<td>3.4470</td>
<td>0.0691</td>
</tr>
<tr>
<td>3</td>
<td>D\textsubscript{3h}</td>
<td>3.1972</td>
<td>0.1902</td>
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<tr>
<td>4</td>
<td>T\textsubscript{d}</td>
<td>3.0218</td>
<td>0.3871</td>
</tr>
<tr>
<td>5</td>
<td>D\textsubscript{3h}</td>
<td>3.1448</td>
<td>0.3851</td>
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<tr>
<td>6</td>
<td>C\textsubscript{2v}</td>
<td>3.2117</td>
<td>0.4111</td>
</tr>
<tr>
<td>7</td>
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<td>8</td>
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<td>9</td>
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<td>0.6676</td>
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<tr>
<td>11</td>
<td>C\textsubscript{3}</td>
<td>3.0356</td>
<td>0.6676</td>
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bonding distance \( \langle d \rangle \) and binding energy per atom \( E_b \). We can see that, for \( \text{Mg}_2 \) dimer, the calculated interatomic bonding distance \( \langle d \rangle \) and the binding energy per atom \( E_b \) of 3.447 Å and 0.069 eV/atom are in general agreement with the experimental values of 3.891 Å and 0.025 eV/atom, respectively [23] and recent DFT-GGA calculation results of 3.56 Å and 0.07 eV/atom [19]. The most stable structure of \( \text{Mg}_3 \) is an equilateral triangle, whose energy is about 0.083 eV/atom lower than its isomer with a linear structure. This implies that the clusters favor to maximize coordination number. This trend is continued for bigger clusters as well. The lowest-energy structure of \( \text{Mg}_4 \) is a compact tetrahedron, rather than its isomers with linear or planar structure (square or rhombus). This indicates that the transition from planar to three-dimension structure begins. The slightly elongated triangular bipyramid is the most stable structure for \( \text{Mg}_5 \). From \( \text{Mg}_6 \) the dimension structure begins. The slightly elongated triangular structure any more. The ground-state structures of \( \text{Mg}_6 \) and \( \text{Mg}_7 \) are a fused bipyramid and a pentagonal bipyramid, respectively. The former is different from the result of Reuse et al. [18] that the ground-state structure was the square bipyramid octahedron. The ground-state structure of \( \text{Mg}_8 \) can be considered as an atom capped on the pentagonal bipyramid of \( \text{Mg}_7 \). These results are in a good agreement with previous researches [16,19,20]. From \( \text{Mg}_9 \) a new trigonal prism-based structure starts. \( \text{Mg}_9 \) can be obtained by adding one atom to each of the three prism planes. Adding an atom to one of the two triangular faces of the trigonal prism of \( \text{Mg}_9 \) cluster results in \( \text{Mg}_{10} \), while adding another atom to the remaining triangular face of the prism within the \( \text{Mg}_{10} \) cluster leads to the structure of \( \text{Mg}_{11} \).

Table 1 also shows the optimized geometries of singly charged cationic \( \text{Mg}_n^+ \) and anionic \( \text{Mg}_n^- \) clusters. The cationic and anionic dimers are more bound and compact as compared to the neutral dimer. The ground-state structures of singly charged cationic \( \text{Mg}_n^+ \) and singly charged anionic \( \text{Mg}_n^- \) clusters are not very different from those obtained for corresponding neutral clusters. Exceptions are observed for small clusters, where the ground-state geometries of \( \text{Mg}_3^+ \) and \( \text{Mg}_4^+ \) are linear chains due to the Jahn–Teller distortion [29] and that of \( \text{Mg}_6^- \) is a pentagonal pyramid the reason is not clear here.

To quantitatively look into the structures of \( \text{Mg} \) clusters, the average bonding distance \( \langle d \rangle \) as a function of the cluster size \( n \) is shown in Fig. 1, the \( \langle d \rangle \) is defined as

\[
\langle d \rangle = \frac{1}{N} \sum_{ij} d_{ij}
\]

where \( d_{ij} \) is the interatomic bonding distance between the \( i \)th atom and its neighbor \( j \) atom, \( N \) is the count number of \( d_{ij} \). We consider an atom \( j \) to be the neighbor of atom \( i \) if the distance \( d_{ij} \) is smaller than a cutoff radius \( r_c = 1.2a = 3.85 \) Å, \( a \) is the lattice constant of the bulk \( \text{Mg} \).

