# Density functional theory study of $Mg_2Ni_n$ ($n = 1$–8) clusters*

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The density functional theory B3PW91 with LANL2DZ basis sets has been used to study the possible geometries of $Mg_2Ni_n$ ($n = 1$–8) clusters. For the lowest energy structures of the clusters, stabilities, electronic properties, and natural bond orbital (NBO) are calculated and discussed. The results show that the doped Mg atoms reduce the stabilities of pure Ni clusters. The $Mg_2Ni_2$, $Mg_2Ni_4$, and $Mg_2Ni_6$ clusters are more stable than neighboring clusters. The system appears magic number characteristics. In addition, the hybridization phenomenon occurs, owing to the interaction of Mg and Ni. The result of charge transfer is that Ni atom is negative and the Mg atom is positive. We also conclude that the 3p and 4d orbitals of the Ni atom have an effect on the stabilities of the clusters.

**Keywords:** $Mg_2Ni_n$ clusters, density functional theory, geometrical structures, stability

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## 1. Introduction

Ni, as an important transition metal, is not only used as a permanent magnet material but also used extensively in metallurgy and chemical industry. Nickel and its mixed clusters have attracted much attention.[1–12] Sun *et al.*[13] have studied the equilibrium geometries and the bonding energies of $Ni_n$ ($n = 2$–20) clusters by using an empirical many-body potential and a genetic algorithm (GA). Song *et al.*[14] investigated the magnetic property and electronic properties of the $Ni_n$ ($n \leq 30$) neutral and ionic clusters by using density functional theory (DFT). Adding an appropriate amount of Ni into magnesium metal can significantly change the hydrogen storage property.[15] Experimental and theoretical investigations of Mg–Ni alloys have been reported.[15–17] For example, Jiří and Čermák[15] studied the pure Mg, $Mg_2Ni$ intermetallic, and Mg eutectic alloy (23.5 wt.% Ni). The samples were respectively prepared by ball-milling, compacting, and casting. Structure changes during hydrogenation are also observed. In theory, Prigent and Gupta[16] presented *ab initio* study of the electronic structure of several Mg-based compounds. Ternary compounds of $Mg_2X$ ($X$ = Ni, Si) and YMgNi have been investigated. However, in practical application, $Mg_2Ni$ still has some limitations. For example, the preparation is only available by using mechanical alloying.[15] In this paper, we carry out systematic study on the properties of $Mg_2Ni_n$ clusters up to $n = 8$, and analyze the equilibrium geometries, stabilities, electronic properties, and the natural bond orbital (NBO). Our main purpose is to give a theoretical support to the preparation and application of the Mg–Ni alloy material.

## 2. Computational method

The structure optimizations and energy calculations of $Mg_2Ni_n$ ($n = 1$–8) clusters are computed by using P3BW91 with LANL2DZ basis sets. In this work, all the calculations are performed based on Gaussian03 program package.[18] In searching for the ground-state structures of $Mg_2Ni_n$ ($n = 1$–8) clusters, a large number of initial structures have been considered. These configurations are also investigated under different spin multiplicities. The frequency analysis of all configurations has been taken into account. The structures we chose do not include imaginary frequency. In our calculations, the convergence criteria of energy is $10^{-7}$ a.u., force and displacement are set as $10^{-4}$ a.u./Bohr and $1\times10^{-3}$ Bohr, respectively.

In order to further verify the accuracy of the calculation method, we carry out the calculations of the $Mg_2$ and $Ni_2$ dimers. The bond lengths of $Mg_2$ and $Ni_2$ are 0.3626 nm and 0.2369 nm, respectively, which are in good agreement with the bond lengths estimated at B3LYP/LANL2DZ level[19] (0.3961 nm for $Mg_2$ and 0.2376 nm for $Ni_2$). For MgNi cluster, the bond length is 0.2495 nm. The obtained value is also close to 0.2489 nm computed at B3LYP/TZVP level. The good agreement shows that the method we choose is suitable for describing $Mg_2Ni_n$ systems.

