A single palladium atom immerses in magnesium clusters: PdMg$_n$ ($n = 2-20$) clusters DFT study

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Abstract

The structure, stability, charge transfer, and chemical bonding properties of palladium-doped magnesium clusters, PdMg$_n$ ($n = 2-20$), are comprehensively researched by CALYPSO software within first-principles DFT computations. It is shown that the cluster structure evolved from a tetrahedral-based structure to a cage-like structure, and interestingly, the single Pd atom always immerses in the Mg$_n$ clusters except for PdMg$_2$ and PdMg$_3$. Stability studies indicate that PdMg$_4$, PdMg$_7$, PdMg$_{10}$, and PdMg$_{15}$ clusters have relative robust stability and can be identified as ‘magic’ clusters. Most importantly, chemical bonding studies reveal that Pd–Mg is always non-covalent bond (closed-shell) interaction in all PdMg$_n$ ($n = 2-20$) clusters, and PdMg$_6$ and PdMg$_7$ are the critical sizes at which Mg–Mg covalent interactions occur. The geometric structure database of transition metal-doped Mg clusters will be enriched by this study, and it also provides, at least theoretically, new members of cage-like structures for magnesium-based hydrogen storage nanomaterials.

1. Introduction

Cluster science, which can be dated back to the 1950s and has been flourished since the 1980s, is an interdisciplinary subject of condensed matter physics, atomic-molecular physics, chemical physics and materials science [1]. Its research, initially, started as a way to satisfy a basic scientific curiosity about how microscopic atoms transition to bulk matter. However, with the increase in the number of studies reporting various amazing cluster structures, researchers find that nanocluster science is opening up new avenues in the search for novel nanomaterials. For example, the well-known fullerene C$_{60}$ with a cage-like structure is one of the carbon clusters that can exist at room temperature [2–4]. Fullerene has many derived complex clusters favored by researchers, one is the impurity atom doping type [5, 6], and the other is the substitution type, where the impurity atom directly replaces the C atoms in the fullerene [7, 8]. Interestingly, these clusters always possess some amazing physical and chemical properties, like strong magnetic properties, superconductivity, etc, which strongly indicates that they have attractive application prospects in the fields of light, electricity and magnetism. The study of boron clusters is another interesting research area contributing to the transition from cluster science to nanomaterials technology. It was shown that boron clusters with less than 36 boron atoms exhibited a two-dimensional planar structure similar to graphene [9–11], which inspired the experimentalists to synthesize borophene and eventually succeeded [12]. Boron-based clusters have attracted a great deal of interest in recent years in the field of nanomaterials science [13–15]. Furthermore, the structures of gold clusters show diversity, specifically, small-sized gold clusters consisting of less than 13 gold atoms exhibit a two-dimensional planar structures [16], and the cluster of 20 gold atoms has a tetrahedral pyramidal geometry while larger-sized, like Au$_{32}$, Au$_{75}$, Au$_{101}$, Au$_{146}$, gold clusters exhibit solid cage-like shapes [17–19]. The size-dependent nature of these clusters structures shows us a
Figure 1. The ground state structures of PdMg$_n$–PdMg$_{11}$ clusters and atom distance range of Pd–Mg and Mg–Mg (in Å) are contained in each isomer.

fantastic microscopic world, and at the same time provides so many potential novel materials for the field of nanomaterials.

Theoretically, the composition of the clusters selected for the study could be any element in the periodic table or any combination thereof. There is no doubt that any such cluster would certainly be of academic research value. However, the research priority of nanoclusters based on application possibilities should be higher. Interestingly, magnesium-based nanoclusters are one of such nanomaterials that are worthy studied for their promising hydrogen storage applications [20, 21]. Some researchers have studied the adsorption of hydrogen atoms on pure magnesium clusters [22, 23], while others have studied the hydrogen storage in doped magnesium clusters, such as oxygen-doped [24], metallic cobalt-doped [25], rhodium-doped [26], zirconium-doped [27], and scandium-doped magnesium clusters [28]. One of the motivations for these studies is that the structures of magnesium-based clusters as hydrogen storage materials change depending on their size, resulting in materials of different sizes exhibiting differential hydrogen storage capacity. In other words, any magnesium-based nanocluster material has hydrogen storage properties that are worth, at least theoretically, investigating. Palladium–magnesium materials also have good prospects for hydrogen storage applications [29]. Many studies have shown that the hydrogen storage capacity of Pd–Mg alloys [30] and thin-film materials [31] are significantly improved compared to ordinary materials. However, surprisingly, not much research has been done on the structure and hydrogen storage properties of Pd–Mg nanoclusters. The study of the hydrogen storage and other properties of Pd–Mg clusters of different sizes presupposes the understanding of their structures, and this paper aimed at completing such work. Specifically, a palladium atom doped into magnesium clusters of different sizes, PdMg$_n$ ($n = 2–20$), will be systematically studied. We shall focus on the geometric structure evolution mechanism, relative energetic stability, electronic structure and chemical bonding properties of the lowest energy state of the PdMg$_n$ ($n = 2–20$) clusters. These studies can, on the one hand, fill the gap in the theoretical study of Pd-doped Mg clusters and, on the other hand, can also help to investigate their hydrogen storage properties in the future.
2. Computational method details

