ARTICLE

Unbiased Fuzzy Global Optimization of Morse Clusters with Short-Range Potential for $N \leq 400$

Liping Chen$^{a,b}$, Linjun Wang$^c$

$^{a}$ Hangzhou Institute of Advanced Studies, Zhejiang Normal University, Hangzhou 311231, China
$^{b}$ Key Laboratory of Excited-State Materials of Zhejiang Province, Zhejiang University, Hangzhou 310027, China
$^{c}$ Key Laboratory of Excited-State Materials of Zhejiang Province, Department of Chemistry, Zhejiang University, Hangzhou 310027, China

(Dated: Received on October 24, 2021; Accepted on November 12, 2021)

Global optimization of Morse clusters with short-range potential is a great challenge. Here, we apply our recently developed unbiased fuzzy global optimization method to systematically study Morse clusters with the potential range $\rho = 14$ and the number of atoms $N$ up to 400. All the putative global minima reported in the literature have been successfully reproduced with relatively high success ratios. Compared to the available results for $N \leq 240$ and several larger Morse clusters, new global minima (and local minima) with lower energies have been found out for $N = 164, 175, 188, 193, 194, 197, 239, 246, 260, 318$, and $389$. Clusters with magic numbers are figured out through fitting the size-dependent global minimum energies. The cluster structures tend to be close-packed for short-range potential with large $N$.

Key words: Unbiased fuzzy global optimization, Morse clusters, Short-range potential

I. INTRODUCTION

Nanometer-sized clusters are aggregates of atoms or molecules. They may exhibit novel size-dependent chemical and physical properties, which are significantly different from those of isolated atoms or molecules and bulk materials [1–6]. Thereby, clusters have attracted a lot of attention both in experiment and theory [5, 7]. While the properties are intrinsically determined by the structures, the lowest-energy structure corresponding to the global minimum (GM) on the potential energy surface (PES) is of the most importance to understand the intrinsic origin of macroscopic properties [8]. In experiment, it is difficult to identify the detailed atomic structure of clusters, especially when the cluster is relatively large. Since the number of local minima generally grows exponentially with the cluster size, global optimization (GO) to search the GM among all the local minima is regarded as a nondeterministic polynomial-time hard (NP-hard) problem [9–11]. Although it is a challenging task, theory has played a more and more important role in structure prediction [12–14].

A lot of efforts have been devoted to developing reliable and efficient GO methods [15–34], which can be either biased or unbiased. In biased GO methods, extra conditions (such as symmetries) of the structure are presumed. As a large number of structures are filtered out from the search space, large clusters can be more efficiently dealt with. Considering that the true GM
structure may be excluded due to the specified conditions, unbiased GO methods have broader applicability. In simulated annealing [15, 16], it is easy to go across barriers on the PES and accept new structures because the initial temperature is generally high. As the temperature decreases gradually, the structure search becomes localized in certain regions. As a result, the efficiency of simulated annealing strongly relies on the variable temperature setup. Genetic algorithms follow the spirit of the Darwinian evolution process but utilize energies as the criteria of fitness [17, 18]. In an iterative way, the optimized structures are mated to generate potential structures with lower energies. Basin hopping is also a widely used GO method [19, 20], where the original PES is replaced by a set of basins through transformation, but the GM keeps the same. Due to the reduced energy barriers, it is generally easier to find out the GM in the modified PES. Dynamic lattice searching (DLS) is another efficient GO method [21, 22]. Starting with a random local minimum structure, a DLS run includes a circulation of construction and searching of the dynamic lattice. The dynamic lattice construction identifies all possible positions for atoms which are added to the surface of the local minimum structure. In dynamic lattice searching, the occupied atom with the highest energy is moved to the vacant site with the lowest energy repeatedly to obtain lower energy structures. As each DLS run converges at a specific funnel of the PES, the GM structure can be found with a number of independent DLS runs. In addition to these traditional approaches, there exist many other new or variant GO methods [23–34].

