Global minima of transition metal clusters described by Finnis–Sinclair potentials: A comparison with semi-empirical molecular orbital theory

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We present putative global minimum energy structures for nanoscopic transition metal clusters, with sizes ranging from \(N = 3\) to 100 atoms, described by the original embedded atom potential of Finnis and Sinclair (FS), using their parameter sets for molybdenum and iron, and compare selected results with predictions from semi-empirical molecular orbital (SE-MO) theory via further optimization using the AM1* and PM6 Hamiltonians. We find that, for Fe clusters, the global minima found for the FS potential consist mainly of polyicosahedral structures with magic numbers \(N = 13, 19, 23, 26, 29, 39, 60\) and 78, whereas, for Mo clusters with sizes \(N > 30\), they are more likely to be bcc terminated by \{110\} and \{100\}-type surface facets. We find that the global minimum energy structures obtained for the FS potential are, in general, very good starting points for further SE-MO optimization, although the relative ordering of the resulting structures by energy compared to those obtained from global minima of other potentials used to model metal clusters does not, in general, agree.

Keywords: Finnis–Sinclair potential; transition metal; nanosized clusters; numerical simulation; global optimization; basin-hopping; semi-empirical molecular orbital theory; AM1*; PM6

1. Introduction

The structures of transition metal nanoclusters (with diameters between 1 and 10 nm) are of significant theoretical and practical interest due to their potential use in ultra-high density magnetic recording materials [1], catalytic particles in the synthesis of carbon nanotubes [2–5], and other applications in electronics and optics. Due to their small size, nanoclusters can remain in a ‘liquid-like’ state at temperatures well below the bulk melting point [6–8], and their magnetic moments can exceed bulk values up to cluster sizes of several hundred atoms [9]. In general, the geometric structures
of the clusters do not resemble those of the bulk metals since there are no constraints on rotational symmetry from the crystallographic restriction theorem. Instead, stable clusters with sizes corresponding to ‘magic numbers’ of aperiodic motifs (e.g. icosahedra, decahedra and tetrahedra) are commonly observed. While there exists much previous work on global optimization of metal clusters described by a variety of different potentials, which is briefly reviewed in Section 1.1, to date there has been no systematic study of clusters described by Finnis–Sinclair (FS) potentials, as originally proposed for bcc metals, such as iron and molybdenum. In view of the current widespread use of these potentials to describe transition metal clusters, we have therefore undertaken such an investigation to mark the 25th anniversary of the first publication of the FS potential.

1.1. Global optimization of metal clusters

The number of distinct structures (disregarding permutational isomers) corresponding to local minima on the potential energy surface (PES) of a cluster containing \( N \) atoms is expected to grow exponentially with \( N \) [10,11]. Systematic global optimization techniques are therefore essential to identify favorable morphologies [12]. In fact, the computational expense of locating the global minimum with some degree of confidence is not a monotonic function of \( N \), even for values of \( N \) much larger than those considered in the present work. At sizes where there is a single favorable morphology, the potential energy landscape corresponds to a single funnel topology. Such landscapes correspond to good ‘structure-seekers’, where global optimization is generally a straightforward task [13]. In contrast, numerous cases have been found where the landscape exhibits two or more potential energy funnels corresponding to competing morphologies. If the global potential energy minimum is entropically disfavored, then such systems exhibit low temperature solid–solid transitions between different phase-like forms, associated with different regions of configuration space [14–18]. Global optimization is generally much more difficult in this situation [12,18–20].

The basin-hopping approach to global optimization is based upon large steps in configuration space between local minima [19], generalizing the ‘Monte Carlo plus energy minimization’ procedure of Li and Scheraga [21]. A key feature of the method is that a local minimization is performed after every proposed step, and that steps are accepted or rejected based upon the potential energy (and perhaps other properties) of the new minimum and the previous one in the sequence. The local minimization was recognized [12,19] as an essential step on examination of previous studies for clusters bound by the Lennard-Jones (LJ) potential, including genetic algorithms [22,23]. The minimization has been compared to Lamarckian rather than Darwinian evolution [24], where parents pass on features that they have acquired, rather than inherited, to their ‘offspring’.

Perhaps the most attractive feature of the basin-hopping approach is that only a small number of adjustable parameters need to be specified to produce acceptable results for a wide range of different systems, ranging from atomic and molecular clusters [12,18,19,25,26] to peptides [27–33], polymers [34], a glass-forming solid [35],
1.2. Application of the FS potential to transition metal clusters

The FS potential interaction is defined, for an ensemble of $N$ atoms with separations $r_{ij}$, by Equation (1):

$$E = \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} V_{ij}(r_{ij}) - A \sum_{i=1}^{N} \sqrt{\rho_i},$$

