RESEARCH ARTICLE

The influence of the composition of eight-atom Pt–Ir clusters on the magnetic properties

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The energetic stability, electronic structure and magnetic properties of Pt8−nIrnn clusters have been investigated by employing the spin-polarised generalised gradient approximation. The cubic structure is expected to be the effective building block in Ir-rich clusters after optimisation extensively. The average binding energy of all the clusters presents the linear increment trend with iridium atoms, due to the stronger interaction between Ir atoms than Pt atoms. Bader charge analysis shows how tiny charge transfers from iridium to platinum. The atomic moments of Ir are larger than that of Pt, and the Ir-rich clusters show greater moments than the Pt-rich cluster, with the exception of Ir8 and Ir7Pt. A unique magnetic property is found in the Pt4Ir4 cluster, where two Pt atoms show antiferromagnetic alignment and the other atoms are found to be aligned ferromagnetically.

Keywords: Pt–Ir clusters; stability; electronic properties; magnetic moments

1. Introduction

As compared to atomic and bulk counterparts, clusters always receive extensive attention because of exhibiting remarkably different physical and chemical properties, which may be tuned by varying the composition and the size, as well as by the atomic ordering of the clusters. Especially, noble metallic nanoclusters always attract great interest on account of their potential application in the field of catalysis [1–3]. To a large extent, their catalytic performance is due to their high surface area-to-volume ratio and distinct quantum effect of the surface atoms. Pt–Ir bimetallic nanoparticles often exhibit better catalytic performance and higher stability than their monometallic counterparts, and thus, they act as the most effective catalyst in the field of catalysis and fuel cells [4–11]. In unitised regenerative fuel cell) performance, among the catalysts of Pt black, Pt–Ir, Pt–Ru and PtRuOx, Yim et al. [5] found that the Pt-Ir catalyst with 1 wt% Ir reveals the best bifunctional electrocatalytic efficiency. Moreover, Hu et al. [6] investigated that the addition of an appropriate amount of Ir improves the catalytic activity of pure Pt and the best catalytic activity is exhibited by a hydrophobic catalyst with a Pt/Ir molar ratio of 4/1. Recently, Wang et al. [8] studied the influence of Ir content on the behaviour of Pt–Ir/C catalysts for hydrogen iodide decomposition in the iodine–sulphur thermochemical water-splitting cycle, and they demonstrated that the bimetallic 2.5% Pt–2.5% Ir/C exhibited the highest catalytic activity toward HI decomposition among the Pt, Ir and binary Pt-Ir catalysts.

Additionally, Small et al. [12] reported that the supported Pt–Ir nano-clusters of the average diameter 1.7 nm were synthesised. Both their experimental and theoretical calculations showed the hemispherical cuboctahedral geometry with surfaces enriched in Pt atoms and with cores occupied by Ir atoms to be an energetically favourable conformation for the alloy cluster. Tigger et al. [13] also predicted that Pt–Ir 923-atom nanoparticles prefer the compositional structure of cuboctahedron and suggested Pt segregation to the nanoparticle surface sites as well by employing based on the density functional theory (DFT) coordination dependence of bond energy variations combined with the highly efficient statistical–mechanical free energy concentration expansion method. Similarly, within the DFT framework, other theoretical studies focused mostly on the surface segregation effect of Pt–Ir nanoparticles with the surface sites occupied by Pt atoms [14–18]. On the other hand, Sondón et al. [19] have investigated the magnetic properties of Pt1−xIrx (0 ≤ x ≤ 1) nanowires by using the wien2k code, and the result exhibited the linear increasing behaviour for alloy nanowires with the increase of Ir content without spin-orbit coupling (SOC), but the nanowires displayed irregular variation tendency with high Ir magnetic moment values at intermediate concentrations, taking into account SOC. Guo et al. [20] have studied the structure and stability of PtIr0.5n (n = 0–5) clusters and found that Ir atoms play a major role in the energetic stability of the binary clusters and the Pt dopant could weaken the interaction between Ir atoms.
However, to the best of our knowledge, no theoretical investigations on the fundamental properties of Pt–Ir clusters have been performed so far. In order to understand the catalytic processes and design more efficient catalysts, it is worthwhile exploring the structural stability, electronic and magnetic properties of Pt–Ir clusters. To understand the influence of the composition of bimetallic clusters on the magnetic property, a fixed size of eight atoms has been determined in this paper.