## 3. Results and discussion

### 3.1. Geometry

The calculated results of $Mg_2Ni_n$ ($n = 1$–8) clusters are listed in Fig. 1. The dark spheres represent the Mg atoms, while the light color spheres stand for the Ni atoms. The clusters are designed as *n*a, *n*b, *n*c, and *n*d, where *n*a refers to the ground-state structures and others are related to metastable configurations. The corresponding geometrical parameters of the lowest energy clusters are summarized in Table 1.

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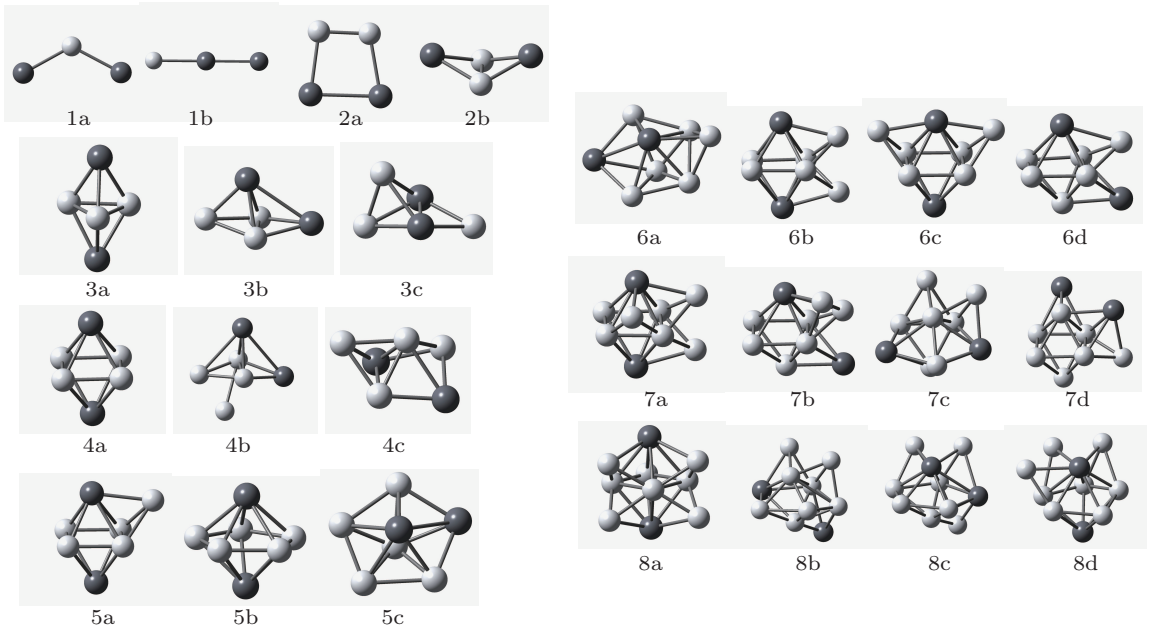



**Fig. 1.** Geometries of $Mg_2Ni_n$ ($n = 1$–8) clusters.

**Table 1.** Geometric parameters and energies of the ground-state structures of $Mg_2Ni_n$ ($n = 1$–8) clusters.

| Cluster | Multiplicity | Symmetry | $E_b$/eV | HLG/eV | $\Delta_2E$/eV | IP/eV | EA/eV |
|---|---|---|---|---|---|---|---|
| $Mg_2Ni$ | 3 | $C_{2v}$ | 0.3861 | 1.7581 | | 5.5418 | 1.2305 |
| $Mg_2Ni_2$ | 3 | $C_s$ | 0.6709 | 2.4112 | –0.1130 | 6.2416 | 0.8120 |
| $Mg_2Ni_3$ | 1 | $D_{3h}$ | 0.8644 | 1.6528 | –1.6043 | 4.6507 | 2.2416 |
| $Mg_2Ni_4$ | 5 | $D_{4h}$ | 1.2608 | 1.7780 | 1.4373 | 6.1166 | 1.8000 |
| $Mg_2Ni_5$ | 3 | $C_s$ | 1.3386 | 1.1739 | –0.5819 | 5.0727 | 2.1534 |
| $Mg_2Ni_6$ | 3 | $C_s$ | 1.4696 | 0.6933 | 2.6254 | 5.3067 | 1.7806 |
| $Mg_2Ni_7$ | 1 | $C_1$ | 1.2799 | 1.3524 | –2.1079 | 2.4505 | 3.7403 |
| $Mg_2Ni_8$ | 1 | $C_{2v}$ | 1.3389 | 1.2495 | | 2.6480 | 3.5682 |