(1)

where the total electronic charge at the site of atom $i$ is

$$\rho_i = \sum_{j=1, j \neq i}^{N} \phi_{ij}(r_{ij}),$$

(2)

and

$$V_{ij}(r_{ij}) = \begin{cases} (r_{ij} - c)^2 \left( c_0 + c_1 r_{ij} + c_2 r_{ij}^2 \right), & r \leq c, \\ 0, & r > c \end{cases}$$

(3)
is a repulsive two-body interaction, interpreted in the context of tight-binding theory as the repulsion between core electrons on neighboring atoms, and

\[
\phi_{ij}(r_{ij}) = \begin{cases} 
(r_{ij} - d)^2 + \beta \frac{(r_{ij} - d)^3}{d}, & r \leq d, \\
0, & r > d
\end{cases}
\]

is a cohesive term related to the sum of squares of overlap integrals for the valance electrons. For each atom (or atom pair), there are seven variable parameters determined empirically by Finnis and Sinclair for bcc metals: \(A\) is the binding energy, \(c_0, c_1,\) and \(c_2\) are free parameters used for fitting to experimental data, \(c\) and \(d\) are cut-off parameters assumed to lie between the second-nearest- and third-nearest-neighbor atoms, and \(\beta\) is a parameter used to introduce a maximum value of \(\phi\) within the first-nearest-neighbor distance. This parameter is used to reproduce the anomalously low value of the Cauchy pressure, which is a function of \(\phi\), for iron and chromium.

The forms of the repulsive two-body interaction (Equation (3)) and cohesive term (Equation (4)) as a function of atomic separation are shown in Figure 1 for the parameters given by Finnis and Sinclair for molybdenum [62] and iron (revised in [63]), which are reproduced for reference in Table 1. In the case of iron, a maximum in \(\phi\) is observed at \(r_{ij} = 2.25\,\text{Å}\), which is within the first-nearest-neighbor distance, 2.49 Å. This difference has some significant consequences for the type of clusters produced by basin-hopping (see Section 2.1) and also the ease of finding the global minimum structure. In order to introduce this maximum for both Fe and Cr, which is required to reproduce their anomalously low Cauchy pressures, Equation (4) contains a cubic correction term that may give rise to incorrect behavior at small \(r\). In most normal applications of the potential, such small values of \(r\) do not arise, but during basin-hopping the searches described in Section 2.1, when \(\beta > 0\), it was necessary to restrict \(r_{ij} \geq d(\beta - 1)/\beta\) in Equation (4) to avoid \(\phi\) becoming negative and hence resulting in an undefined energy in Equation (1).
The FS potential is one of the most commonly used interatomic potentials for
bcc metals, since it can correctly reproduce their bulk material properties despite its
empirical form and short cut-off distance. A comparison of the lattice parameters,
binding energies, bulk moduli and selected elastic constants calculated for bulk bcc
Fe using FS potential with equivalent experimental and
\textit{ab initio} calculations using DFT with GGA functional.

<table>
<thead>
<tr>
<th>Property</th>
<th>(a_0) [Å]</th>
<th>(E_0) [eV/atom]</th>
<th>(K) [GPa]</th>
<th>(c_{11}) [GPa]</th>
<th>(c_{12}) [GPa]</th>
<th>(c_{44}) [GPa]</th>
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<td>173.1</td>
<td>243.1</td>
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<td>121.9</td>
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<tr>
<td>Experiment [64,65]</td>
<td>2.8665</td>
<td>-4.28</td>
<td>178.3</td>
<td>242.0</td>
<td>146.5</td>
<td>112.0</td>
</tr>
<tr>
<td>\textit{Ab initio} (DFT) [66]</td>
<td>2.84</td>
<td>-4.28</td>
<td>186.0</td>
<td>279.0</td>
<td>140.0</td>
<td>99.0</td>
</tr>
</tbody>
</table>

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binding energies, bulk moduli and selected elastic constants calculated for bulk bcc
Fe using FS potential with equivalent experimental and \textit{ab initio} results is shown
in Table 2. However, for fcc metals, the alternative long-range form of the FS
potential due to Sutton and Chen [42] is more widely used.

Although the FS potential was originally fitted to the material properties of
bulk bcc systems, in which the coordination number is generally higher than that of
a small cluster, the FS potential was applied by Marville and Andreoni [67] to
examine the size-dependence of the structural properties of transition metal clusters.
They showed that the dodecahedral structure, which is a type of bcc cluster, is more
stable than cuboctahedral and icosahedral structures in clusters up to 3000 atoms
in size. However, their calculations mainly assumed a fixed structure for the cluster,
with only the ‘lattice constant’ allowed to relax as a function of size. More recently,
Shibuta and Suzuki [68] carried out explicit molecular dynamics simulations of the
phase transition from liquid droplet to solid nanoparticle for clusters, ranging in size
from 2000 to 31,250 atoms for iron, chromium, molybdenum, and tungsten
described by FS potentials. These simulations confirmed that only nanoparticles with
a bcc structure were observed, independent of particle size and elemental
composition.

