Structure and magnetic properties of Os$_n$ $(n = 11 \sim 22)$ clusters

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The structure and magnetic properties of Os$_n$ $(n = 11 \sim 22)$ clusters are systematically studied by using density functional theory (DFT). For each size, the average binding energy per atom, the second-order differences of total energies and the highest occupied molecular orbital (HOMO)–the lowest unoccupied molecular orbital (LUMO) gaps are calculated to analyze the stability of the cluster. The structures of Os$_{14}$ and Os$_{18}$ clusters are based on a close-packed hexagonal structure, and they have maximum stabilities, so $n = 14, 18$ are the magic numbers. The 5d electrons play a dominant role in the chemical reaction of Os$_n$ clusters. The magnetic moments of Os$_n$ clusters are quenched around $n = 12$, and when $n = 18 \sim 22$ the value approximates to zero, due to the difference of electron transfer.

Keywords: density functional theory, Os$_n$ clusters, structure, magnetic properties

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1. Introduction

The cluster plays its role the same as a bridge linking molecule and bulk. The electronic structures and magnetic properties of clusters are very important parts in academic research. Among them, the transition metal (TM) clusters have been of special interest both theoretically and experimentally because of their potential as catalysts and high-density magnetic data storage materials.$^{[11–10]}$ However, compared with the clusters with 3d or 4d electrons, TM clusters with 5d electrons have been theoretically studied very little. Osmium as a member of the 5d electronic elements is one of the most important parts of organic catalytic activity, but the investigations of its relevant clusters and complexes are few and far between.

In previous investigations, the hardness of osmium complexes and the catalytic activity of osmium carbonyls are the most popular projects. Ahrens et al.$^{[11]}$ studied the reactions of [Os$_3$(CO)$_{18}$(MeCN)$_2$]$_2$ with ethynyl thiophenes. The result indicates that the highest occupied molecular orbital (HOMO)–the lowest unoccupied molecular orbital (LUMO) gap decreases only marginally and suggests that the degree of conjugation in the cluster complexes is not much greater than that in the free ligands. Jackson and Walls$^{[12]}$ studied the catalysis of osmium metal clusters by using a combination of analytical techniques; an overall picture and the chemisorption and catalytic studies all show behavior fundamentally different from that obtained with conventional metal catalysts. Zhang et al.$^{[13]}$ studied the chemical bondings, elastic behaviors, phase stabilities, and hardness values of OsB, OsB$_2$, OsC, OsO$_2$, OsN, and Os$_2$N$_2$ by using first-principles calculations. The calculations suggest that the chemical bondings in these compounds are a mixture of covalent and ionic components. The results indicate that the hexagonal tungsten carbide structure is more stable, the large occupations and high strength of the covalent bonds are crucial for a superhard material, and there is no clear connection between bulk modulus and hardness in these osmium compounds. Yang et al.$^{[14]}$ investigated the structure in the frame of the generalized gradient approximation (GGA) and (local density approximation (LDA) by using CASTEP code, elastic properties, and elastic anisotropy of orthorhombic OsB$_2$ under pressure. They found that the elastic constants, bulk modulus, and Debye temperature of OsB$_2$ tend to increase with pressure increasing. It is predicted that OsB$_2$ is not a superhard material. Ji et al.$^{[15]}$ studied the mechanical properties and chemical bonding of the Os–B system, and the results indicate that high hardness values in Os$_x$B$_y$ and OsB$_3$ are mainly attributed to the occurrence of strong B–B covalent bonds and the disappearance of some ductile Os–Os metallic bonds.

Our research group$^{[16–19]}$ also studied the Os–N, Os–B cluster system and pure osmium clusters with small sizes $(n = 2 \sim 10)$, but there have been hardly any other studies of pure osmium clusters so far, so we will continue this research. In this paper, we pay attention to structures, relative stabilities, and magnetic properties of Os$_n$ clusters with $11 \leq n \leq 22$ by using density functional theory (DFT), so as to make a research foundation of the osmium application.