The ground-state configuration of $Mg_2Ni$ cluster is an angular structure, which has triplet spin multiplicity. The energies of singlet and quintet spin multiplicities are higher than those of the ground state by 0.4750 eV and 0.8725 eV, respectively. It has a big difference from the flat triangular structures of pure $Ni_3$ cluster[9] and the linear structure of $MgNi_2$.[19] Beginning from $n = 2$, the system appears three-dimensional configuration. The most stable structure of $Mg_2Ni_2$ cluster 2a is tetragonal structure and two Mg atoms occupy the same side. This geometry also differs greatly from the tetrahedron of $Ni_4$ cluster[9] and the rhombus of $MgNi_3$ in Ref. [20]. Isomer 2b has a three-dimensional form and the energy is 0.2483 eV higher than that of 2a. Starting from the $Mg_2Ni_3$ cluster, all the configurations are three-dimensional (3D) structures. The optimized ground-state structure of $Mg_2Ni_3$ has singlet spin multiplicity. It can be seen as the top atoms of pure $Ni_5$ cluster[9] are replaced by two Mg atoms. The lowest energy structure of $Mg_2Ni_4$ is quadrangular bipyramid structure with two Mg atoms occupying the top positions, which has quintet spin multiplicity and the symmetry is $D_{4h}$. The configuration conforms to the pure $Ni_6$ cluster.[9] The most stable isomer of $Mg_2Ni_5$ cluster (5a) is based on the 4a by a Ni atom capping on one side of the quadrilateral bipyramid. It accords with the geometry of pure $Ni_7$ cluster.[9] The energies of the metastable structures 5b and 5c with Mg atom replacing the different locations of pentagonal bipyramid are higher than those of 5a. The ground-state configuration of $Mg_2Ni_6$ cluster is based on the metastable isomer 5c that an Ni atom caps on the top of pentagonal bipyramid. It makes a big difference compared with the pure $Ni_8$ cluster.[9] Ni–Mg atoms separately capping on the different positions of 5a are the low-lying isomers 6b, 6c, and 6d. From $n = 7$, the lowest energy configurations each have a singlet spin multiplicity and the geometries are different from the pure $Ni_{n+2}$ clusters.[14] The most stable structure of $Mg_2Ni_7$ is derived from adding a Ni atom on one side of 6b. Two Mg atoms are respectively located at the apex position of the octahedral, and other Ni atoms distribute around it. The particular configuration with four Ni atoms successively capping on the top and bottom of quadrilateral bipyramid is the most stable structure of $Mg_2Ni_8$ cluster. The symmetry is $C_{2v}$. The energies of other metastable structures, which are based on the pentagonal bipyramid, are higher than those of

the ground-state structure.

From the discussion above, it is clear that the clusters begin to appear three-dimensional structure when $n = 2$ ($Mg_2Ni_2$) and pyramidal structure dominates the growth. For the parameter n ranging from 3 to 5, the ground-state structures are formed by two Mg atoms replacing the tops of the pure $Ni_{n+2}$ clusters. The combination of Ni cluster which relates to the localized d electrons and quasi-free sp electrons may give an explanation of this phenomenon. For small Ni cluster, the combination is probably determined by localized d electrons. The corresponding structure may be close-packed and the combination of electrons can be described as covalent bonding. Adding one more atom into the cluster cannot obviously change its structure. As to larger Ni cluster, which shows metallic character, additional atoms may cause significant deformation of the original cluster and a new cluster may form.[13] It is no surprise that the elements of pure $Ni_{n+2}$ clusters cannot be found in the ground-state structures of $Mg_2Ni_n$ ($n = 1$–8) clusters when $n \geq 6$. The Ni atoms remain at the surface of the clusters to form symmetrical structures with the increasing of Ni atoms. Two Mg atoms tend to occupy the tops of the structures so as to achieve the lowest energy structure.

