Reduction of Dimerization Tendency Due to the Decrease in Hybridization Index by Inclusion of 4s and 4p Semicore States as Valence States in Mo\(n\) (\(n=2–18\)) Clusters: A First-Principles Study

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Owing to the unique structural, electronic, and physico-chemical properties, molybdenum clusters are expected to play an important role in future nanotechnologies. However, their ground states are still under debate. In this study, the crystal structure analysis by particle swarm optimization (CALYPSO) approach is used for the global minimum search, which is followed by first-principles calculations, to detect an obvious dimerization tendency in Mo\(n\) (\(n=2–18\)) clusters when the 4s and 4p semicore states are not regarded as the valence states. Further, the clusters with even number of atoms are usually magic clusters with high stability. However, after including the 4s and 4p electrons as valence electrons, the dimerization tendency exhibits a drastic reduction because the average hybridization indices \(H_{sp}\), \(H_{sd}\), and \(H_{pd}\) are reduced significantly. Overall, this work reports new ground states of Mo\(n\) (\(n=11, 14, 15\)) clusters and proves that semicore states are essential for Mo\(n\) clusters.

Key words: Density functional theory, First-principles calculations, Mo clusters, Hybridization indices, 4s and 4p Semicore states

I. INTRODUCTION

Due to its excellent thermal and electrical conductivity, high strength at elevated temperatures, low thermal expansion, and high corrosion resistance, Mo is widely used in high-strength alloys [1], organic electronics [2], substrates in thin-film solar cells [3], and other coating industries [4]. Besides, its sulfide (MoS\(_2\)) is a two-dimensional material that has been applied in solid lubricant [5, 6], phototransistor [7], catalyst to dehydrogenate complex hydrocarbon [8], optoelectronics, and energy harvesting [9]. Owing to their large surface-volume ratio and novel electronic structures, transition metal clusters can exhibit better physical, chemical, and catalytic properties than their bulk phases [10–13]. From the perspective of efficiency and cost-effectiveness, a thorough investigation of Mo clusters is important. Experimentally, absorption/emission spectra [14] and mass-selective resonant two-photon ionization spectra [15] have been used to determine the bond length of Mo\(_2\) as 1.929 and 1.940 ± 0.009 Å, respectively. Theoretically, Mo\(_2\) is usually studied to validate the experimental methodologies. Zhang et al. [16] and Aguilera-Granja et al. [17] calculated the bond length of Mo\(_2\) to be 1.80 and 1.65 Å, respectively, which are inconsistent with the experimental values. However, Min et al. [18],

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Plá et al. [19], and Chaves et al. [20] calculated it as 1.94, 1.93, and 1.92 Å, respectively, which are in excellent agreement with the experimental results. Moreover, they pointed out that the dimerization tendency of Mo\(_n\) \((n=2\sim10)\) clusters observed in previous theoretical calculations is significantly reduced when the 4s and 4p semicore states (SCSs) are explicitly included as the valence states. For convenience, in this work, if SCSs are (are not) included as the valence states, the method is labeled as “with (without) SCS”. Without (with) SCS, the valence electrons of Mo atom are \(4d^55s^1\) \((4s^24p^64d^55s^1)\).

However, the underlying physical mechanism of the above intriguing phenomena in Mo clusters is still not understood completely, and some key questions need to be elucidated: (i) What is the characteristic difference between clusters with and without SCS? (ii) What is the reason for the reduction or disappearance of dimerization tendency? (iii) What are the growth modes of large Mo\(_n\) \((n>10)\) clusters? Resolving these questions is crucial for an in-depth study on the geometric and electronic properties of Mo clusters. In this study, we analyzed the crystal structure by particle swarm optimization (CALYPSO) approach for global minimum search, followed by first-principles calculations, to find that the dimerization tendency of Mo\(_n\) \((n=2\sim18)\) clusters observed in previous theoretical calculations is significantly reduced after including SCSs as the valence states due to the considerable decrease in the hybridization index. Furthermore, with (without) SCS, Mo\(_n\) \((n=2\sim18)\) clusters exhibit metallic (nonmetallic) growth mode.