Recently, we have proposed a novel unbiased fuzzy global optimization (FGO) method [32]. On the basis of a randomly generated initial structure, directed Monte Carlo (DMC) and surface Monte Carlo (SMC) are carried out in the discrete space to obtain low-energy candidate structures, which are further optimized in the real space to get the GM. FGO has been applied to Lennard-Jones (LJ) clusters with up to 1000 atoms [32]. All the GM structures reported previously have been obtained with a low scaling of CPU time as a function of the cluster size, and new GM structures for LJ clusters with 894, 974, and 991 atoms have been found out. The results show that FGO is an unbiased GO method with both high efficiency and robustness [32].

In clusters, the interaction between atoms can be described by different potentials. Especially, pair-wise LJ and Morse potentials have been widely adopted. Compared with LJ clusters, the GO of Morse clusters has been less extensively investigated [25, 35–46]. For a \(N\)-atom Morse cluster denoted as \(M_N\), the total potential energy can be described by the sum of all pair-wise interactions as

\[
E_{\text{tot}} = \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} V_M(r_{ij})
\]

(1)

\[
V_M(r_{ij}) = \varepsilon \phi(1-r_{ij}/r_0)\left[\phi(1-r_{ij}/r_0) - 2\right]
\]

(2)

where \(\varepsilon\) is the well depth, \(r_0\) is the equilibrium distance, \(r_{ij}\) is the distance between atoms \(i\) and \(j\), and \(\rho\) characterizes the potential range. By definition, large \(\rho\) characterizes short-range interaction, and \textit{vice versa}. For the sake of simplicity, reduced units with \(\varepsilon=r_0=1\) are used throughout this work.

In 1995, Doye and coworkers studied all Morse clusters with 25 atoms or less and a selection of sizes for \(35 < N < 80\) with different range of potential \((i.e., \rho=3, 6, 10, \text{and } 14)\) [35]. They showed that large \(\rho\) tends to destabilize the strained structures, and the GM structures change from icosahedral to decahedral to face-centered cubic (fcc) with increasing \(\rho\). Since there is no common strain-free close-packed (scp) lattice, it is generally very difficult to optimize the scp structures. In 2007, Cheng and Yang developed an efficient method to study the scp structures of Morse clusters with short-range potential \(\rho=14\) for \(N<250\) [41]. They demonstrated that the optimal scp structures are lower in energy than the fcc structures in most cases. Cheng, Feng, and coworkers have also used the DLS method to investigate the GM structures of Morse clusters for \(N<240\) with different range of potential \((i.e., \rho=3.0, 3.5, 4.0, 4.5, 5.0, 6.0, 8.0, 10.0, \text{and } 14.0)\) [42, 43]. They successfully located new GM structures and found that as \(\rho\) increases, the GM structures change from disordered to icosahedral to decahedral to close-packed, and the size effect on structures is weaker. In 2012, Marques and coworkers applied the big-bang method to study Morse clusters with different \(\rho\) [44]. They showed that the GM structures can always be obtained with small \(\rho\), and reported a new GM structure for \(N=240\) with \(\rho=3\). However, the method failed to obtain the GM structures for Morse clusters with relatively large \(\rho\) even for small \(N\) \(\text(e.g., } N=27 \text{ and 36 with } \rho=10, \text{ and } N=27, 28, 34-37, \text{ and 40 with } \rho=14\) [45]. In 2013, Shang and Liu developed the stochastic surface walking method (SSW) and studied Morse clusters with up to 103 atoms and \(\rho=14\) [25, DOI:10.1063/1674-0068/cjcp2110210 ©2021 Chinese Physical Society
Morse clusters with algorithm \[32\] to systematically study the GM structures of Morse clusters with short-range potential, namely, there exist many local minima \[35\text{–}38\]. Besides, the number of local minima increases rapidly with the cluster size. Hence, searching the GM structure presents a great challenge as both \(N\) and \(\rho\) increase in Morse clusters. To the best of our knowledge, the GM structures of Morse clusters with short-range potential \(\rho=14\) have been investigated only for \(N\leq240\) \[35\text{–}45\] and some selected large sizes with \(N=241\text{–}244, 247, 260, 318,\) and \(389\) \[46\]. Especially, the energies of scp and fcc structures are compared for \(N=244, 247, 260, 318,\) and \(389\).

As pointed out by Doye and coworkers, the PES is very “noisy” for Morse clusters with short-range potential. In this work, we use the recently developed FGO algorithm \[32\] to study the GM structures of Morse clusters with \(\rho=14\) and up to 400 atoms.