### 3.2. Stability

In order to study the relative stabilities of the lowest energy structures of $Mg_2Ni_n$ ($n = 1$–8) clusters, we calculate the average binding energy ($E_b$), the second-order energy difference ($\Delta_2 E$), and the HOMO–LUMO energy gap in this section. The $E_b$ is a parameter used to describe the stability of clusters. It is defined as

$$E_b(Mg_2Ni_n) = [2E(Mg) + nE(Ni) - E(Mg_2Ni_n)]/(n+2),$$

where $E(Mg_2Ni_n)$, $E(Mg)$, and $E(Ni)$ are the energies of $Mg_2Ni_n$ cluster, an Mg atom, and an Ni atom, respectively. In order to make a comparison between $Mg_2Ni_n$ and pure Ni clusters, the average binding energies of the ground-state clusters and pure Ni clusters in Ref. [13] are displayed in Fig. 2. The binding energies of $Mg_2Ni_n$ clusters almost linearly increase and then reach the maximal value of 1.47 eV at $n = 6$. For pure Ni clusters, the values also reflect an upward trend. When the number of atoms is the same, the $Mg_2Ni_n$ cluster bonding energies are lower than those of pure Ni clusters. It is noted that two doped Mg atoms reduce the stabilities of pure Ni clusters. It can be explained by the metallic characteristic of Mg. The doping has an influence on the interaction of Ni–Ni bonds.

The second-order energy difference $\Delta_2 E$ sensitively reflects the relative stability of the clusters. The higher the value is, the more stable the cluster will be. It can be calculated as

$$\Delta_2 E(Mg_2Ni_n) = E(Mg_2Ni_{n+1}) + E(Mg_2Ni_{n-1}) - 2E(Mg_2Ni_n),$$

where $E$ represents the energy of the ground-state clusters. Figure 3 shows the value of $\Delta_2 E$ of $Mg_2Ni_n$ ($n = 1$–8) clusters. The $\Delta_2 E$ of the clusters clearly indicates oscillations and $n = 2$, 4, and 6 correspond to peaks, i.e., the second-order energy differences of the clusters with even numbers are higher. Moreover, it can be deduced that the system appears magic number characteristics.

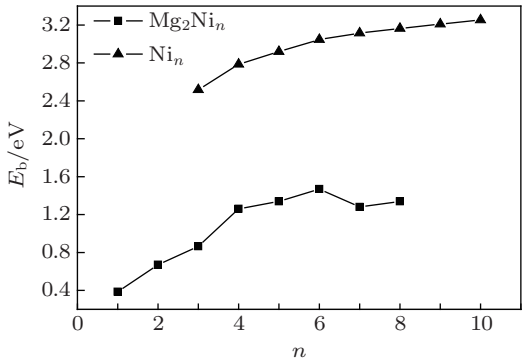



**Fig. 2.** Average binding energies of the ground-state structures of $Mg_2Ni_n$ ($n = 1$–8) clusters and $Ni_n$ clusters ($n = 3$–10).

The HOMO–LUMO energy gap is an important quantity always used to describe clusters' chemical activity. A larger energy gap corresponds to more energy need when the electrons transit from occupied orbital to unoccupied orbital, i.e., the cluster with higher stability. In the present calculation, the values of $n = 2$ and 4 are larger. It can be concluded that the $Mg_2Ni_2$ cluster and $Mg_2Ni_4$ cluster have weaker chemical activities. This is consistent with the analysis of magic number characteristics above.