II. METHODS

The calculations are based on the density functional theory (DFT) [21, 22] with spin-polarized generalized gradient approximation (GGA) [23] implemented in the Vienna \textit{ab initio} simulation package (VASP) code [24, 25]. The wave functions are expanded in a plane wave basis with an energy cutoff of 400 eV. The interaction of valence electrons with the ionic cores is described by projector augmented wave (PAW) method [26, 27]. We used a simple cubic cell with edge length of 20 Å accompanied by a periodic boundary condition and \(\Gamma\) point approximation for Brillouin zone sampling. The total energy is converged to \(10^{-4}\) eV for structural relaxations, and the convergence criterion for the force on each ion is 0.02 eV/Å. The vibrational frequency analysis was also carried out (see FIG. S1 without SCS and FIG. S2 with SCS in supplementary materials), confirming that these structures were also dynamically stable. Here, without semicore orbital, the valence states belonging to the pseudopotential are \(5s^14d^5\). Including the semicore orbital, the valence states belonging to the pseudopotential are \(4s^24p^65s^14d^6\). For the strong-correlation effect, we used GGA+\(U\) \((U=1\sim4)\) to compare with that without \(U\) \((U=0)\), whose details are in Table S1 and FIGs. S3–S5 in supplementary materials.

To test the accuracy of the plane wave basis and the PAW potential used in the VASP code, we calculated the interatomic distance of Mo\(_2\) molecule. Surprisingly, the calculated value is only 1.70 Å without SCS, while it is 1.92 Å with SCS, which are in good agreement with the theoretical [18, 20] and experimental values \((1.93\sim1.94\) Å\) [14, 15]. In this work, the CALYPSO searching method [28–32] coupled with DFT calculations are used for geometrical optimization of Mo\(_n\) \((n=2\sim18)\) clusters with and without SCS. In particular, the structures searched by CALYPSO without SCS have many dimers, while less dimers appear with SCS.

III. RESULTS AND DISCUSSION

A. Structure and average binding energy of Mo\(_n\) \((n=2\sim18)\) clusters

1. Without SCS

Due to their dimerization tendency, the linear Mo\(_n\) \((n=2\sim8)\) clusters [16, 17] are worth exploring. Their structures, average binding energy, energy gap, and spin multiplicity \(M\) \((M=2S+1, S\) is the total spin\) are summarized in Table S1 without SCS in Supplementary materials. In this work, the average binding energy of a cluster is defined as

\[
E_b = E(\text{Mo}_n) - \frac{E(\text{Mo}_n)}{n}
\]  

(1) where \(E(\text{Mo}_n)\) and \(E(\text{Mo}_n)\) represent the total energy of a single Mo atom (in its \(7S\) ground state [15]) and Mo\(_n\) clusters, respectively. Table S2 in Supplementary materials confirms the dimerization tendency, which leads to odd-even oscillation in the average binding energy. The odd-size clusters usually have lower binding energy than their neighbors, indicating relatively lower stability. The structures and properties of linear Mo\(_n\) \((n=2\sim8)\) clusters without SCS are in
agreement with those reported by Zhang et al. [16] and Aguilera-Granja et al. [17].