II. METHODOLOGY

A detailed description of the FGO algorithm has been given in Ref.\[32\], and thus we only briefly discuss about the major steps below. According to Eq.(1) and Eq.(2), the energy of a Morse cluster for a given \(\rho\) is totally determined by the distances between atoms. In the discrete space, the distance-dependent interaction energy in Eq.(2) can be precomputed, stored in an array, and read out directly when needed without recalculation.

Taking this advantage, FGO is mainly carried out in the discrete space to achieve an efficient search of the GM structure. Due to the space discretization error, however, the candidate structures in the discrete space with the lowest energy may differ from the true GM structure. Thereby, the candidate structures with relatively low energies are optimized subsequently in the real space to get the true GM structure. A uniform grid spacing of \(d=0.02\) is utilized along \(x\), \(y\), and \(z\) directions to achieve a good balance between accuracy and efficiency in the optimizations. In FGO, the initial cluster structure is randomly generated by placing the \(N\) atoms on different discrete grids in a sphere with the radius \(R=0.4N^{1/3}\), and then locally optimized in the discrete space.

In the DMC step, the energy of each atom \(i\) interacting with its neighboring atoms within the range \(R_{\text{cut}}=2.1, E_i\), is calculated according to Eq.(2). On the basis of \(E_i\), adjustable parameters \(E_{\text{active}}, E_{\text{target}},\) and \(\sigma_{\text{target}}\) are introduced to define the probabilities of choosing active and target atoms \[32\],

\[
p_{\text{active}}^i = \frac{\exp\left(E_i/E_{\text{active}}\right)}{\sum_j \exp\left(E_j/E_{\text{active}}\right)}
\]

\[
p_{\text{target}}^i = \frac{\exp\left[-(E_i - E_{\text{target}})^2/(2\sigma_{\text{target}}^2)\right]}{\sum_j \exp\left[-(E_j - E_{\text{target}})^2/(2\sigma_{\text{target}}^2)\right]}
\]

Once an active atom and a target atom are selected, a new structure is generated by moving the active atom to the neighborhood of the target atom. Due to the atom move, the active atom experiences an energy change \(\delta E\). If \(\delta E<0\), the new structure is accepted directly and then locally optimized in the discrete space. Based on the new cluster structure, the probabilities of active and target atoms are updated by Eq.(3) and Eq.(4) accordingly. If \(\delta E\geq0\), the new structure is also accepted when \(\eta<\exp(-\delta E/E_{\text{active}})\), where \(\eta\) is a uniform random number and \(E_{\text{active}}\) is a parameter; otherwise, the new structure is rejected, and the active atom stays in its original position. These procedures are repeated until the cluster energy cannot be reduced within \(P_{\text{stop}}^{\text{DMC}}N^2\) steps, where \(P_{\text{stop}}^{\text{DMC}}\) is a parameter.

Two layers of DMC have been proposed in FGO for LJ clusters and are also adopted here due to the similarity between LJ and Morse clusters. For each run, the cluster structure with the lowest energy obtained from the first-layer DMC (DMC1) are used as the initial cluster structure in the second-layer DMC (DMC2). For Morse clusters in this study, we set, \(E_{\text{active}}=0.5, E_{\text{target}}=-2.1, \sigma_{\text{target}}=1.25, E_{\text{DMC}}^a=0.4,\) and \(P_{\text{stop}}^{\text{DMC}}=6.0\) in DMC1, and \(E_{\text{active}}=0.5, E_{\text{target}}=-5.5, \sigma_{\text{target}}=1.3, E_{\text{DMC}}^a=0.3,\) and \(P_{\text{stop}}^{\text{DMC}}=4.0\) in DMC2. After DMC2, we obtain the lowest cluster energy \(E_{\text{lowest}}\). Then, the structures with energies smaller than \(E_{\text{lowest}}+2.0\) are reoptimized in the real space, and the one with the lowest-energy is regarded as the initial structure in SMC.