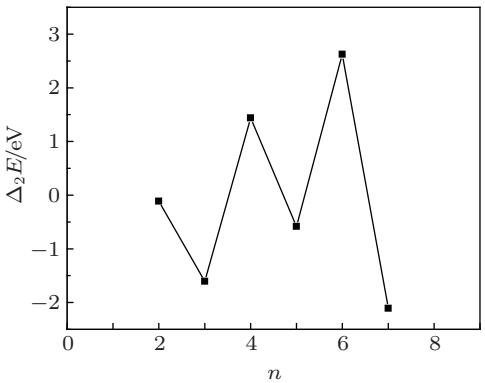



**Fig. 3.** The second-order energy difference of the ground-state structures of $Mg_2Ni_n$ ($n = 1$–8) clusters.

### 3.3. Electronic properties

The ionization potential (IP) and electron affinity (EA) are two useful parameters to identify the electronic property of the clusters. The IP is related to the energy of a neutral cluster losing an electron, and the larger value of IP normally yields a highly stable cluster. The EA refers to the bonding

energy of a neutral cluster receiving an electron. Calculation formulas are respectively defined as

$$\mathrm{IP}(\mathrm{Mg_2Ni}_n) = E(\mathrm{Mg_2Ni}_n^+) - E(\mathrm{Mg_2Ni}_n),$$
$$\mathrm{EA}(\mathrm{Mg_2Ni}_n) = E(\mathrm{Mg_2Ni}_n) - E(\mathrm{Mg_2Ni}_n^-),$$

where $E(\mathrm{Mg_2Ni}_n^+)$, $E(\mathrm{Mg_2Ni}_n^-)$, and $E(\mathrm{Mg_2Ni}_n)$ correspond to the energies of $\mathrm{Mg_2Ni}_n^+$, $\mathrm{Mg_2Ni}_n^-$, and $\mathrm{Mg_2Ni}_n$ clusters, respectively.

As shown in Fig. 4, the IPs and EAs of $\mathrm{Mg_2Ni}_n$ clusters exhibit odd–even oscillations for the cluster size $n = 1$–8. In the IP curve, the peaks locate at $n = 2$, 4, and 6. The valence electrons may account for this phenomenon. For a cluster with an even number of valance electrons, gaining or losing an electron can produce a single electron. It results in the effect that the corresponding cluster owns higher energy. In the case of our calculation, the valence shell for Mg is $2p^6 3s^2$, and for Ni atom is $3d^8 4s^2$. When $n$ is even, the energy of $\mathrm{Mg_2Ni}_n^+$ clusters is higher and its IP is larger. It suggests that the clusters with even numbers possess higher stabilities than neighboring clusters. For the EA curve, $n = 2$, 4, and 6 correspond to valley values, respectively. It can be deduced that $\mathrm{Mg_2Ni_2}$, $\mathrm{Mg_2Ni_4}$, and $\mathrm{Mg_2Ni_6}$ clusters are more stable than odd-size clusters. In terms of the clusters with larger EAs, they have a stronger tendency to receive an extra electron, i.e., their chemical activities are higher.

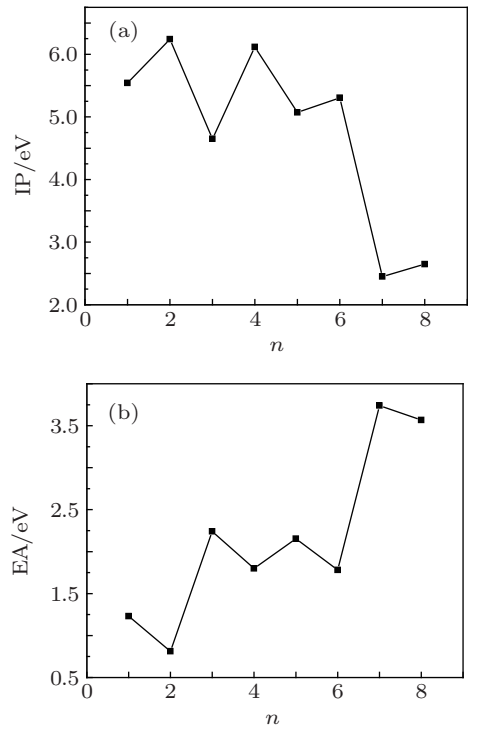



**Fig. 4.** (a) Ionization potential (IP) and (b) electron affinity (EA) of the ground-state structures of $\mathrm{Mg_2Ni}_n$ ($n = 1$–8) clusters.