The structures and average binding energy ($E_b$) of Mo$_n$ ($n$=2–18) clusters without SCS are shown in FIG. 1, where “na” and “n(b–f)” represent the ground state and low-lying isomers, respectively. For a clear visualisation, the atoms forming dimers (less than 2.2 Å) are shown in green, the other atoms are shown in magenta. Further, the bonds of dimers are indicated in red. Besides, some bond lengths are marked from Mo$_2$ to Mo$_6$. In view that there are so many structures, we mainly focus on the ground states. In details, the bond length of Mo$_2$ is 1.70 Å with $E_b$=3.089 eV/atom. Mo$_{2a}$ forms an isosceles triangle with bond lengths of 1.92 and 2.31 Å. Mo$_{2b}$ forms a parallelogram, whose $E_b$ is 0.017 eV/atom higher than the rectangular structure Mo$_{2c}$. Mo$_{2a}$ can be seen as a combination of a dimer and a trimer with spin triplet, which is in agreement with the result of Aguilera-Granja et al. [17]. Mo$_{2a}$ includes three dimers (about 1.75 Å) connected by two bonds (2.91 Å), while Mo$_{2b}$ is obtained by adding a dimer above Mo$_{2c}$. Mo$_{2a}$ is formed by adding an atom on Mo$_{2a}$, while Mo$_{2b}$ exhibits an open structure with an unpaired atom connecting three dimers. Mo$_{2a}$ is obtained by adding a dimer on Mo$_{2a}$, which can also be obtained by adding an atom on Mo$_{2a}$. Mo$_{2b}$ is obtained by adding a dimer to the left of Mo$_{2a}$. Unexpectedly, the binding energy of Mo$_{2a}$ is lower than that of Mo$_{2a}$, indicating that Mo$_{2a}$ is a magic cluster. Mo$_{10a}$ (Mo$_{10b}$, Mo$_{10c}$) exhibits a quasi-cage structure, containing five dimers, while the least stable Mo$_{10d}$ has only three dimers. Mo$_{11a}$ (Mo$_{11b}$) can be regarded as five dimers connected by an unpaired atom. Mo$_{14a}$ shows a larger structural relaxation than Mo$_{15a}$, Mo$_{16a}$, and Mo$_{17a}$ with seven dimers.

For clusters in which $n$ is a small even number such as Mo$_{2a}$, Mo$_{6a}$, Mo$_{8a}$ and Mo$_{10a}$, all the atoms form dimers. From Mo$_{13a}$ to Mo$_{18a}$, the inner atom appears in the ground state structures. Mo$_n$ ($n$=2–18) clusters without SCS exhibit obvious dimerization tendency, indicating their nonmetallic properties. Interestingly, highly symmetrical and compact structures such as Mo$_{4b}$ and Mo$_{15d}$ (Mo$_{15e}$, Mo$_{14f}$) are not necessarily the ground state structure of Mo clusters.

2. With SCS

Table S3 in Supplementary materials shows the structures, average binding energy, energy gap, and the spin multiplicity of linear Mo$_n$ clusters with SCS. The dimerization tendency weakens after the inclusion of SCS. The bond length of dimer (other bonds) increases (decreases) by nearly 0.2 Å (0.1 Å), while the binding energy decreases from 3 eV/atom to 2 eV/atom. It is important to note that the bond length of the same-group atom Cr$_2$ (W$_2$) increases from 1.51 Å (1.86 Å) without SCS to 1.60 Å (2.02 Å) with SCS, where the SCS results are close to the experimental value for Cr$_2$ [33, 34] and theoretical value for W$_2$ [35].