On the other hand, Besley et al. [69] examined the transition between fcc and bcc
structures as the most stable form for an iron cluster using a Murrell–Mottram
(MM) potential and found the stability order: icosahedral > rhombic dodecahedral
(bcc) > decahedral > cuboctahedral (fcc) for clusters with fewer than 2000 atoms.
Furthermore, Tománek et al. [70] examined the structural stability of small bcc
clusters by formulation of the cohesive energy, including surface energy, and found
that fcc clusters are more stable below some critical size: for example, 580 atoms
for chromium. In view of these previous studies, and the considerable uncertainty that still remains in determining the most stable structures for transition metal nanoclusters, a systematic search of the global minima of small clusters described by the FS potential is desirable. Furthermore, since the FS potential cannot explicitly take into account interactions between atomic and electronic degrees of freedom in the clusters, a comparison with structures calculated using semi-empirical molecular orbital theory has been performed. A brief summary of the latter is given in the following section, and the reader is referred to [71–73], and references therein, for a fuller discussion of the approximations involved.

1.3. Semi-empirical molecular orbital (SE-MO) theory

Until relatively recently, semi-empirical molecular orbital (SE-MO) methods based on the neglect of diatomic differential overlap (NDDO) approximation, such as AM1 [74], were restricted to main group elements containing only s and p electrons. However, Voityuk and co-workers first described an extension of AM1 to d orbitals, which they called AM1/d, and recently reported parameters for Mo [75]. Their approach was based on an extended multipole–multipole interaction scheme [76] and the introduction of two bond-specific parameters for Mo into the core–core repulsion term [75]. The Mo parameters in AM1/d were later incorporated in a slightly modified form by the Clark group into their AM1* Hamiltonian [77], which used a distance-dependent core–core repulsion for some interactions. More recently, Stewart [73] has published parameter sets for 70 elements, known as PM6 and including the transition metals Fe, Co, Ni and Mo, which use a very similar core repulsion function to AM1/d and AM1*, given by

\[ E_n = Z_A Z_B \langle s_A s_A | s_B s_B \rangle \left[ 1 + \delta_{AB} \exp \left[ -\alpha_{AB}(R_{AB} + 0.0003R_{AB}^6) \right] \right] \],  

where \( Z_A, Z_B \) are the atomic numbers, \( R_{AB} \) is the separation, and \( \langle s_A s_A | s_B s_B \rangle \) are the two-electron, two-center integrals between species \( A \) and \( B \). The bond-specific parameters \( \delta_{AB} \) and \( \alpha_{AB} \) were determined by fitting to experimental enthalpies of formation and geometries for selected molecules [73], and determine the range of the repulsions between core electrons in an analogous way to Equation (3) for the FS potential. For transition metals, the bonding character of the interactions is provided by the overlap of d electrons in the valence band.

Thus, in principle, the empirical form of the FS potential should be compatible with the description of electronic bonding in SE-MO methods such as AM1* and PM6, or alternatively density-functional based tight binding (DFTB) approaches [78]. However, the advantages of SE-MO methods are that they give a self-consistent calculation of the ground-state energy and an explicit representation of the electronic wave function and spin density without the computational expense of a full density functional theory (DFT) calculation. Also, due to the way in which they are parameterized, as opposed to an exact Hartree–Fock (HF) approach, SE-MO Hamiltonians implicitly include the effects of electron correlation [79], which is required to describe phenomena such as ferromagnetism [80]. However, without performing a full configuration interaction (CI) calculation, which is prohibitive for even modestly sized systems, it is difficult to determine the precise electronic
ground state and, for open shell unrestricted calculations without projection, there
is a risk of spin contamination from excited states. For these reasons, we have
not attempted here a detailed comparison of the magnetic moments predicted for
different clusters by SE-MO methods. However, in Section 3.2, some of the global
minimum cluster structures calculated using FS potentials are compared with those
obtained after further optimization using SE-MO theory, in an attempt to isolate
the structural changes caused by the inclusion of exchange-correlation energy.

2. Methodology

2.1. Global optimization

All the global optimization calculations in the present work were carried out using
the GMIN package [38], which implements the basin-hopping algorithm with a
variety of options for the step-taking strategy. Two independent runs were carried
out for $10^6$ basin-hopping steps (minimizations) at a temperature of $k_B T = 0.8$ eV; the
first starting from known global minimum structures for Gupta potential from the
CCD [40], and the second starting from putative global minimum structures for the
FS potential for other elements (i.e. starting from Fe for Mo, and vice versa). Runs
were continued for a further $10^7$ steps if the first two runs did not produce the same
prediction for the global minimum.

Each step consisted of a random perturbation to the Cartesian coordinates
of every atom in the range $[-\text{max}, \text{max}]$, where the value of \text{max} was adjusted every
50 steps to give an average acceptance ratio of 0.5. A suitable initial value for \text{max}
at the chosen temperature is 0.6 Å. A spherical container was used to prevent
evaporation during the local minimizations. The convergence parameter for
minimization during the basin-hopping runs was taken as $10^{-3}$ eV Å$^{-1}$ for the root
mean-square (RMS) gradient, and the lowest 20 minima were converged to an RMS
gradient less than $10^{-6}$ eV Å$^{-1}$ at the end of each run.