The initial PdMg\(_n\) (\(n = 2–20\)) isomers structures were searched through CALYPSO quantum chemistry software in the global potential energy surface [32, 33]. Once the compound composition and external conditions are given, numerous reports, including crystal, functional material under high pressure, two-dimensional laminate material and cluster studies, successfully confirm the scientific usefulness of CALYPSO software [34–40]. In particular, the aromaticity of Mg\(_{17}\) [41] and the tubular drum-shaped MgB\(_{18}\) [42] clusters were successfully first found in the study of pure Mg clusters and Mg-doped boron clusters using CALYPSO. The main parameters of the PdMg\(_n\) cluster structure search at each size are given as follows: 80% and 20% of the geometric structures are generated using the local particle swarm optimization and random algorithm, respectively, and then the structure optimization is performed in Gaussian09 software [43], with 20 structures for one generation and a total of 50 generations for the search and optimization. Theoretically, using CALYPSO according to the above settings, for each size of PdMg\(_n\), 1000 structures can be searched out. However, it should be noted that these 1000 structures are not completely different, and many of them have the same energy and the same structure, so they need to be censored. The obtained isomers close in energy and structure were censored using the CALYPSO auxiliary function and finally ranked by energy. The different isomers with an energy difference of 3 eV were again subjected to structural optimization and frequency calculation using B3PW91 functional in Gaussian09 together with DFT. The pseudopotential mixed group 6-311g(d) basis set is applied to the magnesium atom and the Lanl2tz(f) basis set [44] is used for the palladium atom. For each isomer, different spin multiplicities are considered to ensure that it is the global minimum. Specifically, structural optimization and frequency calculations were performed for each PdMg\(_n\) isomer with 1, 3, 5, and 7 spin multiplicities. In
addition, if the frequency calculation result contains imaginary frequencies, it means that this structure is a transition state and not a local or global minimum in potential energy surface. Such structure will be optimized again by eliminating the imaginary frequencies until there are no imaginary frequencies.

The structural stability of the optimized PdMgₙ (n = 2–20) clusters in the lowest energy state were investigated by the average binding energy (Eₐ in eV), the second-order energy difference (Δ₂E in eV) and the HOMO–LUMO energy gap (E_{gap} in eV) by the following equations:

\[ Eₐ(PdMgₙ) = \frac{nE(Mg) + E(Pd) - E(PdMgₙ)}{n + 1} \]  
\[ Δ₂E(PdMgₙ) = E(PdMgₙ₋₁) + E(PdMgₙ₋₂) - 2E(PdMgₙ) \]  
\[ E_{gap}(PdMgₙ) = E_{LUMO}(PdMgₙ) - E_{HOMO}(PdMgₙ), \]

where \( E(Mg) \) and \( E(Pd) \) are the total energies of free Mg and Pd atoms, \( E(PdMgₙ) \) is the total energy of the corresponding cluster, \( E_{LUMO} \) and \( E_{HOMO} \) are energies of the lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) of the corresponding cluster.

Charge population analysis for the ground state of PdMgₙ (n = 2–20) clusters was performed by atomic dipole moment corrected Hirshfeld (ADCH) atomic charges method [45]. Natural bond orbital (NBO) was used to analyzed molecular orbital composition [46]. The interactions between atoms in each ground state cluster were discussed by topological analysis of the electron density \( ρ(r) \) and Laplacian function of electron density \( \nabla^2 ρ(r) \) at their bond critical points (BCP) [47], and electron localization function (ELF) [48] values of these BCPs were calculated simultaneously to understand the existence of covalent bonds between atoms. The ADCH on Pd and Mg atoms and BCPs values were directly calculated through Multiwfn software [49].