The structures, symmetry information, average binding energy per atom, and spin multiplicity for Mo$_n$ ($n$=2–18) clusters with SCSs are presented in Table S4 (supplementary materials) and FIG. 2, where “na” and “n(b–f)” represent the ground state and some low-lying isomers, respectively. For the ease of visualization, the atoms forming dimers (less than 2.2 Å) are indicated in green, and the other atoms are shown in green. The electronic structure of the ground state of Mo atom is 4d$^{5}$s$^{1}$ (with six unpaired valence electrons). This just half-filled electronic configuration leads to the formation of a strong sextuple bond [36, 37] in the Mo dimer, which may explain its shortest bond length (1.92 Å) among some 4d transition metal dimers (Ru$_2$: 2.07 Å [38], Rh$_2$: 2.20 Å [39], Pd$_2$: 2.49 Å [40], and Ag$_2$: 2.58 Å [32]). The $E_b$ of Mo dimer is 2.008 eV/atom. Mo$_{2a}$ includes an isosceles triangle with bond lengths of 2.16 and 2.41 Å. Mo$_{2a}$ (D$_{2h}$) is 0.060 eV/atom more stable than the planar structure Mo$_{4b}$, showing a transition from two to three dimension. The buckled square pyramid structure Mo$_{2a}$ (C$_2$) is obtained by adding an atom to Mo$_{2a}$ with optimization, leading to a binding energy of 2.973 eV/atom. Mo$_{2a}$ (C$_{3v}$) is a buckled square and Mo$_{2a}$ is a distorted face-capped octahedron. The nearly degenerate Mo$_{8a}$ (C$_2$) and Mo$_{8b}$ (C$_2$) can be obtained by adding an atom on Mo$_{2a}$ and Mo$_{2b}$, respectively. Mo$_{8a}$ (C$_{3v}$) is obtained by adding an atom on Mo$_{8a}$, and Mo$_{10a}$ is obtained by capping two atoms on Mo$_{8b}$, which is nearly degenerate with Mo$_{10b}$ (D$_{2h}$). Table S4 in Supplementary materials presents the average binding energy ($E_b$), electronic spin multiplicity, and equilibrium bond lengths ($R_c$: shorter, longer, and average bond lengths) for the most stable Mo$_n$ ($n$=2–10) clusters, where the values in italic are from Ref.[19]. It is clear from FIG. 1(a) and Table S5 in supplementary materials that our results are consistent with those of Ref.[19]. Apart from Mo$_8$ and Mo$_9$, the spin multiplicity is also in agreement with that reported

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FIG. 1 Structure (the bond length cutoff is 3 Å) and the average binding energies of the ground state of Mo$_n$ ($n=2$–18) clusters without SCS. For clusters in which $n$ is a small even number such as Mo$_4$, Mo$_6$, Mo$_8$ and Mo$_{10}$, all the atoms form dimers. From Mo$_{12}$a to Mo$_{18}$a, the inner atom appears in the ground state structures. Mo$_n$ ($n=2$–18) clusters without SCS exhibit obvious dimerization tendency, indicating their nonmetallic properties. Interestingly, highly symmetrical and compact structures such as Mo$_{14}$b and Mo$_{18}$d, Mo$_{18}$e, Mo$_{18}$f are not necessarily the ground state structure of Mo clusters. The atoms involved in the formation of dimer are shown in green. The other atoms are shown in magenta, and the dimer bonds (less than 2.2 Å) are indicated in red.

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FIG. 2 Structures (the bond length cutoff is 3 Å) with symmetry information and the average binding energies of the ground state of Mo$_n$ ($n=2–18$) clusters with SCS. The atoms forming dimers (less than 2.2 Å) are shown in magenta, the other atoms are indicated in green, and the dimer bonds (less than 2.2 Å) are indicated in red.

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in Ref.[19]. In fact, the energy difference contributed by spin multiplicity is negligible, where the $E_b$ of Mo$_8$ (Mo$_9$) between $M=1$ ($M=3$) and $M=5$ ($M=1$) is only 0.004 eV/atom (0.003 eV/atom).

Mo$_{11}a$ is obtained by adding an atom on Mo$_{10}b$, it has a dimer and is more stable than Mo$_{11}b$ ($C_s$) and Mo$_{11}c$ ($C_1$). Mo$_{12}a$ ($C_{5v}$) can be obtained by moving a surface atom from the regular icosahedrons in Mo$_{13}$ after optimization. As reported for the ground state in Ref.[20], Mo$_{13}a$ ($C_s$) is more favorable than the other four isomers with lower symmetry. Mo$_{14}a$ ($C_{5v}$) has an inner atom, and it is more stable than Mo$_{14}b$ (Mo$_{14}c$) (with one dimer) and Mo$_{14}d$ (with three dimers). With $C_{2v}$ symmetry, Mo$_{15}a$ is more stable than the other five isomers with lower symmetry. Mo$_{16}a$ has low symmetry, while Mo$_{17}a$ ($C_s$) and Mo$_{18}a$ ($C_{2v}$) exhibit high symmetry. The obtained ground states of Mo$_n$ ($n=2$–7, 12, 13) clusters are in agreement with those reported in Ref.[20]. Further, the second most stable isomers of Mo$_8$ ($n=8$–11, 14) obtained in this work are consistent with the ground states in Ref.[20], and the third most stable isomers of Mo$_{15}$ are similar to that in Ref.[20].