In our analysis of IP and EA, the clusters with even numbers of Ni atoms show good stabilities. This conforms to the analysis of the second-order energy difference and the magic number characteristics. However, the value of energy gap for the $\mathrm{Mg_2Ni_6}$ cluster is smaller than neighboring clusters. We will give an explanation combined with the NBO analysis.

### 3.4. Natural bond orbital analysis

In order to understand the bonding properties of $\mathrm{Mg_2Ni}_n$ ($n = 1$–8) clusters, the natural bond orbital (NBO) analysis is performed here. The NBO results of the ground-state structures are summarized in Table 2.

According to the Pauli exclusion principle and the lowest energy principle, the outer electronic orbitals of Mg atom and Ni atom are $2s^2 2p^6 3s^2$ and $3s^2 3p^6 4s^2 3d^8$, respectively. As can be seen from Table 2, the charge distribution of 3s orbital for Mg atom is between 1.01 and 1.70. The 3p orbital electrons range from 0.08 to 0.21. The charges of 4s and 4p orbitals are rare. From the data above, the 3s orbital of Mg atom loses electrons. The 3p, 4s, and other orbitals gain electrons. It indicates that the sp orbital hybridization happens in Mg atom. As to Ni atoms, the charge distribution of 4s orbital is between 0.79 and 1.37. The electrons of Ni atom mainly distribute in the 3d orbital. The number of 3d orbital electrons is from 8.96 to 9.41. The 4p orbital only has a small amount of electrons (between 0.01 and 0.16). The maximum number of the electrons distributed in the 5p orbital is 0.14. These data illustrate that the 4s orbital of Ni atom loses electrons, the 3d, 4p, and other orbitals obtain electrons. It indicates that Ni atom has spd orbital hybridization. For Ni atom, the electrons that the 3d, 4p, etc. obtained are more than its 4s orbital lost. As to Mg atom, it is just opposite. It can be deduced that some electrons of 3s orbital for the Mg atom transfer to the Ni atom. The result of charge transfer is that the Ni atom is electronegative and the Mg atom is electropositive. In the process of forming alloy clusters, Mg atom acts as an electron donor. The reason is that the electronegativity of Ni atom (1.91) is higher than that of Mg atom (1.31). Ni atom is the receptor. Combining with Fig. 1 and Table 1, it can be concluded that the NBO charge distribution of a cluster is also affected by the cluster's symmetry. When the cluster has higher symmetry, the NBO charge distributions of the atoms which are in the same relative position are also the same. It is consistent with Ref. [21]. For instance, the symmetry of $\mathrm{Mg_2Ni_4}$ cluster is $D_{4h}$ and the electronic arrangements of two Mg atoms in the cluster are 3s (1.30) 3p (0.12) 4S (0.01) 4p (0.01).

Finally, we discuss the relationships between the stabilities, energy gaps, and the electron distribution of 3d, 4p orbitals for Ni atom when $n = 2$, 4, and 6. $\mathrm{Mg_2Ni_2}$ and $\mathrm{Mg_2Ni_4}$ clusters have higher stabilities compared with the neighbouring clusters. Moreover, the energy gaps are also larger. It can be seen that the charge numbers of 3d orbital for the Ni atom in $\mathrm{Mg_2Ni_2}$ and $\mathrm{Mg_2Ni_4}$ clusters are respectively less than those of their neighbouring clusters. For $\mathrm{Mg_2Ni_2}$ cluster, there is a

**Table 2.** Natural electron configuration and atomic charge of the ground-state structures of $Mg_2Ni_n$ ($n = 1$–8) clusters.