2.2. Semi-empirical optimization

Semi-empirical calculations were carried out using the VAMP software package,
which is part of Materials Studio from Accelrys [81]. Geometry optimizations were
carried out with standard eigenvector-following (EF) optimization techniques [82],
with the convergence criterion being a gradient norm of 0.1 kcal mol$^{-1}$ Å$^{-1}$, using
a self-consistent field (SCF) unrestricted Hartree–Fock (UHF) calculation with full
Hessian. Each stationary point was verified to be a true minimum by performing
a vibrational frequency analysis.

3. Results

We first describe the putative global minima for Fe$_N$ and Mo$_N$ clusters with the
FS potential, and then report on their relative stability after further optimization
with SE-MO methods.
The relative energies, $E(N) - E_{\text{avg}}$, of putative global minimum structures for Fe and Mo clusters for $N=3$–100 are plotted in Figure 2a, together with the second differences, $\Delta_2E(N) = E(N-1) + E(N+1) - 2E(N)$, between these energies in Figure 2b. In order to remove the effects of increasing cluster size, the absolute cluster energies were reduced by the average energy, $E_{\text{avg}}$, computed from a four-parameter fit to the absolute energies. Parameters for the average energy expression are given for reference in Table 3. A complete set of atomic coordinates and energies for all the suggested global minima is available from the Cambridge Cluster Database [40].

3.1. Finnis–Sinclair (FS) putative global minima

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It is clear from Figure 2a that the global minima for both Fe and Mo clusters have very similar energies for $N < 26$, but begin to diverge with increasing $N$. In general, the variation of energy with $N$ is rather smoother in the case of Fe for $N > 50$, indicating that the structures may be less symmetrical than for Mo. However, there are two large coincident troughs in the energy around $N \approx 60$ and $N \approx 80$, which will be described in more detail below. The peaks in $\Delta E(N)$ confirm that there are several magic numbers for stability in the range $N = 13–26$ for both Fe and Mo, but, with increasing $N$, it appears that Mo clusters are appreciably more stable than Fe for the range of sizes investigated. It was also found that, for $N > 65$, obtaining consistent minimum energy structures for Fe clusters between different basin-hopping optimizations was considerably harder than for Mo clusters of similar size, requiring several independent runs to achieve.

Figure 3 shows the energies of the most stable minima for $N = 3–30$, together with selected structures. For the majority of clusters with $N < 26$, the geometries and relative energies of the predicted global minima for Fe and Mo clusters are identical. A notable exception is the octahedral cluster $N = 6$ (not shown) which, although isostructural (point group $O_h$), is less stable for Fe than for Mo. For the first two magic numbers, $N = 13$ and $N = 19$, clusters of both Fe and Mo consist of single and double icosahedra, in common with Lennard-Jones (12-6), some Sutton–Chen (12-6, 9-6) and some Gupta (Na, Co) clusters of the same sizes. For the next magic number, $N = 23$, the predicted global minimum structures are again the same for Fe and Mo, but differ from a SC 9-6 cluster of the same size [20], which has point group $C_2$.

Farges et al. [83] first described cluster structures composed of double icosahedra, which they found in rare gas clusters with fewer than 50 atoms [84]. A double icosahedron (DIC) is composed of two interpenetrating 13-atom primitive icosahedra sharing seven atoms, and contains 19 atoms. Larger polyicosahedral clusters can be made by placing atoms on unoccupied tetrahedral and pentagonal sites; for example $N = 23$, which consists of three interpenetrating DIC with slightly distorted axes. Sakurai et al. have also observed magic number clusters for Fe: $N = 13, 19, 23$ [85,86] using time-of-flight mass spectrometry, which they attributed to polyicosahedra, and Parks et al. have found further evidence for polyicosahedral structures in ammoniated iron, cobalt and nickel structures [87].

For $N = 26$ and $N = 29$, the global minima for Fe and Mo differ somewhat from previous results for metal clusters, and from each other. Whereas Fe$_{26}$ has point group $T_d$, consisting of six interpenetrating DIC aligned with their axes approximately parallel to the vertices of an unfilled central tetrahedron, and is relatively stable compared to other Fe clusters of similar size, Mo$_{26}$ is tetragonal (point group $C_4$) and only of average stability. This result was checked several times by starting

<table>
<thead>
<tr>
<th>Parameter</th>
<th>a</th>
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<td>-0.81613</td>
<td>2.418055</td>
<td>-4.18369</td>
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</table>