In the SMC step, the binding energy of each atom in the cluster is calculated first \[32\]. While \(N_{\text{move}}\) most unstable atoms are chosen based on the binding energies, the rest atoms form the frozen core. New stable
sites bonded to the core atoms are located by adding atoms to the surface of the core one by one, and the number of stable sites is referred as \( N_{\text{site}} \). For each iteration, an unstable atom and a stable site are chosen based on uniform weights, and a new structure is generated by moving the unstable atom to the stable site. Similar algorithms as in DMC are performed to decide whether the new structure is accepted or not based on a parameter \( E^\text{SMC}_a \) to replace \( E^\text{DMC}_a \). These procedures are repeated until the cluster energy cannot be reduced within \( P^\text{DMC}_{\text{stop}}N_{\text{move}}N_{\text{site}} \) steps, and the lowest cluster energy \( E_{\text{lowest}} \) is updated. For Morse clusters in this study, we set \( N_{\text{move}}=30, E^\text{SMC}_a=0.25, \) and \( P^\text{DMC}_{\text{stop}}=5.0 \). Finally, the structures with energies smaller than \( E_{\text{lowest}}+0.3 \) are reoptimized in the real space, and the one with the lowest energy is regarded as a candidate GM structure. In FGO, the atom move acts only on one atom at each time, which cannot always search the whole configuration space of the cluster. Therefore, we perform a number of independent FGO runs for each \( M_N \) cluster, and the structure with the lowest energy among all the FGO runs is regarded as the GM structure of \( M_N \).

III. RESULTS AND DISCUSSION

A. Success ratios of the global minimum structures

For each \( M_N \) with \( \rho=14 \), we carry out 1000 independent FGO runs. The lowest-energy structure obtained in all the runs is considered as the GM structure, while all other structures are local minima. In Table S1 of the Supplementary materials, we list the energies of GM structures for all \( M_N \) clusters with \( N \leq 400 \). Compared with the available results for \( N \leq 250 \) and \( N = 260, 318, \) and 389 [41–43, 46], either the putative GM energy or a lower GM energy has been obtained for each \( M_N \) by FGO. The success ratio is calculated as the total number of GM structures identified in all the runs divided by 1000. In FIG. 1, we show the success ratio as a function of the cluster size \( N \). In general, the success ratio decreases as the cluster size grows due to the rapid expansion of the configuration space. In detail, 80% of the \( M_N \) clusters have success ratios larger than 0.1 for \( N \leq 200 \), while 80% of the clusters have success ratios larger than 0.01 for \( 200 < N \leq 300 \). Especially, only one cluster (i.e., \( M_{288} \)) within \( N \leq 300 \) has a low success ratio of 0.001 because the GM structure is a truncated octahedron with \( T_d \) symmetry. Note that LJ\(_{38} \) has a similar truncated octahedral GM structure and is difficult to obtain by most GO algorithms as well [20, 21, 44]. For \( N = 301–400 \), 24% of the clusters still have success ratios larger than 0.01. However, there are 10 clusters with low success ratio of 0.001. For these clusters, further investigation is needed to confirm whether the true GM has been obtained. Note that the search of the GM structure for relatively large \( N \) with \( \rho=14 \) also becomes difficult for other GO methods. For instance, it has been shown that the GM structure of \( M_89 \) was found only once among 100 independent SSW trajectories within 104 Monte Carlo (MC) steps [25, 45], which means that the success ratio is about 0.01. Besides, the hit number of the GM structure for \( M_{200} \) in \( 10^4 \) DLS runs is about 20, corresponding to a success ratio around 0.002 [43]. In comparison, the success ratios of \( M_{89} \) and \( M_{200} \) are respectively 0.193 and 0.188 in the present study, implying the high efficiency of FGO in searching the configuration space of \( M_N \) with \( \rho=14 \).