3. Results and discussion

3.1. Geometric structure of PdMgₙ clusters

Using the computational method mentioned in the previous section, we have obtained the lowest-lying structures of PdMgₙ (n = 2–20) clusters and show them in figures 1, 2, S1 and S2 (https://stacks.iop.org/NJP/23/103002/mmedia) in the supplemental materials. Figures 1 and 2 show the ground state geometric structures, symmetries, electronic states and the ranges of Pd–Mg and Mg–Mg atomic distances (not chemical bonds!) of the PdMgₙ clusters, while figures S1 and S2 display the structures, symmetries, electronic states and their energy differences (in eV) from the ground state clusters for the three lowest energy isomers. The isomers in figures S1 and S2 are named as 'N − i', where \( N \) denotes the number of Mg atoms in the isomer and \( i \) can be 1, 2 and 3, which denotes the energy order. It is noted that the information for the ground state clusters can also be found in table 1, and in addition, the atomic coordinates of the ground state clusters are shown in table S1 of the supplementary materials to enable the readers to repeat this work. The vibration frequency results in table 1 confirm that none of the structures contain imaginary frequencies.

As figure 1 displayed, the lowest-energy isomer of PdMg₂ cluster has \( C_{2v} \) symmetry with \( 1A_1 \) electronic state, and it shows an isosceles triangular geometry. The ground state of the PdMg₂ cluster presents a similar tetrahedral structure, and its electronic state is \( 1A_1 \) and possesses \( C_{3v} \) symmetry. The geometry of the lowest-energy isomer of the PdMg₄ cluster, which has \( T_d \) symmetry with a \( 1A_1 \) electronic state, shows a palladium atom imprisoned in the center of a tetrahedron of four magnesium atoms. It should be emphasized that the palladium atom is immersed inside the magnesium clusters starting from the ground state of the PdMg₄ cluster, i.e. the lowest-energy structure states of the PdMgₙ (n = 4–20) clusters all exhibit this commonality, the only difference being in the shape of the external magnesium clusters and the different points of palladium imprisonment. It is not common for magnesium clusters to have dopant atoms completely immersed inside them. For example, the available reports of Be doping [50–52], Si doping [53], Ge, C, Sn doping [54], Zn doping [55], etc indicate that these dopant atoms are still on the cluster surface at many sizes. The lowest-energy isomer of the PdMg₅ cluster, which possesses \( C_{4v} \) symmetry and \( 1A_1 \) electronic state, shows a pyramid geometry of five magnesium atoms with a palladium atom immersed near the bottom. The geometry of the lowest-energy state of the PdMg₅ cluster is octahedral, it has \( O_h \) symmetry as well as \( 1A_1 \) electronic state. The ground state isomer of PdMg₇ cluster possesses \( C_{3v} \) symmetry with \( 1A_1 \) electronic state, and its structure can be easily obtained by the adsorption of a magnesium atom on the lower right side of the lowest-energy isomer of PdMg₆ cluster. For the ground state
Table 1. Electronic state, symmetry, average binding energy, second-order energy difference, HOMO–LUMO energy gap, vibration frequency range, ADCH charges on Pd atom, and VIP, VEA values in the lowest energy states of PdMgₙ (n = 2–20) clusters.