The features that deserve particular attention are the following: (1) The evolution of \( \langle d \rangle \) with increasing cluster size presents essential difference for the neutral \( \text{Mg}_n \), singly charged cationic \( \text{Mg}_n^+ \) and singly charged anionic \( \text{Mg}_n^- \) clusters while the size \( n < 6 \), but behaves similarly when \( n > 7 \). This can be understood by considering that the addition or removal of an electron produces little change in a system with larger numbers of the electrons; however, such an addition or removal may have large effects in smaller clusters and produce a change in geometry. Therefore we can deduce that with the increase of cluster size \( n \) the average interatomic bonding distances of \( \text{Mg}_6^+ \) and \( \text{Mg}_{10}^- \) will gradually close each other and converge to the nearest-neighbor distance of 3.21 Å of HCP lattice [30]. (2) The appearance of the minima in the size-dependence curve of the average bonding distance of the neutral cluster at \( \text{Mg}_4 \) and \( \text{Mg}_{10} \) shows that \( \text{Mg}_4 \) and \( \text{Mg}_{10} \) clusters (with 8 and 20 valence electrons, respectively) are more tightly packed than their neighbors. This is resulted from the closure of electronic shells of the delocalized electrons. Compared with the neutral clusters, the evolutions of \( \langle \langle d \rangle \rangle \) for cationic \( \text{Mg}_n^+ \) and \( \text{Mg}_n^+ \) and anionic \( \text{Mg}_n^- \) clusters behave different trends are due to the structural rearrangements.

In order to investigate the size dependence of cluster stability and electronic properties, the calculated binding energy per atom, the second differences of total energy, HOMO–LUMO gap and DOS are shown in Figs. 2–5, respectively, for the ground-state structures obtained above. The binding energy per atom and the second differences of total energy of the neutral \( \text{Mg}_n \) clusters behave different trends are due to the structural rearrangements.

\[
E_b = E_1 - E_n/n
\]

where \( E_1 \) and \( E_n \) are the total energy, non-interacting and interacting electronic states.
where $D$ is the singly charged cation and $D$ is the singly charged anion.

The results of Akola et al. [19] for the neutral Mg are well agreed with the mass spectrum experiment [8].

From Fig. 2 we can see that the binding energy per atom for the neutral Mg clusters increases nonmonotonically with cluster size, similar trend was also obtained by Akola et al. [19]. This is because both the average coordination number and the effective hybridization increase with increasing of the cluster size and thus consequently enhances the binding energy. Up to the bulk Mg, it is with the highest coordination number and s-p hybridization and thus the highest binding energy. This indicates that the promotion of electrons from 3s to 3p states is an important mechanism responsible for the bonding in both the cluster and the metal. It is noteworthy that, even for the largest cluster Mg$_{11}$, the binding energy per atom of 0.6676 eV is only 44.2% of the bulk value of 1.51 eV [31]. This fact confirms the conclusion on the slow and nonmonotonous evolution of metallic properties in Mg clusters. Similar to neutral Mg$_n$ clusters, the binding energies per atom dependent on the cluster size for both singly charged cationic Mg$_n^+$ and singly charged anionic Mg$_n^-$ clusters also present a nonmonotonically increasing behavior. Compared with the binding energy of the singly charged cationic Mg$_n^+$ and singly charged anionic Mg$_n^-$ clusters with identical cluster size $n$, the binding energy of the neutral clusters is found to be very small. The reason is that the neutral Mg clusters have full filled 3s$^2$ electronic shell while the singly charged Mg$_n^+$ and Mg$_n^-$ clusters always have an open electronic shell due to their odd number of the valence electrons. The similar low binding energy has been seen in other neutral clusters too, e.g. Be [32] and Mn [33,34] clusters. The fact that the binding energy of the cationic cluster is larger than that of an identical size $n$ anionic cluster indicates the increasing stability for the cationic cluster resulted from the removal of an antibonding electron is larger than that for the anionic cluster by promoting an extra electron to occupy a bonding orbital.