B. Bond distribution function of Mo$_n$ ($n=2$–18) clusters

For further clarifying the structural characteristics of Mo$_n$ ($n=2$–18) clusters, the bond distribution function (BDF) of the ground states of Mo$_n$ ($n=2$–18) clusters without SCS is shown in FIG. 3, where the two dotted lines denote bond lengths of 2 Å and 3 Å, respectively. It is clear that less coordinated atoms are related with smaller bond length, and simpler BDF corresponds to higher symmetry. Besides, several bond lengths are less than 2 Å, indicating strong dimerization tendency. The spectra of Mo$_{2}$–8 are noticeably clear with higher symmetry, and that of Mo$_8$ is dispersed.

The bond distribution function (BDF) of the ground states of Mo$_n$ ($n=2$–18) clusters with SCS is shown in FIG. 4, where the bonds with length less than 2 Å decrease significantly, indicating the weakening of dimerization tendency. The spectrum of Mo$_{10}$ becomes more dispersed, manifesting lower symmetry for $n<10$.

C. Stability of Mo$_n$ ($n=2$–18) clusters

The stability properties of the ground states of Mo$_n$ ($n=2$–18) clusters without SCS (black triangles) and those with SCS (red stars) are systematically analyzed in FIG. 5. FIG. 5(a) shows the variation in average binding energy ($E_b$) as a function of the cluster size. It is evident that the $E_b$ of Mo$_n$ clusters usually increases as the cluster size increases. The $E_b$ of Mo$_3$ without SCS is even lower than that of Mo$_2$, which is not reasonable, while the $E_b$ value of Mo$_3$ with SCS is higher than that of Mo$_2$. To exhibit the relative stabilities of these clusters, FIG. 5(b) displays the second-order difference of energies, i.e.,

$$d^2E = E_{n+1} + E_{n-1} - 2E_n$$

(2)

As shown in FIG. 5(b), clusters with even number of atoms usually exhibit peaks in the $d^2E$ curve, in-
FIG. 5  (a) Average binding energy, $E_b$. (b) Second-order dierence of energies, $d^2E = E_{n+1} + E_{n-1} - 2E_n$. (c) Average bond length, $R$. (d) Energy gap ($E_g$), which is the energy dierence between HOMO and LUMO. The triangles and stars represent the ground states of Mo$_n$ ($n=2$–18) clusters without SCS and that with SCS, respectively.

indicating higher stability than their neighbors. It may be noted that the odd-even oscillation of $d^2E$ without SCS is more obvious than that with SCS due to the dimerization effect. Such oscillation in electronic properties also induces oscillation in geometrical structures without SCS in FIG. 5(c) (black triangles), where the average bond lengths exhibit odd-even oscillation with respect to the cluster size $n$. This implies that higher stability usually corresponds to shorter average bond length. However, the odd-even oscillation in average bond lengths does not appear in the ground state with SCS (in FIG. 5(c), red stars). FIG. 5(d) shows that the HOMO-LUMO gap usually decreases as cluster size increases, and it shows odd-even oscillation with or without SCS. Such odd-even oscillation is also shown on chemical hardness (or fragmentation energy, originally based on bond dissociation energy), one of the highly useful concepts which enable chemists to understand reactivities without reference to large supercomputers and databases. To elaborate the reason that Mo$_n$ clusters become more reactive as size increases, we calculated the fragmentation energy of Mo$_n$ of an $n$-atom cluster into $p$-atom and $q$-atom ($n=p+q$) fragments,

$$E_f(\text{Mo}_n) = E(\text{Mo}_p) + E(\text{Mo}_q) - E(\text{Mo}_n) \quad (3)$$

in which the fission is assumed to occur along the lowest energy pathways with no activation barrier [41].