| Cluster   | State | Symmetry | E₀ (eV) | ΔE (eV) | E萩 (eV) | Highest frequency (cm⁻¹) | Lowest frequency (cm⁻¹) | Charges on Pd atom (eV) | VIP (eV) | VEA (eV) |
|-----------|-------|----------|--------|--------|---------|--------------------------|--------------------------|-------------------------|---------|---------|
| PdMg₂     | Cᵥ     | ¹A₁      | 0.78   | —      | 2.40    | 263                      | 67                      | −0.11                   | 6.28    | 0.95    |
| PdMg₃     | Cᵥ     | ¹A₁      | 0.82   | −0.08  | 2.39    | 249                      | 53                      | −0.14                   | 6.17    | 1.14    |
| PdMg₄     | T₁      | ¹A₁      | 0.86   | 0.38   | 2.57    | 265                      | 35                      | −0.39                   | 6.18    | 1.17    |
| PdMg₅     | Cᵥ     | ¹A₁      | 0.83   | −0.04  | 1.16    | 264                      | 26                      | −0.28                   | 4.97    | 1.12    |
| PdMg₆     | Cᵥ     | ¹A₁      | 0.81   | −0.27  | 1.09    | 226                      | 81                      | −0.19                   | 4.78    | 1.74    |
| PdMg₇     | T₁      | ¹A₁      | 0.82   | 0.51   | 1.65    | 254                      | 42                      | −0.30                   | 5.23    | 1.42    |
| PdMg₈     | Cᵥ     | ¹A₁      | 0.78   | −0.36  | 0.71    | 250                      | 21                      | −0.21                   | 5.17    | 1.67    |
| PdMg₉     | Cᵥ     | ¹A₁      | 0.78   | −0.30  | 1.43    | 249                      | 18                      | −0.28                   | 5.17    | 1.65    |
| PdMg₁₀    | Cᵥ     | ¹A₁      | 0.81   | 0.60   | 1.75    | 278                      | 51                      | −0.26                   | 5.17    | 1.19    |
| PdMg₁₁    | Cᵥ     | ¹A₁      | 0.78   | −0.11  | 1.35    | 251                      | 41                      | −0.23                   | 5.02    | 1.62    |
| PdMg₁₂    | Cᵥ     | ¹A₁      | 0.77   | −0.23  | 0.71    | 246                      | 34                      | −0.22                   | 5.06    | 1.63    |
| PdMg₁₃    | Cᵥ     | ¹A₁      | 0.77   | −0.02  | 1.33    | 256                      | 18                      | −0.30                   | 5.15    | 1.82    |
| PdMg₁₄    | Cᵥ     | ¹A₁      | 0.78   | −0.13  | 1.19    | 228                      | 38                      | −0.25                   | 4.93    | 1.77    |
| PdMg₁₅    | Cᵥ     | ¹A₁      | 0.79   | 0.70   | 1.30    | 257                      | 48                      | −0.24                   | 4.95    | 1.75    |
| PdMg₁₆    | Cᵥ     | ¹A₁      | 0.76   | −0.35  | 0.94    | 279                      | 15                      | −0.25                   | 4.93    | 1.95    |
| PdMg₁₇    | Cᵥ     | ¹A₁      | 0.75   | −1.29  | 1.15    | 258                      | 27                      | −0.12                   | 4.86    | 2.03    |
| PdMg₁₈    | Cᵥ     | ³A       | 0.82   | 1.29   | 0.81    | 285                      | 13                      | −0.39                   | 4.68    | 2.17    |
| PdMg₁₉    | Cᵥ     | ³A       | 0.81   | −0.36  | 0.82    | 275                      | 26                      | −0.31                   | 4.59    | 2.19    |
| PdMg₂₀    | Cᵥ     | ³A       | 0.81   | —      | 0.97    | 291                      | 26                      | −0.20                   | 4.51    | 2.13    |

isomer of PdMg₉ cluster, it has Cᵥ symmetry and ¹A electronic state. Its geometry is a deformation based on the lowest-energy isomer of PdMg₅ cluster with the addition of one magnesium atom. As the ground-state structures for the sizes n = 9, 10, and 11, they are essentially based on the addition of one, two and three magnesium atoms to the lowest-energy isomer of PdMg₅ cluster as some kind of deformers. The above three clusters have Cᵥ, Cᵥ and Cᵥ symmetries, and the corresponding electronic states are 1A, ¹A and ¹A, respectively.

As figure 2 showed, the structures of the lowest-energy isomers of PdMg₁₂–PdMg₂₀ clusters present more complex multilayer-cage-like geometries with a palladium atom is immersed in them. Interestingly, these kinds of multilayer-cage-like structures are very similar to the previous reports of Xia [41] and Heidar [56] on pure Mg clusters. The ground state isomers of PdMg₁₂, PdMg₁₄, PdMg₁₆ and PdMg₁₇ clusters have Cᵥ symmetry and ¹A electronic state. Other isomers have Cᵥ symmetry. The lowest-energy isomers of the PdMg₁₈, PdMg₁₉ and PdMg₂₀ clusters possess ³A electronic states and all others have ¹A electronic states.

The distribution range values of the Pd–Mg and Mg–Mg atomic distances in the lowest-energy isomers of PdMgₙ clusters are also shown in figures 1 and 2. These data are intended only to display the cluster spatial size and the position of the Pd atom in those clusters, and they cannot represent the chemical bonding interactions between the corresponding atoms. From the atomic distance data, it can be seen that the Mg–Mg atomic distance has a significant increase with the increase of cluster size, while the shortest distance of Pd–Mg does not change much because the Pd atom is always immersed in the Mg atom. The lowest-energy isomer of the PdMg₁₄ cluster has the largest spatial size of 8.50 Å, while the ground state isomer of the PdMg₁₉ cluster has the smallest spatial size of 4.00 Å.