B. Structure distributions of \( M_{100}, M_{200}, M_{300}, \) and \( M_{400} \)

FIG. 2(A–D) show the structure distribution (i.e., the number of a specified structure found out in 1000 independent FGO runs as a function of the corresponding cluster energy) for \( M_{100}, M_{200}, M_{300}, \) and \( M_{400} \), respectively. To simplify the discussions, the energies of the corresponding GM structures are all shifted to zero. The unbiased nature of FGO allows us to capture different types of structures. For \( M_{100} \) and \( M_{200} \) with \( \rho=14 \),

\[ \text{DOI:10.1063/1674-0068/cjcp2110210} \]

©2021 Chinese Physical Society
FIG. 2 Number of structures in 1000 FGO runs as a function of the cluster energies for (A) M\textsubscript{100}, (B) M\textsubscript{200}, (C) M\textsubscript{300}, and (D) M\textsubscript{400} with $\rho=14$. The GM energies of the four clusters (i.e., $-439.070547$, $-944.800223$, $-1463.964377$, and $-1993.525153$) are shifted to zero. The structures of the GM, the local minima around 0.5 and 7 with relatively high hit numbers are shown in each inset and labelled as I, II, and III, respectively. The corresponding energy positions are also indicated.

it has been shown that the structures with relatively high energies around 7 are the most predominant conformations in DLS calculations [42, 43]. In FGO, these structures (labeled by III) also have relatively high hit numbers, implying that they are locally very stable and act as major bottlenecks for GO. However, the local minimum with the second lowest energy around 0.5 (labeled as II in FIG. 2(A)) and the GM with the lowest energy (labeled as I in FIG. 2(B)) now have the highest hit numbers for M\textsubscript{100} and M\textsubscript{200}, respectively. Thereby, FGO could capture low-energy structures more easily.

As the cluster size grows, the number of local minima increases significantly. As shown in FIG. 2(C) and 2(D), the overall hit numbers for major conformations decrease, and more and more local minima appear for M\textsubscript{300} and M\textsubscript{400}. Thereby, the search of GM becomes extremely difficult for large clusters with short-range potential (e.g., $\rho=14$), agreeing with previous studies [35–38]. In the insets of FIG. 2, we show the structures of the GM, the local minima around 0.5 and 7 with relatively high hit numbers, which are labelled as I, II and III, respectively. The corresponding energy positions are also indicated. The GM structure changes from tetrahedron in M\textsubscript{100} (see FIG. 2(A)) and decahedron in M\textsubscript{200} (see FIG. 2(B)) to close-packed structures in M\textsubscript{300} and M\textsubscript{400} (see FIG. 2(C) and 2(D)). In all cases, the structures with the highest hit numbers are decahedral, but antilayers are present in M\textsubscript{300}.

C. New global and local minimum structures

In Table I, we summarize the new GM and local minima obtained by our FGO, which possess energies lower than the reported GM structures in Refs.[41–43, 46]. While new GM structures are denoted as $N_A$, new local minima are expressed as $N_B$, $N_C$, and so on. The corresponding structures of these new GM and local minima are shown in FIG. 3, where the structures of the reported GM for M\textsubscript{N} in the literature are referred as $N$ and also shown for comparison. The coordinates of the new GM structures are given in the Supplementary materials.

The GM structures for M\textsubscript{N} with $\rho=14$ and $N\leq240$ have been systematically investigated by DLS [42, 43]. Besides, the energies of the scp and fcc structures are compared for $\rho=14$ and $N\leq250$ through constructing...
TABLE I  Energies of the new GM and local minima by FGO that are lower than those of the corresponding GM reported in the literatures for Morse clusters with \( \rho = 14 \). The first column lists the number of atoms \( N \) in Morse clusters. While NA expresses the new GM of \( M_{231} \), NB and NC denote new local minima by FGO. The second column gives the energies of the structures listed in the first column. The third column shows energies of the corresponding GM structures reported in the literature.