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optimizations for Fe and Mo clusters from different initial conditions, including the global minimum for the other element and, in each case, no other lower energy structures were found. The $T_d$ structure for Fe most resembles those of the LJ 12-6 and Gupta (Co) and Murrell–Mottram (Na) clusters of the same size, but is distinct from SC clusters, which have dihedral or $C_3$ symmetry only. However, the $C_4$ structure for Mo has no analogue in any metal cluster studied by classical potentials.
to date, although it is still based on multiple interpenetrating DIC with non-parallel axes. The final magic cluster for $N \leq 30$ is the $D_{3h}$ structure of Fe$_{29}$, which again resembles that of the LJ 12-6 cluster, whereas Mo$_{29}$ has point group $C_2$ and more resembles SC 9-6 or 10-8 clusters of the same size. Both are polyicosahedral, with the DIC in Fe$_{29}$ arranged with their axes around a trigonal bipyramidal core, and those in Mo$_{29}$ with their axes approximately at right angles. These results for small clusters demonstrate that the short-range interactions in the FS potential can give rise to structures with a diverse range of optimal geometries. For Fe, the more weakly repulsive nature of the FS potential at short range (see Figure 1a) results in optimal short-range repulsions in Mo clusters.

Moving on to consider larger clusters, Figure 4 shows the energies of the most stable minima for $N = 30-60$, together with selected structures. From the point of view of comparison with previous metal cluster optimization studies, the most surprising observation for FS potentials is the absence of a stable magic number structure for $N = 38$, which is usually found to be a truncated octahedron (point group $O_h$) for a very wide range of potentials, including LJ, Gupta, SC, although not MM (Na). Again, this result was checked by starting optimizations for Fe and Mo clusters from different initial conditions, including the $O_h$ structure (which is hard to locate without a transformation of the PES [15,88]), and found to be robust – it is not simply due to a failure of the basin-hopping algorithm to locate the $O_h$ structure. In fact, in Section 3.2, we show that for Fe$_{38}$, there is a high symmetry minimum with point group $T_h$ that is even lower-lying than the $O_h$ structure for the FS potential, and which is likely to be the global minimum for PM6. However, for $N = 39$, there do exist stable high symmetry clusters for both Fe and Mo described by the FS potential. Although their structures are markedly different (Fe$_{39}$, hexagonal, point group $C_{6v}$; Mo$_{39}$, pentagonal, point group $D_5$), their energies relative to the average are approximately equal, indicating that they are very similar in stability. Whereas Fe$_{39}$ consists of 12 interpenetrating DIC, with their axes perpendicular to the six-fold axis, the $D_5$ structure of Mo$_{39}$ is most unusual, and has no analogue in any metal cluster studied by classical potentials to date. It is based around a distorted central DIC, surrounded by five mutually interpenetrating, partially complete DIC aligned with their axes at approximately 13.8° to the five-fold axis. Although it is only slightly more stable than average, Mo$_{55}$ bound by a FS potential also has a very similar structure with five-fold rotational symmetry (point group $D_5$) in which the surrounding DIC are now complete, whereas all other metal cluster potentials studied to date (with the exception of SC 10-8) predict a very stable Mackay icosahedral ($I_h$) configuration for $N = 55$. In contrast, FS Fe$_{55}$ is polyicosahedral ($C_s$) with the DIC axes arranged approximately parallel, and not particularly stable.

For $N = 59-60$, there is a broad coincident trough in energy for both Fe and Mo clusters, mentioned earlier, which can be seen most clearly in Figure 2a. Although similar in their relative stabilities and high symmetry, the structures of Mo$_{59}$ and Fe$_{60}$ are very different. Whereas Mo$_{59}$ is a complete four-shell bcc particle with octahedral symmetry (point group $O_h$), Fe$_{60}$ is still polyicosahedral (point group $C_{3v}$). In Figure 4, the atoms on $\{110\}_{bcc}$-type faces of the $O_h$ structure of Mo$_{59}$ have been highlighted. Although characteristic of bulk crystalline Mo, this structure has
Figure 4. (Color online). Energies of putative global minima, $E(N)$ for FS Fe and Mo clusters as a function of size, $N=30-60$, relative to the average energy, $E_{\text{avg}}$, and corresponding structures for clusters with particularly low energy (with point groups indicated in square brackets). For Mo$_{59}$, atoms defining a $\{110\}_{\text{bcc}}$-type face are highlighted. Fe$_{55}$ and Mo$_{55}$ are also shown, for comparison, despite not being particularly stable.
not been seen in any finite metal clusters by classical potentials to date. In contrast, the C\textsubscript{3\texttimes} structure of Fe\textsubscript{60} is trigonal, and more resembles the global optima for SC 9-6 and 10-8 clusters. Its polyicosahedral character is evident when examining the cluster perpendicular to the one of the four three-fold axes and the corresponding mirror plane, and it appears to be built up from interpenetrating DIC arranged around a distorted filled tetrahedral core, with the remaining atoms attached in symmetric positions. The most likely explanation for this difference in structure between clusters of Fe and Mo with N = 59 bound by FS potential is again the contrast between short-range repulsions, which allows Fe clusters to adopt a polyicosahedral structure, which maximizes nearest-neighbor packing at the expense of incorporating larger amounts of bulk strain.