Summarily, the geometric growth mechanism of the lowest energy states of PdMgₙ (n = 2–20) clusters can be summarized as follows: except for the PdMg₂ cluster, which has a two-dimensional structure, all the others prefer to form three-dimensional geometries. The lowest energy isomers of the PdMg₅–PdMg₉ clusters are all based on tetrahedral geometry growth. While the ground state structures of PdMg₁₀–PdMg₂₀ clusters show multilayer-cage-like deformation geometry. Interestingly, in PdMg₁₄–PdMg₂₀ clusters, the single palladium atom in all the lowest energy isomers is immersed inside the magnesium cluster with a different orientation. Furthermore, the symmetry of the PdMgₙ clusters decreases significantly with increasing size, suggesting that the Jahn–Teller effect influence increases with the cluster size. In addition, the geometric growth mechanism of the second and third lowest-energy isomers presented in figures S1 and S2 in the supplemental material is somewhat similar to that of the first lowest-energy isomer, but the size of the Pd atom immersed into the Mg clusters starts at PdMg₅ cluster. Finally, as stated in the introduction, such cage-like structures of Mg-based nanoclusters have a high value for theoretical hydrogen storage studies due to their structural features. Researchers can fix any PdMgₙ cluster structure and then examine the adsorption of hydrogen atoms on its surface based on the first nature principle and investigate whether Mg–H is bonded to determine whether H is stored by PdMgn under DFT structure optimization calculations.
Figure 3. (a) Average binding energy $E_b$, (b) the second-order difference energy $\Delta_2E$, (c) the HOMO–LUMO energy gap $E_{\text{gap}}$ for the lowest energy state of PdMg$_n$ ($n = 2–20$) clusters.

3.2. The relative stability and HOMO–LUMO energy gap of the ground state of PdMg$_n$ clusters

The average binding energy, the second-order energy difference and the HOMO–LUMO energy gap for all the PdMg$_n$ ($n = 2–20$) clusters in figure 1 are calculated using equations (1)–(3). The results are presented in table 1, and their size-dependent curves are shown in figures 3(a)–(c). As can be seen in figure 3(a), the $E_b$ curve shows local peaks at $n = 4, 7, 10, 15$ and $18$, in which PdMg$_4$ has the largest $E_b$ value (0.86 eV) and the smallest $E_b$ value can be found at PdMg$_{17}$ (0.75 eV). The clusters corresponding to the localized peaks show higher stability than their neighbors. Figure 3(b) displays the evolution of the $\Delta_2E$ with size. The second-order energy difference is a parameter related to experimental observations, specifically, it is related to the experimental relative abundance of the corresponding element in the mass spectrometry experiment. The local peaks of the oscillating $\Delta_2E$ curve appear at the PdMg$_4$, PdMg$_7$, PdMg$_{10}$, PdMg$_{13}$, PdMg$_{15}$ and PdMg$_{18}$, suggesting that these clusters may have higher stability. It is easy to find a perfect agreement between the peaks of the $\Delta_2E$ and $E_b$ curves of PdMg$_n$ ($n = 2–20$) clusters, except for PdMg$_{13}$ which does not have a local maximum $E_b$ value. In addition, the $\Delta_2E$ curve points out that the PdMg$_n$ clusters have no similar odd–even oscillation property like magnesium-doped neutral boron clusters [42]. However, a comparison with the study of neutral Mg clusters reported by Xia [41] reveals that the trend of the $\Delta_2E$ curve of PdMg$_n$ and Mg$_n$ clusters coincides perfectly below $n = 15$. This indicates that below a medium-sized cluster of 15 Mg atoms, Pd doping has little effect on the second-order energy of Mg$_n$ clusters, but beyond this critical size, the situation changes, with Mg$_{17}$ and PdMg$_{18}$ possessing local $\Delta_2E$ peaks, respectively. Another parameter that can characterize the size dependence of cluster is the HOMO–LUMO energy gap, where a larger $E_{\text{gap}}$ value corresponds to higher chemical stability. The $E_{\text{gap}}$ curve of PdMg$_n$ ($n = 2–20$) clusters is plotted according to their size and shown in figure 3(c). The PdMg$_n$ clusters with $n = 4, 7, 10, 13, 15$ and $17$ have a local maximum $E_{\text{gap}}$ value, implying that their chemical stabilities are higher than other clusters. Interestingly, the energy gaps of the PdMg$_n$ ($n = 2–20$) clusters and the corresponding Mg$_n$ clusters [41] have similar trends, i.e. $E_{\text{gap}}$ oscillates smaller as the cluster size grows, suggesting that the oscillatory nature of the energy gap to size originates from the structural characteristics of the magnesium clusters. However, the $E_{\text{gap}}$ values of PdMg$_n$ are significantly smaller than those of their corresponding Mg$_n$ clusters. This is because, after Pd doping, the 4$d$ orbital of the Pd atom will make the HOMO energy level of the Mg$_n$ cluster increase while the LUMO energy level becomes smaller. Interestingly, it is found that the energy gap decreases in an oscillatory manner as the cluster size increases. The potential reason for this abnormal phenomenon can be explained to some extent by the particle-in-a-box model [57]. Based on this model, the energy gap is inversely proportional to the mass of the particle and the square of the particle’s range of motion. As the cluster size increases, the mass of the cluster and the range of motion of the electrons increase. So the overall cluster energy gap decreases accordingly. However, the decrease of energy gap is not linear and always oscillate locally as shown in figure 3(c), which may due to the discrepancies of the clusters geometries.