| Clusters | Atom | Natural electron configuration | Net-charge |
|---|---|---|---|
| $Mg_2Ni$ | Ni1 | [core]4S(1.37)3d(8.98)4p(0.05)5S(0.01) | –0.4092 |
| | Mg2, Mg3 | [core]3S(1.70)3p(0.08)4S(0.01) | 0.2046 |
| $Mg_2Ni_2$ | Ni1 | [core]4S(1.18)3d(8.98)4p(0.07) | –0.2354 |
| | Ni2 | [core]4S(1.22)3d(8.96)4p(0.07) | –0.2615 |
| | Mg3 | [core]3S(1.63)3p(0.12)4S(0.01) | 0.2414 |
| | Mg4 | [core]3S(1.62)3p(0.12) | 0.2555 |
| $Mg_2Ni_3$ | Ni1, Ni2, Ni3 | [core]4S(0.81)3d(9.41)5S( 0.01)5p(0.08) | –0.3144 |
| | Mg4, Mg5 | [core]3S(1.38)3p(0.13)4S(0.01)4p(0.01) | 0.4716 |
| $Mg_2Ni_4$ | Ni1, Ni2 | [core]4S(1.17)3d(9.03)4p( 0.09)5S(0.01) | –0.2989 |
| | Ni3, Ni4 | [core]4S(1.11)3d(9.05)4p(0.10)5S(0.01) | –0.2724 |
| | Mg5, Mg6 | [core]3S(1.30)3p(0.12)4S(0.01)4p(0.01) | 0.5712 |
| $Mg_2Ni_5$ | Ni1 | [core]4S(0.96)3d(9.07)4p(0.14)5S( 0.01)5p(0.01) | –0.1888 |
| | Ni2, Ni3 | [core]4S(1.02)3d(9.17)4p(0.09)5S(0.01)5p(0.01) | –0.2979 |
| | Ni4 | [core]4S(0.87)3d(9.30)4p(0.03) | –0.2102 |
| | Ni5 | [core]4S(0.96)3d(9.07)4p(0.14)5S(0.01)5p(0.01) | –0.1888 |
| | Mg6 | [core]3S(1.18)3p(0.14)4p(0.01) | 0.6666 |
| | Mg7 | [core]3S(1.35)3p(0.11)4S(0.01)4p(0.01) | 0.5171 |
| $Mg_2Ni_6$ | Ni1, Ni4 | [core]4S(1.03)3d(9.21)4p(0.11)5p( 0.01) | –0.3562 |
| | Ni2, Ni3 | [core]4S(1.00)3d(9.01)4p(0.09)5S(0.01)5p(0.01) | –0.1168 |
| | Ni5 | [core]4S(1.12)3d(8.96)4p(0.16)5p(0.01) | –0.2535 |
| | Ni6 | [core]4S(0.93)3d(9.12)4p(0.04) | –0.0993 |
| | Mg7 | [core]3S(1.05)3p(0.21)4p(0.01) | 0.7301 |
| | Mg8 | [core]3S(1.23)3p(0.19)4S(0.01) | 0.5688 |
| $Mg_2Ni_7$ | Ni1 | [core]4S(0.86)3d(9.28)5p(0.03) | –0.1799 |
| | Ni2 | [core]4S(0.88)3d(9.23)4p(0.01)5p(0.15) | –0.2747 |
| | Ni3 | [core]4S(0.85)3d(9.23)5p(0.04) | –0.1363 |
| | Ni4 | [core]4S(0.85)3d(9.22)4p(0.01)5p(0.13) | –0.2139 |
| | Ni5 | [core]4S(0.90)3d(9.23)4p(0.01)5S(0.01)5p(0.12) | –0.2590 |
| | Ni6 | [core]4S(0.88)3d(9.23)5S(0.01)5p(0.05) | –0.1663 |
| | Ni7 | [core]4S(1.00)3d(9.29)4p(0.01)5S(0.01)5p(0.06) | –0.3586 |
| | Mg8 | [core]3S(1.11)3p(0.12)4S(0.01)4p(0.01) | 0.7553 |
| | Mg9 | [core]3S(1.01)3p(0.15)4p(0.01) | 0.8335 |
| $Mg_2Ni_8$ | Ni1, Ni2 | [core]4S(0.83)3d(9.24)4p( 0.01)5p(0.14) | –0.2177 |
| | Ni3, Ni4, Ni5, Ni6 | [core]4S(0.79)3d(9.26)4p(0.01)5p(0.04) | –0.0919 |
| | Ni7 | [core]4S(0.99)3d(9.20)4p(0.08)4d(0.01)5p(0.14) | –0.4151 |
| | Mg8, Mg10 | [core]3S(1.08)3p(0.14)4p(0.01) | 0.7709 |
| | Ni9 | [core]4S(0.97)3d(9.27)4p(0.01)5p(0.07) | –0.3237 |