<table>
<thead>
<tr>
<th>( N )</th>
<th>FGO</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>164A</td>
<td>-758.088521</td>
<td>-758.088391 [43]</td>
</tr>
<tr>
<td>175A</td>
<td>-815.017100</td>
<td>-815.007921 [43]</td>
</tr>
<tr>
<td>175B</td>
<td>-815.013069</td>
<td>-815.007921 [43]</td>
</tr>
<tr>
<td>188A</td>
<td>-881.845600</td>
<td>-881.836606 [43]</td>
</tr>
<tr>
<td>193A</td>
<td>-908.742729</td>
<td>-908.727339 [43]</td>
</tr>
<tr>
<td>194A</td>
<td>-913.749840</td>
<td>-913.713089 [43]</td>
</tr>
<tr>
<td>197A</td>
<td>-928.775119</td>
<td>-928.775109 [43]</td>
</tr>
<tr>
<td>197B</td>
<td>-928.775111</td>
<td></td>
</tr>
<tr>
<td>239A</td>
<td>-1144.548217</td>
<td>-1144.532820 [43]</td>
</tr>
<tr>
<td>239B</td>
<td>-1144.548047</td>
<td></td>
</tr>
<tr>
<td>246A</td>
<td>-1181.181104</td>
<td>-1181.168892 [41]</td>
</tr>
<tr>
<td>260A</td>
<td>-1255.600136</td>
<td>-1254.298339 [46]</td>
</tr>
<tr>
<td>260B</td>
<td>-1254.393704</td>
<td></td>
</tr>
<tr>
<td>260C</td>
<td>-1254.298648</td>
<td></td>
</tr>
<tr>
<td>318A</td>
<td>-1560.161618</td>
<td>-1560.11539 [46]</td>
</tr>
</tbody>
</table>

the motifs [41]. In comparison, the GM energies in Refs.[42, 43] are the same as or lower than the corresponding scp energies in Ref.[41] for \( N \leq 240 \) except \( M_{231} \), where both the optimal scp and fcc structures are lower in energy. All the energies of the reported GM structures are exactly reproduced in the present FGO study. Especially, the first and second lowest energies for \( M_{231} \) by FGO correspond to the lower energies of the optimal scp and fcc structures reported in Ref.[41], respectively. In addition, new GM structures are obtained for \( N = 164, 175, 188, 193, 194, 197, \) and 239, and new local minima are found out for \( N = 175, 197, \) and 239 with \( \rho = 14 \) and \( N \leq 240 \). For all these systems, the energy difference between new GM/local minima and the reported GM is small (see Table I) and the corresponding structural change is related to only a few atoms on the surface highlighted in red (see FIG. 3).

For instance, the energy difference between 164A and 164 (197B and 197) is only 0.000130 (0.000002), and the two corresponding structures can be transformed to each other by moving only one atom on the surface (see FIG. 3).

A heuristic algorithm based on the Strongin method has been applied to calculate the GM energies for several \( M_N \) with \( \rho = 14 \) and \( N > 240 \), namely, \( N = 241, 242, 243, 244, 247, 260, 318, \) and 389 [46]. Note that Cheng and Yang have systematically studied \( M_N \) with \( \rho = 14 \) and \( N \leq 250 \) through constructing the scp and fcc motifs [41], and demonstrated that optimal scp structures are lower in energy than fcc structures in most cases. For \( N = 241, 242, 243, 244, \) and 247, the GM energies by FGO are all lower than those in Ref.[46], but the same as those reported in Ref.[41]. It is important to emphasize that there exist 15 local minima in FGO with lower energies than that reported in Ref.[46] for \( N = 241, 32 \) for \( N = 242, 5 \) for \( N = 243, \) and 34 for \( N = 247 \), further highlighting the complex PES for Morse clusters with both large \( N \) and \( \rho \). In fact, all the energies of the scp structures in Ref.[41] have been reproduced by FGO for \( N = 241 \) in an unbiased manner. Especially, a new GM structure with lower energy (i.e., 246A) is obtained for \( M_{246} \). As shown in FIG. 3, both 246A and 246 are dense-packed but associated with a big structure change. As a result, the energy difference 0.012212 is relatively large.

For \( N > 250 \) with \( \rho = 14 \), actually only three Morse
Clustering (i.e., M_{260}, M_{318}, and M_{389}) have been studied in the Ref.[46]. For all these three systems, however, we obtain new GM structures by FGO (i.e., 260A, 318A, and 389A in Table I). In FIG. 3, three structures of M_{260} are given in FIG. 3, where the energy of 260A is the lowest, the energy of 260B is the second lowest, and 260C has the closest energy to 260. 260A, 260B, and 260C have respectively decahedral, tetrahedral, and close-packed structures, further demonstrating the unbiased feature of our FGO algorithm. The energy difference between 260A/260B/260C and 260 is 1.301746/0.095314/0.000258, and the new GM (i.e., 260A) is associated with the highest hit number in the structure distribution. It is important to emphasize that there are actually 15 extra new local minima with energies locating between those of 260B and 260C (see Table II), which demonstrates the large number of local minima with close energies and the difficulty to make GO for large clusters with large $\rho$. In addition, 318A is the new close-packed GM with $C_{4v}$ symmetry and 389A is decahedral with $D_{5h}$ symmetry.