The vertical ionization potential (VIP) and vertical electron affinity (VEA) values of each ground state of the PdMg$_n$ cluster are also listed in table 1. VIP $= E_+ - E_0$ and VEA $= E_0 - E_-$, where $E_0$ is the neutral cluster energy, $E_-$ denotes the energy after ionization of an electron from a neutral cluster without changing its structure, while $E_+$ is the energy after gaining an additional electron without changing the structure of
the neutral cluster. As shown in figure 4, on the one hand, the peak VIP values appear in PdMg₄, PdMg₇, and PdMg₁₃, corresponding to 6.18 eV, 5.23 eV and 5.15 eV, respectively, implying that these clusters require higher energies to lose electrons relative to their neighbors and therefore have higher relative stability. On the other hand, it is well known that low VEA values mean the clusters are relatively stable since they only need to release less energy to acquire additional electrons. The low local minimum VEA values of the PdMg₅ (1.12 eV), PdMg₇ (1.42 eV), PdMg₁₀ (1.19 eV) and PdMg₁₅ (1.75 eV) clusters reveal that they are more stable relative to their neighboring clusters.

From the above analysis, we can conclude that the PdMg₄, PdMg₇, PdMg₁₀ and PdMg₁₅ clusters possess robust local stability than others, and therefore, they can be identified as ‘magic’ clusters. In addition, the PdMg₁₁ and PdMg₁₈ clusters have two local higher stability parameters simultaneously, and thus, only below the high stability of the magic clusters, they also have relatively high local stability.

3.3. Charge transfer property of PdMgₙ clusters

Atomic dipole moment corrected Hirshfeld (ADCH) atomic charges method can effectively analyze atomic charge transfer properties in the cluster. Table 1, figure 5 and table S2 of the supplemental materials show the calculation results of ADCH charges on Pd and Mg atoms of PdMgₙ (n = 2–20) clusters. In all clusters, the palladium atoms are negatively charged ranging from −0.39 e to −0.11 e, while most of the magnesium atoms are positively charged with a range of 0.131 e−0.004 e. The charged properties of the palladium and magnesium atoms are also shown in figure 5 using atomic coloring, with blue indicating the negative charge properties and different reds indicating different amounts of positive charged. On the one hand, in the PdMgₙ (n = 2–6) clusters with high symmetry, the magnesium atoms play electron donor and in symmetric positions lose an equal number of electrons, while the palladium atoms receive all the charges.
lost by the magnesium atoms. On the other hand, table S2 of the supplemental materials shows that some magnesium atoms in PdMg\(_n\) (\(n = 7–20\)) clusters start to gain electrons in the range of \(-0.121\) e to \(-0.004\) e, and become electron receivers. The palladium atoms received the most electrons in the PdMg\(_4\), PdMg\(_7\), PdMg\(_8\), PdMg\(_{13}\) and PdMg\(_{18}\) clusters and the least in the PdMg\(_6\), PdMg\(_8\), PdMg\(_{12}\) and PdMg\(_{17}\) clusters. The palladium atoms in the more stable clusters get relatively more electrons, indicating that the charges are transferred more in these clusters and the structures formed are relatively stable. The electronegativity of the palladium atom is 2.20, while that of the magnesium atom is 1.31, which determines that palladium usually becomes the electron acceptor when they two interact.