Considering the largest group of cluster sizes, Figure 5 shows the energies of the most stable minima found for N = 60–100, together with selected structures. It is clear that for the larger clusters, the variation of the reduced energy, E(N), for N > 60 is qualitatively different for the two elements studied, with the curve for Mo showing more precipitous peaks and troughs than for Fe, where the variation is rather smoother. The reason for this behavior can be seen by contrasting the structures of stable clusters with N = 78 for the two elements. Fe\textsubscript{78} is again polyicosahedral (point group D\textsubscript{6\texttimes}), consisting of six sets of four interpenetrating DIC with their axes, which are slightly distorted, pointing perpendicular to the six-fold axis, giving 24 interpenetrating DIC in total. Each set of four DIC has a two-fold axis, which is contained by the mirror plane perpendicular to the six-fold axis, and there are eight additional atoms occupying hexagonal sites surrounding the DIC array. Such a highly symmetrical arrangement is not only relatively stable, but can also accommodate loss or gain of atoms around the DIC array, giving rise to a wide basin of stability around N = 78 for Fe clusters. In contrast, Mo\textsubscript{78} is based around a truncated fragment of a bcc lattice, with a twin plane bisecting the three-fold and two-fold axes (which are highlighted in Figure 4). Similar, but lower symmetry bcc fragments (point group C\textsubscript{s}) are also the stable structures found for Mo\textsubscript{71} and Mo\textsubscript{93}. In each case, the Mo nanoclusters are truncated by \{110\}_bcc-type facets. These structures contrast greatly with the behavior found for Fe, which continues to prefer polyicosahedral structures even for large N, including Fe\textsubscript{93} (point group C\textsubscript{2\texttimes}) which, although not particularly stable, is shown for comparison with Mo\textsubscript{93}. Finally, it should be noted that for other types of metal cluster potential, including LJ, Gupta, SC and MM, the stable clusters of size N = 78 and 93 have low symmetry (point groups C\textsubscript{s} and C\textsubscript{1}). Also, for N = 98, there is no sign of the Leary tetrahedron [89], which is the most stable structure for the LJ potential, for clusters bound by the FS potential.

For some of the larger iron clusters, the structures can be described in terms of disclinations. A disclination occurs when a nearest-neighbor edge belongs to more (negative disclination) or fewer (positive disclination) than five tetrahedra. Such structures have been analyzed in detail for clusters bound by long-ranged Morse potentials, where the global minima were found to have an excess of negative disclinations for values of the Morse range parameter $\rho$ around 3 or less [43,90]. Polytetrahedral global minima have also been characterized for aluminium clusters [55] bound by a glue model [51], and for binary Lennard-Jones clusters [91] and nanoalloys [59]. The strain associated with polytetrahedral packing in these
structures is relieved either by the packing of atoms that have different sizes, or a long range interatomic potential [43,90,92–95]. Bulk polytetrahedral crystals, known as Frank–Kasper phases, are found in some alloys [96].

Negative disclinations are evident in the FS global minima of Fe$_{55}$, Fe$_{60}$, and Fe$_{78}$, described above. In each case we relaxed the corresponding structure for the aluminium glue potential [51] and for the Morse potential with $\rho = 3$. We also performed the reverse relaxation from the global minima of the aluminium and
Morse clusters using the FS potential for iron. The initial geometries were uniformly scaled before each relaxation according to the mean nearest-neighbor distance. For Fe$_{55}$, the structure of the corresponding Al$_{55}$ cluster is a low-lying minimum for the FS potential, and vice versa, but relaxation from the Morse global minimum with $\rho = 3$ involves a significant change in structure. For Fe$_{60}$, the Morse $\rho = 3$ global minimum and the FS global minimum each relaxed rapidly to a low-lying local minimum with the alternative potential. The aluminium and FS global minima correspond to the same structure. For Fe$_{78}$, the aluminium global minimum relaxes in a few steps to the previously identified FS global minimum. Conversely, when the FS global minimum was relaxed with the aluminium potential, it produced a structure only of order $10^{-3}$ eV higher in energy than the aluminium global minimum, with a slight change in radial distances for some atoms.

We then relaxed all the previously reported [55] lowest minima for the aluminium glue potential [51] for the size range $3 \leq N \leq 100$, and in no case was a lower minimum produced. In the size range $3 \leq N \leq 50$, it was found that 34 of the aluminium structures relax to the lowest minimum found with the FS potential, while only six structures are the same for $51 \leq N \leq 100$, and none above $N = 78$. It is likely that the FS global minimum structure corresponds to a low-lying minimum for the aluminium potential for the sizes where the global minima are different. These results clearly illustrate that a ‘knowledge-based’ approach to global optimization for clusters, where known structures are relaxed with a new potential, can be a very efficient method, although there is the obvious danger of missing a new structural motif.