For FIG. S6(a) in supplementary materials, without SCS, Mo$_n$ dissociates to a Mo$_2$ and Mo$_{n-2}$. For FIG. S6(b) with SCS, other than Mo$_4$ to Mo$_2$ and Mo$_2$, Mo$_n$ dissociates to a single Mo$_1$ and Mo$_{n-1}$, in accordance with the experiment results that Mo single atom has the highest photon intensity [15]. Besides, Mo$_8$ appears as a peak point, in accordance with its high photon intensity in experiment [15]. For both methods (with or without SCS), the other dissociation path (decomposed product is not Mo$_1$ or Mo$_2$) is not favorable. Interestingly, without SCS (see FIG. S6(a)), the fragmentation energy shows obvious odd-even oscillation (the value of even size is usually smaller than that of odd size clusters), because of the relatively stability for even size clusters. While with SCS (see FIG. S6(b)), the fragmentation energy did not manifest obvious odd-even oscillation, because of the reduction of dimerization tendency. In conclusion, the fragmentation behavior showed the reduction of the dimer tendency after including the 4s and 4p electrons as valence electrons.

D. Average number of electrons in s, p, and d orbitals of Mo$_n$ ($n=2$–18) clusters

To elucidate the role of odd-even oscillation in the stability of Mo$_n$ clusters with and without SCS, we obtained the average number of s, p, and d electrons in the Mo$_n$ clusters by projecting the valence charge in the Wigner-Seitz sphere onto the atomic orbitals, which are shown in FIG. 6. Here, we acknowledge that the space division is somewhat arbitrary, but the obtained result is almost independent of Wigner-Seitz-sphere radius and can provide useful qualitative information on the electronic structures of the ground state clusters presented in FIGs. 1 and 2. The valence atomic orbital with SCS is 4s$^2$4p$^6$4d$^5$5s$^1$, which is obviously different from that without SCS (4d$^5$5s$^1$). It is clear from FIG. 6(a) that the average number of s electrons with SCS is always around 2.15 from Mo$_2$ to Mo$_{18}$, while it shows odd-even oscillations around 0.50 without SCS, where the clusters with odd (even) atoms have more s electrons when $n<12$ ($n\ge12$) with a crossover at $n=12$. In FIG. 6(b), the average number of p electrons with
SCI is usually 5.90, while it increases from nearly 0.10 to 0.30 without SCS. It is evident in FIG. 6(c) that the average number of d electrons with SCS is always around 3.30 from Mo$_2$ to Mo$_{18}$, while it shows odd-even oscillations around 4.70 without SCS, where the clusters with even (odd) atoms have more d electrons when $n<12$ ($n\geq12$) with a crossover at $n=12$. Interestingly, without SCS, the average number of d electrons shows the opposite oscillation tendency as that of the s electrons, indicating strong hybridization between s and d orbitals. Atomic orbital with SCS is 4s$^2$4p$^5$4d$^5$5s$^1$, which is obviously different from that without SCS (4d$^5$5s$^1$).

E. Hybridization index of Mo$_n$ ($n=2$–18) clusters

1. Hybridization index of the ground state of Mo$_n$ ($n=2$–18) clusters

FIG. 7 shows the s-p (s-d, p-d) hybridization indices of the ground state of Mo$_n$ ($n=2$–18) clusters, which are defined as

\[ H_{sp} = \sum_{i=1}^{n} \sum_{I} \text{occ} w_{i,s}^{(I)} w_{i,p}^{(I)} \]  
\[ H_{sd} = \sum_{i=1}^{n} \sum_{I} \text{occ} w_{i,s}^{(I)} w_{i,d}^{(I)} \]  
\[ H_{pd} = \sum_{i=1}^{n} \sum_{I} \text{occ} w_{i,p}^{(I)} w_{i,d}^{(I)} \]