3.4. The chemical bond analysis of PdMg\(_n\) clusters
The study of the chemical bonding properties helps to further understand cluster formation. Here we calculate the bond critical point (BCP) of the clusters to probe the chemical bonding properties of Pd–Mg and Mg–Mg interaction in PdMg\(_n\) (\(n = 2–20\)) clusters. Specifically, the Laplace of electron density (\(\nabla^2 \rho \rho \)) and ELF were computed for each cluster’s BCPs. If the \(\nabla^2 \rho > 0\) of BCP indicates that the formation of this chemical bond is a non-covalent bond (closed-shell interaction), and the ELF \(> 0.5\) of BCP corresponds to a covalent bonding interaction. Tables S3 and S4 of the supplemental materials present all the results, and the tables also show the label of all atoms and the distances between the corresponding bond-forming atoms. The number of covalent and non-covalent bonding in PdMg\(_n\) and the range of \(\nabla^2 \rho\) and ELF values for the corresponding BCP are given in figures 6 and 7. As figure 6 displayed, 2, 3, 4, 5, 6 BCPs are found in PdMg\(_2\), PdMg\(_3\), PdMg\(_4\), PdMg\(_5\), and PdMg\(_6\) clusters, respectively. The ELFs of these BCPs are all less than 0.5 and \(\nabla^2 \rho\) are greater than 0, indicating that only Pd–Mg closed-shell interactions (non-covalent bonds) are formed in these clusters, and no covalent bonds are formed between Mg–Mg. However, as displayed in figure 7, starting from PdMg\(_7\), all PdMg\(_n\) (\(n = 7–20\)) clusters have both ELF \(< 0.5\) with \(\nabla^2 \rho > 0\) (corresponding to the BCPs of Pd–Mg) and ELF \(> 0.5\) with \(\nabla^2 \rho < 0\) (corresponding to the BCPs of
Figure 7. $\nabla^2 \rho$ analysis of BCPs for the ground state of PdMg$_n$ ($n = 11–20$) clusters.

Figure 8. 2D ELF distributions of PdMg$_4$, PdMg$_7$, PdMg$_{10}$, PdMg$_{13}$, PdMg$_{15}$ and PdMg$_{18}$ clusters.

Mg–Mg). PdMg$_6$ and PdMg$_7$ are the critical sizes at which Mg–Mg covalent interaction occurs. Interestingly, the PdMg$_{15}$, PdMg$_{16}$ and PdMg$_{17}$ clusters have the highest number of Pd–Mg BCPs (9), suggesting that at a cluster size of 20 Mg atoms, one Pd atom can attract up to 9 surrounding Mg atoms, while the other Mg atoms no longer have direct bonding interactions with Pd atom. Moreover, according to
Figure 9. Theoretical calculation infrared (IR) spectrum for the ground-state of PdMg$_n$ ($n = 11–20$) clusters.

The larger $\nabla^2 \rho$ value, the stronger the corresponding bonding interaction, one can find that the strength of Pd–Mg interactions in PdMg$_n$ ($n = 2–6$) clusters is decreasing with size. However, when the Mg–Mg interaction appears, the strength of the Pd–Mg interaction depends on the position of the palladium atom, the closer the palladium atom is to the geometric center of the cluster, the stronger of Pd–Mg interactions, for example, PdMg$_{13}$, PdMg$_{14}$, PdMg$_{15}$ and PdMg$_{17}$ clusters have smaller $\nabla^2 \rho$ averages than PdMg$_{10}$, PdMg$_{16}$, PdMg$_{18}$, PdMg$_{19}$ and PdMg$_{20}$ clusters.

To further investigate the electron–electron interaction in the PdMg$_n$ clusters, in addition to the calculation of the ELF values of the BCPs between two atoms, the ELF distribution within the cluster was also calculated and displayed in figure 8 and figures S3 and S4 of the supplementary materials. The white connecting lines between the two atoms in figures 9, S3 and S4 indicate that they are bonded, and the colors corresponding to 0.50 to 1.00 indicate the electron high-localized regions, while the colors 0.50 to 0.00 are the electron low-localized regions. To highlight the Pd atom doping, the ELF 2D distribution of Pd atoms in all the PdMg$_n$ clusters is also shown separately in the figures. The 2D distribution of the ELF clearly shows that low-localized electrons (ELF $< 0.50$) are present in all the Pd–Mg bonding regions of the PdMg$_n$ cluster, while high-localized electrons (ELF $> 0.50$) in the Mg–Mg bonding regions exist in some of the Mg atoms of PdMg$_7$–PdMg$_{20}$ clusters. This indicates that Mg–Mg bonding is formed by the interaction of their outer 3$s$-orbital electrons, while the Pd atom turns them into non-valent electrons after obtaining the electrons transferred from Mg atoms. Pd–Mg bonding is not the result of electron–electron interactions in their valence layers, they should be ionic bonds, which deserves further study in the follow-up work.