It is interesting to note that many of the putative global minima we have located display relatively high point group symmetry. This observation provides further support for the predicted correlation between high symmetry and either particularly low or particularly high energy [18,97,98]. Furthermore, compared to Fe, the larger Mo$_N$ nanoclusters ($N > 60$) have mainly $\{110\}_{bcc}$ and $\{100\}_{bcc}$-type surface facets, which may be significant in influencing their graphitization ability in carbon nanotube synthesis [99]. However, since the FS potential was originally parameterized for bulk metals, and does not take into account the electronic effects of unfilled d orbitals, we have carried out further optimization of selected global minima described above using SE-MO theory to test the robustness of the structures found.

3.2. SE-MO optimization from FS global minima

As demonstrated in a previous study by some of the present authors [100], the use of basin-hopping algorithms using classical potentials to prepare initial structures for further optimization using SE-MO theory is an efficient strategy for exploring the quantum mechanical PES. Despite the approximations made by NDDO methods, such as AM1* and PM6, optimizing the structure of a transition metal cluster with $N \approx 100$ atoms still requires of order several minutes of CPU time, assuming that the starting point is close to an energy minimum (and, if not, the initial self-consistent field calculation will most likely fail to converge), making it impractical at present to carry out basin-hopping directly on the SE-MO PES. In the Conclusions section, we
discuss a possible method for overcoming this difficulty, but at this stage we simply note that the putative global minimum energy structures found in the previous section using the FS potential are easily optimized by AM1* or PM6, and in most cases result in stable structures with similar geometries to classical potential, except for some Jahn–Teller distortion in systems with unfilled d electron shells. However, the relative energies of the SE-MO minima are not always the same as for the FS optimum structures, and in this section we explore this phenomenon by focusing on clusters of size $N = 38$ and $N = 55$. We used both AM1* (for Mo) and PM6 (for Fe), since, although the binding energies of Mo clusters calculated using PM6 agree well with AM1*, their geometries are rather compact and AM1* has been parameterized more extensively for Mo [75] than PM6 [73]. In a previous study by some of the present authors [101], SE-MO results for a Mo$_{35}$ cluster using AM1* were compared directly with DFT using a hybrid exchange functional (B3LYP) and the geometries were found to be in good agreement.

Figure 6 shows the results from a series of geometry optimizations of Fe$_{38}$ clusters using PM6, starting from different initial conditions. The first of these, shown in Figure 6a, is the polyicosahedral FS global minimum for Fe$_{38}$ found in Section 3.1. After optimization with PM6, the geometry of the cluster is only slightly

![Figure 6](image)

Figure 6. (Color online). Comparison of relative energies for Fe$_{38}$ clusters after geometry optimization using PM6, starting from three different initial conditions: (a) $D_{6h}$ global minimum for FS Fe$_{38}$ found in Section 3.1, (b) fcc LJ $N = 38$ global minimum scaled for Fe atomic radius, and (c) the $T_h$ (distorted fcc) subsidiary minimum for FS Fe$_{38}$ found during global optimization process. In each case, the new space group, root mean square deviation (RMSD) from initial structure and binding energy (BE) of the new structure are given below it. All energies shown are calculated at the UHF/PM6 level.
changed (RMSD = 0.0274 Å atom⁻¹, although this is sufficient to reduce the point symmetry to C₁), which indicates that the original structure was very close to a minimum on the PM6 PES. Moreover, starting from the fcc LJ global minimum structure for N=38 (actually, a similar structure is metastable for FS Fe₃₈ at 3.437 eV above the global minimum), shown in Figure 6b, a heavily distorted (RMSD = 0.9498 Å atom⁻¹) low symmetry cluster was obtained in which the atoms are slightly less tightly bound, albeit by only about 8 meV atom⁻¹ (≈0.3 k_BT at 298 K). However, a previous study by some of the current authors [100] found that a distorted fcc structure for Mo₃₈ is lower in energy than any icosahedral structure at the AM1* level. This might suggest that the final structure in Figure 6a is not the only candidate for the global minimum structure of PM6 Fe₃₈. Indeed, starting from a symmetrically distorted (Tₐ) metastable fcc structure, shown in Figure 6c, which lies 2.682 eV above the global minimum for the FS potential, it was possible to arrive at a structure that is −146.1 meV (≈5.7 k_BT at 298 K) below the original candidate at the PM6 level. Although it is not possible to be certain that this is the global minimum energy structure for PM6 Fe₃₈, we are not aware at this stage of any likely candidates which may lead to lower energy structures. This example also serves as a warning that, although the classical PES described by FS potential may be a good guide for initiating a minimization using quantum methods, the relative ordering of minima on these surfaces should not necessarily be expected to agree.