D. Stability of global minimum structures

The $N$-dependent GM energy by FGO, $E(N)$, for $M_N$ clusters with $\rho=14$ and $N \leq 400$ is fitted with a four-parameter function, $E_{\text{fit}}(N)=aN+bN^{2/3}+cN^{1/3}+d$, where $a$, $b$, $c$, and $d$ are adjustable parameters. In
FIG. 4. Four-parameter fit of the GM energies for Morse clusters with \( \rho=14 \) and \( N \leq 400 \). \( E \) is the GM energy obtained by FGO, and \( E_{\text{fit}} \) is the fitted energy using \( E_{\text{fit}} = -5.99461N + 7.27724N^{2/3} + 1.58031N^{3/3} - 2.84862 \). The numbers of atoms corresponding to some downward peaks are indicated, and close-packed structures are highlighted in red.

FIG. 4 shows the energy difference between the FGO and fitted GM energies, i.e., \( E - E_{\text{fit}} \), as a function of the cluster size \( N \). The clusters with \( E - E_{\text{fit}} < 0 \) are normally considered to be stable, and the downward peaks in the function \( E(N) - E_{\text{fit}}(N) \) indicate the most stable magic numbers. For \( N \leq 240 \), our results are almost the same as those identified previously in Refs. [42, 43]. In general, clusters with magic numbers have high symmetries. For instance, \( M_{38} \), \( M_{305} \), and \( M_{314} \) have truncated octahedral GM structures with \( O_h \), \( C_{4v} \), and \( O_h \) symmetries, respectively. \( M_{75} \), \( M_{101} \), \( M_{146} \), \( M_{192} \), \( M_{238} \), and \( M_{389} \) have decagonal GM structures with \( D_{5h} \) symmetry. \( M_{169} \), \( M_{196} \), \( M_{276} \), and \( M_{292} \) have decagonal GM structures with \( C_{2v} \) symmetry. \( M_{180} \) and \( M_{288} \) have tetrahedral GM structures with \( T_d \) symmetry. With increasing \( N \), more and more stable clusters are close-packed, agreeing with previous studies [42, 43]. Namely, \( M_{201} \), \( M_{260} \), \( M_{302} \), and \( M_{392} \) have close-packed structures with \( D_{5h} \) symmetry, \( M_{316} \), \( M_{372} \), and \( M_{382} \) have close-packed structures with \( C_{2v} \) symmetry, and \( M_{333} \) and \( M_{349} \) have close-packed structures with \( C_s \) symmetry.

IV. CONCLUSION

In summary, we have systematically investigated the global optimization of Morse clusters with \( \rho=14 \) and \( N \leq 400 \) by our recently developed FGO method. Different types of structures have been obtained due to the unbiased nature of FGO. New global minima (and local minima) with lower energies than the corresponding reported global minima have been identified. For \( N \leq 240 \), new global minima have been obtained for \( N=164, 175, 188, 193, 194, 197, \) and \( 239 \), and new local minima for \( N=175, 197, \) and \( 239 \). For the limited available clusters with \( N > 240 \), new global minima have been obtained for \( N=246, 260, 318, \) and \( 389 \). Especially, in addition to the new global minimum, 17 new local minima have been found for \( M_{260} \), demonstrating the great complexity of GO for Morse clusters with short-range potential. Thereby, further improving the FGO algorithm could potentially promote investigation of more complex Morse clusters with \( \rho=14 \) and \( N > 400 \). This study is currently under way.

Supplementary materials: Energies of the global minima for Morse clusters with \( \rho=14 \) and \( N \leq 400 \) by FGO are listed in Table S1. The coordinates of the new GM structures listed in Table I are given in detail.

V. ACKNOWLEDGMENTS

This work is supported by the National Natural Science Foundation of China (No.21803053), the Natural Science Foundation of Zhejiang Province, China (No.LY20B030005), and the Open Project Fund of...
Key Laboratory of Excited-State Materials of Zhejiang Province.