2. Theoretical methods

The structures and magnetic properties of Os$_n$ $(n = 11 \sim 22)$ clusters are computed using DFT semi-core pseudopot
in the DMOL3 package. In the calculation of the electronic structure, we use the spin-polarized generalized gradient approximation (GGA) with PW91 functional for the exchange-correlation interaction and the double numerical basis set that includes d-polarization functions (DND). The direct inversion in an iterative subspace (DIIS) approach is designed for speeding up the self-consistent field (SCF) convergence, and in the structure optimization we consider the smearing. The SCF calculation is done with a convergence criterion of \(10^{-5}\) Hartree (1 Hartree = 2 Ry = 27.2114 eV). The density mixing criteria for charge and spin are taken to be 0.2 and 0.5 respectively. The smearing of molecular orbital occupation is 0.002 Hartree. In the geometry optimization, convergence thresholds are set to be 0.004 Hartree/Å for the forces, 0.005 Å for the displacement and \(10^{-5}\) Hartree for the energy change. We design different initial configurations. Starting with the lowest spin multiplicity for Os\(_n\) cluster, spin-unrestricted calculations are performed to find the low-lying metastable isomers whose frequency is positive, and then some relative properties of ground-state structure are calculated.

To verify the effectiveness of the proposed method, we calculate the dimer Os\(_2\) and find the bond length to be 2.215 nm, which is very close to the experimental value (2.28 nm).[20]

3. Results and discussion
3.1. Geometrical structure

Figure 1 gives the ground-state structures and some low-lying metastable isomers obtained for Os\(_n\) (\(n = 11 \sim 16\)) clusters in this work. The spin multiplicity, symmetry and the relative energy of each structural isomer from the ground state are also labeled below the corresponding structural plot of Fig. 1.

![Fig. 1. (color online) Stable structures of Os\(_n\) (\(n = 11 \sim 16\)) clusters.](attachment:image.png)
Lots of stable structures are obtained in geometry optimization, so we pick out five of the most stable structures in Fig. 1. In the isomers of Os$_{11}$ cluster, pyramid geometry with $C_{3v}$ symmetry (11a) has the lowest energy. The structure combined with cube and triangle with $C_{3h}$ symmetry (11b) lies only 0.057 eV higher than the ground-state structure in total energy. The remaining three structures are very close to the ground-state structure in total energy. The ground-state structure of Os$_{12}$ favors a trigonal prism with $D_{3h}$ symmetry. The second stable structure is 1.527 eV higher than the ground-state structure, so is the third stable isomer. The ground-state structures of Os$_{13}$ are similar, because they are all based on the regular hexagonal prism which is the most stable structure of the Os$_{14}$ cluster. In Os$_{13}$ cluster, the most stable structure is the regular hexagonal prism losing one corner (13a) with $C_{3v}$ symmetry. Adding one atom in the trigonal prism (12a), we obtain a structure (13b) with $C_{2v}$ symmetry which is the second stable structure of Os$_{13}$ cluster. The lowest-energy configuration of Os$_{14}$ cluster is the regular hexagonal prism with two atoms on both undersurfaces, which has $D_{6h}$ symmetry. In total energy, the ground-state structure of Os$_{14}$ cluster is much lower than the second stable configuration (14b) which is added by one atom in the side face of the ground-state of Os$_{13}$ cluster with $C_{1}$ symmetry ($E = 2.134$). In Fig. 1, there are also two structures without symmetry, which are irregular. The ground-state structure of Os$_{15}$ cluster is face-capped hexagonal prism geometry with $C_{2v}$ symmetry (15a). The cage-like geometry with $C_{s}$ symmetry has a high relative energy of $E = 1.735$, and is the second biggest in total energy. The lowest-energy configuration of Os$_{16}$ cluster can be obtained by adding two atoms on the same side face of the ground-state structure of Os$_{14}$ cluster (14a) that has $C_{1}$ symmetry. In Fig. 1, the remaining four isomers are also based on the (14a), and their relative energies are $\Delta E = 0.910$, $\Delta E = 1.170$, $\Delta E = 1.302$, and $\Delta E = 1.744$, respectively.