where $w_{i,s}^{(I)}$, $w_{i,p}^{(I)}$, and $w_{i,d}^{(I)}$ is the square of the projection of the ith Kohn-Sham orbital onto the s (p, d) spherical harmonics centered at atom I, integrated over a sphere of radius equal to half of the shortest NN distance in each cluster [42]. The spin index is implicit in the sum of orbitals $i$ in Eqs. (4–6). The black triangles represent the ground state of Mo$_n$ ($n=2$–18) in FIG. 1 without SCS, and the red stars represent the ground state of Mo$_n$ ($n=2$–18) in FIG. 2 with SCS. FIG. 7(a) shows the variation in hybridization index $H_{sp}$ as a function of cluster size, where $H_{sp}$ with SCS is significantly smaller than that without SCS. Excluding Mo$_3$, odd-even oscillation exits without SCS, where for $n\leq11$, the clusters with odd number of atoms have larger $H_{sp}$, while for $n>11$, the clusters with even number of atoms have larger $H_{sp}$. Surprisingly, the $H_{sp}$ of Mo$_2$ with SCS is significantly larger than that without SCS, which is explained in the later subsection. The value of $H_{sd}$ in FIG. 7(b) without SCS shows obvious odd-even oscillation with crossover at $n=12$, which follows the same trend as the average number of s electrons in FIG. 6(a). The value of $H_{pd}$ in FIG. 7(c) without SCS increases as

![FIG. 6 Variation in the average number of electrons per Mo atom as a function of cluster size for the ground state of Mo$_n$ ($n=2$–18) clusters: (a) s electrons, (b) p electrons, (c) d electrons. The triangles and stars represent the ground states in FIG. 1 without SCS and in FIG. 2 with SCS, respectively.](image)

![FIG. 7 (a) s-p, (b) s-d, and (c) p-d hybridization indices of the ground state of Mo$_n$ clusters ($n=2$–18). The triangles and the stars represent the ground states of Mo$_n$ clusters ($n=2$–18) without SCS and with SCS, respectively.](image)
the cluster size increases, indicating similar oscillation as that shown in FIG. 7(b) from \( n=8 \). With SCS, the odd-even oscillation of the hybridization index is not observed. Compared to \( H_{sd} \) and \( H_{pd} \), \( H_{sp} \) is rather small for both \( Mo_n (n=2−18) \) clusters with and without SCS.

F. Hybridization index of linear \( Mo_n (n=2−8) \) clusters

To explain the reason for large \( H_{sp} \) of \( Mo_2 \), we show the \( s-p \) (\( s-d \), \( p-d \)) hybridization index of linear \( Mo_n (n=2−8) \) clusters in FIG. 8, where the black triangles (red stars) represent the linear structures of \( Mo_n (n=2−8) \) structures without (with) SCS in Table S1 (S2) in supplementary materials. FIG. 8(a) shows that the value of \( H_{sp} \) with SCS is significantly larger than that without SCS, especially for \( n=2, 6−8 \). Besides, the odd-even oscillation is more obvious with SCS than that without SCS. FIG. 8(b) shows that the value of \( H_{sd} \) with SCS is significantly smaller than that without SCS, while the odd-even oscillation with SCS is much weaker than that without SCS. FIG. 8(c) shows that the value of \( H_{pd} \) with SCS is smaller than that without SCS, and the oscillation tendency of \( H_{pd} \) with SCS is the same as that of \( H_{sp} \) with SCS. Compared to \( H_{sd} \) and \( H_{pd} \), \( H_{sp} \) is rather small, indicating that d electrons play a vital role in the hybridization process.

IV. CONCLUSION

We used CALYPSO approach and first-principles calculations to prove that the dimerization tendency of \( Mo_n (n=2−18) \) clusters is weakened if SCS are considered, which was attributed to the reduction in the average hybridization indices. This was consistent with the experimental results and recently published works. Furthermore, new ground states of \( Mo_n (n=11, 14, 15) \) clusters were found. Overall, this work emphasizes that SCS are essential for \( Mo_n (n=2−18) \) clusters, and they may also be important for the clusters of same-group atoms such as Cr and W.

Supplementary materials: The complete electronic structure of the studied \( Mo_n (n=2−18) \) clusters and the detailed information of the properties of ground states of \( Mo_n (n=2−18) \) clusters are given.

V. ACKNOWLEDGMENTS

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