minimum value of 8.96. Ni atoms which get less electrons further illustrate that the $Mg_2Ni_2$ and $Mg_2Ni_4$ clusters are more stable. This reflects the stability of the system and the energy gap characteristics of the clusters are associated with the bonding ability of 3d orbital for the Ni atom. For $Mg_2Ni_6$ cluster, there is no big difference in the charge numbers of 3d orbital for the Ni atom compared with neighbouring clusters. However, the electrons of 4p orbital for the Ni atom increase significantly and reach a maximum value of 0.16. The reason why the $Mg_2Ni_6$ cluster has better stability but smaller energy gap is that the bonding capacity of 4p orbital for the Ni atom is increased. The molecular orbital diagram of these clusters are showed in Fig. 5. It directly reflects the bonding characteristics of clusters. It can be seen that the orbitals of clusters become delocalized as the number of Ni atoms increases.

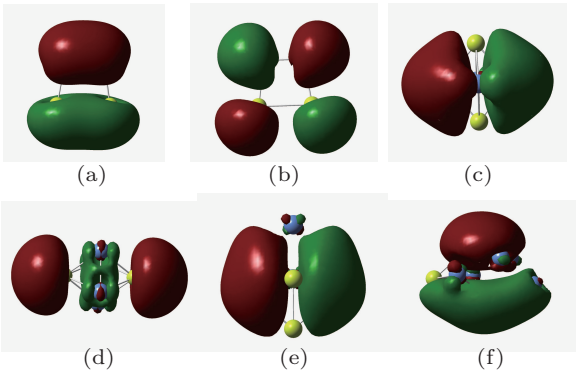



**Fig. 5.** (color online) HOMO orbitals of cluster (a) $Mg_2Ni_2$, (c) $Mg_2Ni_4$, (e) $Mg_2Ni_6$; LUMO orbitals of cluster (b) $Mg_2Ni_2$, (d) $Mg_2Ni_4$, (f) $Mg_2Ni_6$.

## 4. Conclusion

By using the DFT at the P3BW91/LANL2DZ level, the geometrical structures, stabilities, electronic properties, and

NBO of $Mg_2Ni_n$ ($n = 1$–8) clusters are investigated. The results can be concluded as follows.

(i) Pyramidal structure dominates the growth of the clusters. For the ground-state structures, the clusters contain the primitives of pure nickel clusters when $n$ ranges from 3 to 5 while the others do not. The Mg atoms tend to occupy the vertex positions.

(ii) The doped Mg atoms reduce the stabilities of pure Ni clusters. The second-order energy difference, the ionization potential, and the electron affinity exhibit odd–even oscillations. We conclude that $Mg_2Ni_2$, $Mg_2Ni_4$, and $Mg_2Ni_6$ clusters are more stable than neighbouring clusters. The system appears magic number characteristics. The $Mg_2Ni_6$ cluster has lower HOMO–LUMO energy gap, owing to the increase in the bonding capacity of 4p orbital for Ni atom. NBO analysis reveals that the orbital hybridization happens in the Mg atom, Ni atom, and Mg–Ni atoms. The charge transfer results in the effect that the Ni atom is negative and Mg atom is positive.

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