Fig. 2. (color online) Stable structures of Os$_n$ ($n = 17$ ∼ $22$) clusters.
The low-lying geometries and lowest-energy structures of Os\(_n\) clusters with sizes from 17 to 22 are displayed in Fig. 2. Adding one atom on the opposite of the ground-state structure of Os\(_{16}\) cluster (16a) we can obtain the lowest-energy structure of Os\(_{17}\) cluster. Also, when we add one atom on the opposite of the second stable structure of Os\(_{16}\) cluster, we obtain the second stable structure of Os\(_{17}\) cluster, which is only 0.009 eV higher than the ground-state structure in total energy. For Os\(_{18}\) cluster, the quadrangle with undersurface of a rhombus (18a) is found to be the most stable structure, and has \(D_{2h}\) symmetry. Relative to the ground state, figure (18d) is a little different in configuration. The four atoms on both sides are arranged in the direction parallel to the undersurface, but the relative energy is much higher (\(\Delta E = 1.558\)). The second stable structure (18b) is a mixed structure of Figs. (18a) and (18d), its energy is also between those of the two configurations and it has \(C_{2v}\) symmetry. Adding one atom on the center of the (18d) structure, and then folding, there occurs the lowest-energy structure of Os\(_{19}\) cluster. The second and the third stable structure can be obtained by adding an atom on the (18b) and (18a) structures, and their relative energies are \(\Delta E = 0.087\) and \(\Delta E = 0.542\), respectively. From Os\(_{11}\) to Os\(_{18}\) cluster, their structures each turn into a cage that is somewhat compressed, but from Os\(_{19}\) to Os\(_{22}\) cluster, the configurations each seem to favor the globular cage although these cages are still based on the hexagonal prism. This means that with the increase of size, the structure and stability of the clusters change somewhat, and the transition starts from Os\(_{19}\) cluster.

### 3.2. Relative stability

For insight into the relative stabilities, the size-dependent physical properties are discussed in the following. The average binding energies per atom (\(E_b/\text{atom}\)) and the second-order differences of total energies (\(\Delta_2 E\)) are plotted in Figs. 3 and 4, respectively. The quantities of \(E_b\) and \(\Delta_2 E\) are estimated in the following ways:

\[
E_b(\text{Os}_n) = nE(\text{Os}) - E(\text{Os}_n),
\]

\[
\Delta_2E(\text{Os}_n) = E(\text{Os}_{n+1}) + E(\text{Os}_{n-1}) - 2E(\text{Os}_n),
\]

where \(E(\text{Os}_n)\) is the total energy of the Os\(_n\) clusters, and \(E_b(\text{Os}_n)\) is the binding energy of the system.

As shown in Fig. 3, the variation trend of the average binding energies of osmium clusters can be divided into two phases. From the average binding energy curve of Os\(_{11}\) to Os\(_{19}\) clusters, there exhibits the odd–even oscillation effect, and from Os\(_{20}\) to Os\(_{22}\) clusters, the binding energy increases with cluster size increasing generally. For \(n = 12, 14, 16, 18\), the stabilities of Os\(_n\) clusters are higher than those of their adjacent clusters. We plot the values of \(\Delta_2 E\) as a function of cluster size in Fig. 4. From this figure, odd–even oscillation effect also occurs in the same range size. Four prominent peaks are found to correspond to \(n = 12, 14, 16,\) and 18, indicating that the clusters (especially for Os\(_{14}\) and Os\(_{18}\) clusters) possess the stronger stabilities than their neighbors, which is consistent with the trend of binding energies as shown in Fig. 3.
The energy gap between HOMO and LUMO, which is \( E_{\text{gap}} = E_{\text{LUMO}} - E_{\text{HOMO}} \), is generally considered as an important quantity to evaluate the stability of the cluster. The \( E_{\text{gap}} \) indicates the ability for an electron to transit from HOMO to LUMO. The smaller the value, the more easily the electron will transfer, and a larger \( E_{\text{gap}} \) signifies a weaker chemical activity and a higher stability of cluster. The HOMO–LUMO gaps of the ground-state structures of osmium clusters are plotted in Fig. 5. From this figure, one can easily see two prominent peaks at \( n = 14, 18 \), which suggest the tremendous stabilities of Os\(_{14}\) and Os\(_{18}\) clusters, and accord with the conclusions that are drawn from \( E_b \) and \( \Delta_{2}E \). This means that osmium clusters possess magic numbers of \( n = 14, 18 \). The structures of Os\(_{14}\) and Os\(_{18}\) clusters are based on close-packed hexagonal structure, as we know that the crystal lattice of osmium is a hexagonal dense lattice, which indicates that the consistency between theory and practice holds true only under certain conditions.