Fig. 3 shows the evolution of the DOS for the most stable neutral Mg$_n$, singly charged cationic Mg$_n^+$ and singly charged anionic Mg$_n^-$ clusters, Mg$_4$ and Mg$_{10}$ clusters. Since Mg$_4$ and Mg$_{10}$ clusters possessing 8 and 20 valence electrons, according to the spherical jellium model [35–37], which can fill up to the close electronic shells 1s$^2$3p$^6$ and 1s$^2$3p$^6$3d$^{10}$2s$^2$, respectively, and would lead to a high stability. The high stability of Mg$_4$ is resulted from its “closed” pentagonal bipyramidal structure. Structured by such a building block, the first complete Mg$_{13}$ icosahedra cluster has also enhanced stability [33]. So in addition to the electronic shell effects, the “closed” geometrical structure can also enhance the stability of the clusters. The local maxima of the second differences of the total energy for Mg$_5$, Mg$_{10}$, Mg$_4$ and Mg$_{10}$ clusters indicate their enhanced stability. The enhanced stability of the Mg$_4$ and Mg$_{10}$ clusters is well agreed with the mass spectrum experiment [8].

From Fig. 3, we find that for the neutral Mg$_n$, clusters, Mg$_4$, Mg$_7$ and Mg$_{10}$ clusters have relative higher stability. Electronic shell effects will be an important reason for the enhanced stability of Mg$_4$ and Mg$_{10}$ clusters. Since Mg$_4$ and Mg$_{10}$ clusters possessing 8 and 20 valence electrons, according to the spherical jellium model [35–37], which can fill up to the close electronic shells 1s$^2$3p$^6$ and 1s$^2$3p$^6$3d$^{10}$2s$^2$, respectively, and would lead to a high stability. The high stability of Mg$_4$ is resulted from its “closed” pentagonal bipyramidal structure. Structured by such a building block, the first complete Mg$_{13}$ icosahedra cluster has also enhanced stability [33].

Fig. 4 shows the HOMO–LUMO gap for the most stable neutral Mg$_n$, singly charged cationic Mg$_n^+$ and singly charged anionic Mg$_n^-$ clusters. Open-squares present the results of Akola et al. [19] for the neutral Mg$_n$ clusters.

Fig. 5 shows the evolution of the DOS for the most stable neutral Mg$_n$, singly charged cationic Mg$_n^+$ and singly charged anionic Mg$_n^-$ clusters. A broadening of 0.1 eV was used for all the clusters. The zero level of energy is chosen equal to the Fermi level $E_F$. For Mg$_2$, Mg$_3$ and Mg$_5$, the HOMO–LUMO gaps are relatively high (2.36, 2.08 and 1.90 eV, respectively); therefore, there is no
interaction of valence electrons with the 3p state. As cluster size increases the HOMO–LUMO gap decreases, the lowest unoccupied state and the highest occupied state are both shifting toward Fermi level $E_f$. This results in an increase in interaction between valence and unoccupied states and, hence, leads to an increase in s–p hybridization. The most stable clusters Mg$_4$, Mg$_7$, and Mg$_{10}$ possess local maxima in the size dependence of the HOMO–LUMO gap and therefore for such clusters s–p hybridization decreases. The DOS for the neutral Mg$_n$ clusters clearly demonstrates formation of electronic shell structure of small Mg clusters in accord with the spherical jellium model [35–37]. Sharp peaks in the energy spectrum of Mg$_4$ and Mg$_{10}$
correspond to the closed electronic shells 1s\(^2\)p\(^6\) and 1s\(^2\)p\(^6\)d\(^{10}\)s\(^2\), respectively.

4. Conclusions

In summary, under GGA, optimized structure, size dependence of cluster stability and electronic properties of neutral Mg\(_n\), singly charged cationic Mg\(_n^+\) and singly charged anionic Mg\(_n^-\) clusters consisting of up to 11 atoms have been studied systematically by \textit{ab initio} method within the norm-conserving pseudopotential. It is demonstrated that the size-dependent stability and electronic properties of neutral Mg clusters are governed by the interplay of the electronic and geometry shell closures. The enhanced stability for the cationic cluster resulted from the removal of an antibonding electron is larger than that for the anionic cluster by promoting an extra electron to occupy a bonding orbital. The DOS shows the increase in interaction between valence and unoccupied states leads to an increase in s–p hybridization.

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