Next, the structures and relative energies for Fe₅₅ and Mo₅₅ optimized at the AM1* and PM6 levels are compared. In Figure 7a, the polyicosahedral global minimum for Fe₅₅ bound by FS potential is optimized via PM6 to a lower symmetry structure which is quite close to the original (RMSD = 0.0364 Å atom⁻¹). However, in Figure 7b, it can be seen that an equivalent optimization starting from the Mackay icosahedral LJ Fe₅₅ global minimum results in a distorted icosahedral cluster (RMSD = 0.12672 Å atom⁻¹) that is 227.1 meV (≈8.8 k_BT) lower than the one produced from FS global minimum. The situation for Mo₅₅ is similar, with the distorted icosahedral structure lying 137.9 meV (≈5.4 k_BT) lower than the distorted D₅ FS global minimum, as shown in Figures 7c and 7d. However, the AM1* optimized FS structure for Mo₅₅ has undergone a greater distortion (RMSD = 0.0994 Å atom⁻¹) and appears to more resemble the distorted icosahedron, thus accounting for the smaller difference in energy of the final structures as compared with Fe₅₅. In a similar fashion, it was also found that the FS potential ranks the low symmetry global minima of Fe/Mo₇₅ and Fe/Mo₉₈ found in Section 3.1 lower in energy than the decahedral and tetrahedral forms. By contrast, both AM1* and PM6 rank the distorted high symmetry structures as lower in energy than the FS global minima after SE-MO optimization. These results are all consistent with earlier conclusions of Elliott and Shibuta [100], who found that LJ 12-6 potential generally makes global minimum structures more consistent with SE-MO in comparison with LJ 9-6. This may be an indication that FS and LJ 9-6 have core–core interactions that are too soft, since Fe clusters (N ≤ 32) studied using DFT [78] in combination with DFTB showed that Fe₁₀ has a non-icosahedral structure as minimum energy [102]. More recent DFT simulations also show that Fe₅₅ has an icosahedral structure [103].
4. Conclusions

We have calculated the putative global minimum energy structures via basin-hopping for Fe and Mo clusters of size $N = 3$–100 atoms bound by Finnis–Sinclair (FS) potentials, and presented a selection of results for the most stable structures along with those corresponding to magic numbers for other types of potential previously used to study metal clusters. Depending on the parameter sets used, the FS potential can give rise to a great diversity of structures; however, for small clusters, these generally consist of different arrangements of interpenetrating double icosahedra (DIC) for both Fe and Mo. As the cluster size increases, Mo clusters tend to adopt a bcc configuration, terminated by $\{110\}$ and $\{100\}$-type facets, whereas Fe clusters continue to take a polyicosahedral form. This difference is caused by the steeper core–core repulsions for FS Mo potential compared to Fe. Whilst there is considerable experimental evidence to support the existence of stable Fe clusters for smaller magic numbers in the polyicosahedral series, there will clearly be a maximum

Figure 7. (Color online). Comparison of relative energies for FS Fe$_{55}$ and Mo$_{55}$ clusters after geometry optimization using PM6, starting from two different initial conditions for each element: (a) $C_{5}$ global minimum for FS Fe$_{55}$ found in Section 3.1, (b) icosahedral LJ $N = 55$ global minimum scaled for Fe atomic radius, (c) $D_{3}$ global minimum for FS Mo$_{55}$ found in Section 3.1, and (d) icosahedral LJ $N = 55$ global minimum scaled for Mo atomic radius. In each case, the new space group, root mean square deviation (RMSD) from initial structure and binding energy (BE) of the new structure are given below it. Energies shown are calculated at the UHF/AM1* and UHF/PM6 levels, as indicated.
upper limit on the size of such a cluster before it transforms to a more stable structure, e.g. bcc, due to an accumulation of strain energy. Furthermore, SE-MO calculations demonstrate the greater stability of the higher symmetry global minimum structures predicted by pair potentials even for clusters as small as \(N = 38, 55, 75\) and \(98\). Therefore, it would be wise to be cautious in interpreting the global optimum structures predicted by FS potential for transition metal clusters as definitive; ‘different potentials’ lead to ‘different structures’, as found earlier by Doye for lead clusters \([41]\). However, the FS potential at least provides a reasonable approximation to the semi-empirical quantum mechanical PES, and for this reason it would be valuable in future to carry out basin-hopping with either SE-MO or DFTB using FS potentials as a guiding function to steer the optimization process more efficiently. In addition, a more detailed study of the effects of magnetism on cluster structure is required.

Finally, we would like to briefly remark on the potential relevance of the polycosahedral clusters found here for Fe clusters in relation to quasicrystals, which have been described as large-scale quasicrystalline cluster aggregates in which the quasilattice is decorated with atomic clusters of the same point group as the quasicrystal \([104]\). In the same way that the polytetrahedral clusters studied by Doye and Wales \([90]\) may form building blocks of crystalline Frank–Kasper phases or quasicrystals with tetrahedral point groups, the polycosahedral structures found here may play a role in quasicrystals with multishell icosahedral clusters or metallic glasses composed of primitive icosahedral aggregates.

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