The corresponding HOMO and LUMO orbital isosurfaces of Os\(_{14}\) and Os\(_{18}\) clusters.

**Fig. 6.** (color online) Corresponding HOMO and LUMO orbital isosurfaces of Os\(_{14}\) and Os\(_{18}\) clusters.

To explore the size evolution of electronic properties, we analyze the partial densities of states (PDOSs) and total densities of states (TDOSs) for the lowest-energy Os\(_{n}\) clusters with sizes of \( n = 11 \sim 22 \) (provided in Figs. 7–9).

The Fermi level is presented as a vertical line and shifted to zero. Spin-\( \alpha \) (up) and spin-\( \beta \) (down) densities are given in each figure (Figs. 7–9). As shown in most of the DOS figures, the d-orbit curve of PDOS is very similar to the curve of TDOS which is different from the s- and p-orbit curves, and the symmetry of d-orbit curve (except Os\(_{12}\) cluster) is lower, which indicates that there is a greater difference between the spin-up electronic number and the spin-down number, so all the electronic states come mainly from the 5d states compared with other states in Os atoms which are corresponding to the orbital analysis as mentioned before. In all the clusters, each d curve has a great spike, which indicates that the d electron exhibits locality compared with s and p curves. When \( n = 11, 13 \sim 16, 19, 20 \), the symmetry of the DOS curve is much lower. This illustrates that there are many unpaired electrons around the atom. None of their spin multiplicities is 1, which also proves that the unpaired electrons are not very few. The other clusters have very high symmetry, of which the spin multiplicities are all 1. In the total DOSs from Os\(_{11}\) to Os\(_{18}\) cluster, there exist obvious local peaks near the Fermi level, but in the total DOSs from Os\(_{19}\) to Os\(_{22}\) cluster, the number of peaks reduces, and the local peak is less obvious than before, which is mainly because of the structural difference between clusters and accords with the stability analyzed before. Os\(_{12}\) cluster is an exception, the figure has horizontal symmetry, which may contribute to the magnetic moment quenching. The distance between two peaks which stay on each side of the Fermi level is defined as the pseudogap. The pseudogap can directly convey the strength of the covalent properties. The bigger pseudogap they have, the stronger covalent properties there will be. We can find that the pseudogaps of Os\(_{12}\), Os\(_{14}\), and Os\(_{18}\) clusters are bigger than those of the other clusters in Figs. 7–9, which indicates that those clusters have strong covalent bonds and stabilities, which is consistent with the previous analyses.