3.5. The infrared (IR) spectra of PdMg$_n$ clusters

The computed theoretical IR spectra of the ground state of PdMg$_n$ ($n = 2–20$) clusters, which are related to their structures, are calculated to provide data for future experimental observations. For the convenience of discussing the frequencies of the strongest IR absorption spectra, we have shown the IR spectra of all PdMg$_n$ clusters together in figure 9. It is worth noting that although the vertical coordinates in figure 9 are the intensities of the IR spectra, the peak heights of the different clusters cannot be directly compared and they are only distinguished by the intensity of their color cluster. As displayed in figure 9, the strongest peak in the IR spectrum of the PdMg$_2$ cluster is at 253 cm$^{-1}$, while the PdMg$_3$ cluster has three strong IR spectral peaks, the most intense of which appears at 248 cm$^{-1}$. The strongest IR peak of the PdMg$_5$ cluster can be found at 265 cm$^{-1}$, while only a single strong IR peak of the PdMg$_{10}$ cluster is presented at 236 cm$^{-1}$. The
PdMg₆ cluster, which has the highest symmetry O₈ as shown in figure 1, has only one IR peak located at 223 cm⁻¹ while the PdMg₇ cluster has seven IR peaks, the strongest of which is at 235 cm⁻¹. Starting from the PdMg₈ cluster, the IR spectrum of the cluster becomes multi-peaked. The strongest IR peak of the PdMg₈ cluster is located at 183 cm⁻¹, while the strongest IR peak of PdMg₉ cluster is presented at 164 cm⁻¹. The strongest IR peaks from the clusters of PdMg₁₀ and PdMg₁₁ can be found at 51 cm⁻¹ and 182 cm⁻¹ respectively. One can find the strongest IR peaks of PdMg₁₂, PdMg₁₃, PdMg₁₄ and PdMg₁₅ are appeared at 221 cm⁻¹, 241 cm⁻¹, 109 cm⁻¹ and 257 cm⁻¹ respectively. For the strongest IR peaks of PdMg₁₆ and PdMg₁₇ clusters, they would be found at 231 cm⁻¹ and 67 cm⁻¹ respectively. For the three largest clusters in size, the strongest IR peaks of PdMg₁₈, PdMg₁₉ and PdMg₂₀ clusters are located at 263 cm⁻¹, 212 cm⁻¹ and 186 cm⁻¹ respectively.

4. Conclusions

The structure, stability, molecular orbital components, charge transfer and chemical bonding properties of PdMgₙ (n = 2–20) clusters were comprehensively investigated by CALYPSO and GAUSSIAN software together with first-principles DFT computations. All PdMgₙ clusters show a 3D geometry except for the PdMg₂ cluster, which possesses a 2D planar structure. From PdMg₄ to PdMg₈ clusters, the palladium atom is always immersed inside the magnesium cluster. The structures of PdMgₙ (n = 3–9) clusters were based on tetrahedral growth, while the medium-sized PdMgₙ (n = 10–20) had evolved into a kind of cage-like structure. Stability studies had shown that PdMg₄, PdMg₇, PdMg₁₀ and PdMg₁₅ clusters have high stability and can be identified as ‘magic’ clusters. Charge transfer calculations indicated that in all clusters the palladium atoms are always electron receivers while most of the magnesium atoms are electron donors. Chemical bonding studies revealed that Pd–Mg is a non-covalent bond (closed-shell) interaction, and PdMg₆ and PdMg₇ were the critical sizes at which Mg–Mg covalent interactions occur. We believe that these studies cannot only enrich the theoretical study of magnesium-based clusters but also provide some guidance for the future experimental synthesis of palladium-doped magnesium nanomaterials. More interestingly, since palladium atom is always immersed in cage-like magnesium clusters. We believe that the geometric structure database of transition metal-doped Mg clusters will be enriched by this study, and it also provides, at least theoretically, new members of cage-like structures for magnesium-based hydrogen storage nanomaterials.

Authors’ contributions

Ben-Chao Zhu: software, investigation, writing original draft preparation. Ping-Ji Deng: data curation, visualization, investigation. Jia Guo: data curation, visualization. Lu Zeng: software, data curation, investigation, visualization, editing. Jun Zhao: conceptualization, methodology, formal analysis, investigation, writing review & editing.

Conflicts of interest

The authors declare there are no conflicts of interest regarding the publication of this paper.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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