Based on the optimized geometries, the magnetic properties of Os\(_{n}\) clusters are computed. The total and the average magnetic moments are presented in Fig. 9. The total magnetic moments of Os\(_{13}\), Os\(_{15}\), and Os\(_{16}\) clusters are bigger than the others’. The average magnetic moment of Os\(_{11}\) cluster is 0.18 \( \mu_B \), and the average magnetic moment of Os\(_{12}\) cluster is zero, which is called “magnetic moment quenching”. The atomic magnetic mainly comes from the spin of the electron and the movement of the orbital. When it occurs, the “magnetic moment quenches”, and the electron magnetic moment changes its direction and cannot combine with the orbital magnetic moment, so there cannot be a resultant magnetic moment. Also, like the total magnetic moment, the average magnetic moments of Os\(_{13}\), Os\(_{15}\), and Os\(_{16}\) clusters are bigger than the others’. From Os\(_{18}\) to Os\(_{22}\) cluster, the average magnetic moments are very small, most of them are smaller than 0.1 \( \mu_B \), so indeed they can be said to be nonmagnetic approximately. For Os\(_{14}\) and Os\(_{18}\) clusters, they are highly symmetric but their magnetism is not so big. This may be caused by the difference in electron transfer, i.e., by adding an atom into or replacing an atom from a different place for a different structure: the difference in electron transfer may be great.
Fig. 7. Partial densities of states (PDOSs) of s, p, and d orbitals and total densities of states (TDOSs) of osmium clusters with $n = 11 \sim 14$. The vertical line indicates the Fermi level.
Fig. 8. Partial densities of states (PDOSs) of s, p, and d orbitals and total densities of states (TDOSs) of osmium clusters with \( n = 15 \sim 18 \). The vertical line indicates the Fermi level.
Fig. 9. Partial densities of states (PDOS) of s, p, and d orbitals and total densities of states (TDOS) of osmium clusters with $n = 19 \sim 22$. The vertical line indicates the Fermi level.

In order to describe the local magnetic moment of each atom and its contribution to the total magnetic moment, we give the electron spin density maps of four typical clusters in Fig. 11. The bigger the electron spin density of clusters, the more unpaired electrons around the atom and the bigger local magnetic moment there will be. Conversely, their contribu-
tions to the total magnetic moment will become smaller.\cite{21–24}
In Fig. 11, the cluster with an atom staying in its center (es-
specially the close-packed hexagonal cluster with two atoms stay-
ing in its center) has the smallest spin density, almost invisible.
It illustrates the electrons around these atoms are all paired,
forming stable chemical bonds. When \( n = 14 \), the cluster has
very good symmetry, in which all of the electrons around the
atoms are paired, except the two atoms in the center. It means
that their contributions to the total magnetic moment are al-
most the same. But in the Os\(_{20}\) cluster, the contributions of
atoms mainly come from the cage structure in the right as
shown in Fig. 11, which may be because the cage structure
plays a leading role in the chemical properties when \( n = 20 \).
This phenomenon accords with the stability analysis.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{Fig10.png}
\caption{(color online) Size-dependencies of average magnetic moment and total magnetic moment of Os\(_{n}\) clusters for the lowest-energy structure.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{Fig11.png}
\caption{(color online) Electron spin density maps of Os\(_{n}\) \((n = 12, 14, 18, 20)\) clusters at the ground state.}
\end{figure}

4. Conclusion

Using PW91 functional within GGA, the structure and magnetic
properties of Os\(_{n}\) \((n = 11 \sim 22)\) clusters are de-
termined. For each cluster size, an extensive search for the
lowest-energy structure has been conducted by considering a
number of structural isomers. The most favorite geometries
of Os\(_{n}\) clusters with the sizes of \( n = 11 \sim 18 \) each turn into
a cage that is somewhat compressed, most of these cages are
based on the close-packed hexagonal structure, and from Os\(_{19}\)
to Os\(_{22}\) cluster the ground-state seems to favor the globular
cage, with Os\(_{19}\) cluster being the change point. According
the second-order energy difference and the HOMO–LUMO
gaps, Os\(_{n}\) clusters at \( n = 14 \) and 18 might possess relatively
high stabilities, which means that the osmium clusters possess
magic numbers of \( n = 14, 18 \). As the partial DOS and the to-
tal DOS described, the 5d electrons play a dominant role in the
chemical reaction of Os\(_{n}\) clusters. It is found that the magnetic
moment of Os\(_{n}\) cluster is quenched around \( n = 12 \), and when
\( n = 18 \sim 22 \) the values of all magnetic moments approximate
to zero, due to the difference in electron transfer. Also, from
the electron spin density maps, we know that the contribution
to the total magnetic moment mainly comes from the periph-
ery atoms when \( n = 11 \sim 18 \), and from Os\(_{19}\) to Os\(_{22}\) cluster,
they mainly come from the cage structure.

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\end{itemize}