2. Computational details
The calculations were performed in the framework of DFT, implemented in the Vienna ab initio simulation package (VASP) [21–23]. The projector augmented wave (PAW) pseudopotentials [24] were used to describe the interaction between valence electrons and ionic cores. The exchange and correlation energies were calculated using the Perdew–Wang 91 form of the spin-polarised generalised gradient approximation [25]. The 5d and 6s electrons of both Ir and Pt were treated as valence electrons. A cut-off energy of 300 eV was used. The PAW sphere radii for Pt and Ir are set at 1.423 and 1.455 Å, respectively. Periodic boundary conditions were confined within a simple cubic supercell of side 20 Å, and the Brillouin zone integrations were carried out using the Γ point.

We have employed Saunders’ ‘kick’ structural search method [26,27]. This stochastic method can generate structures randomly in a stochastic ‘kick’ way. The maximum and minimum radii of the kick distance are set at 3.0 and 1.0 Å, respectively. And the minimum distance between two random atoms is 1.0 Å. Gaussian 09 [28] was implemented to search the low-energy isomers extensively by using the B3LYP/3-21G basis set, and then we picked out structures of these clusters and took these structures as the initial configurations to be optimised with rough accuracy by using the VASP code. Finally, four most stable structures among them were singled out to reoptimise with convergence accuracy as expected. The rough accuracy of energy and force on each atom is 10^−4 eV and 10^−2 eV/Å, while convergence accuracy is 10^−5 eV and 10^−3 eV/Å, respectively.

3. Results and discussion
3.1. Energetic stability
First, it is necessary to test the reliability of the current methods in the alloy clusters by investigating the dimers and 8-atom pure clusters. For the equilibrium structures of dimers, the bond length, binding energy, spin multiplicity and vibrational frequency are summarised in Table 1. The spin multiplicities of both Ir 2 and Pt 2 are the same as previous values [29–31]. The vibrational frequency of Ir 2 is 282 cm^−1 in our method, showing excellent agreement with the published theoretical values of 279 and 280 cm^−1 predicted with G96PW91 and BP86 functional, respectively. But our predicted value of the binding energy of Ir 2 is much higher than the value estimated by Miedema and Gingerich [32]. The experimental value of Miedema and Gingerich is obtained by empirical correlations using the third-law method, but not directly measured by experiment. Other calculation values are also shown to be significantly larger than the experimental value. Pawluk et al. [36] thought that it might result from the error of measurement in experiment using the third-law method. Otherwise, the interatomic distance of Ir 2 is 2.211 Å, slightly larger than the previous values [29,30]. As for Pt 2 dimer in the vibrational frequency, our predicted value of 231 cm^−1 is close to the experimental value of 223 cm^−1 [35] and the calculated value of 225 cm^−1 [29]. The equilibrium bond length of Pt 2 dimer is 2.334 Å, in excellent agreement with the experimental value of 2.333 Å [35] and the value published by Bhattacharyya and Majumder of 2.33 Å [31]. Similarly, the binding energy of Pt 2 is also larger than the value measured in the experiment. But our result is very close to the value calculated by Bhattacharyya [31], because of using the same pseudopotential and the same exchange-correlation functional. Meanwhile, they believed that the higher binding energy of Pt 2 dimer compared with the experiment is due to the neglect of spin–orbit term in the total energy expression. Table 2 presents bond lengths, binding energies and magnetic moments of both Ir 8 and Pt 8 clusters. For the equilibrium structure of the Ir 8 cluster with Oh symmetry, the average bond length of 2.37 Å, average binding energy of 5.11 eV and magnetic moment of zero are predicted in our method, entirely agreeing with the results reported by Zhang et al. [37]. However, our value of the binding energy of Ir 8 is slightly higher than that of Zhang et al. [37], resulting from using different pseudopotentials.

| Dimer  | Functional  | R (Å) | E_b (eV) | S | Ω (cm^−1) |
|--------|-------------|-------|---------|---|-----------|
| Ir2   | PW91        | 2.211 | 5.53    | 5 | 282       |
| G96PW91 | 2.262     | 3.82  | 279     |   |           |
| BP86  | 2.265      | 4.81  | 280     |   |           |
| Expt. | 3.50        |       |         |   |           |
| Pt2   | PW91        | 2.334 | 3.84    | 3 | 231       |
| G96PW91 | 2.362     | 3.10  | 225     |   |           |
| PW91  | 2.33        | 3.72  | 3       |   |           |
| Expt. | 3.14        |       |         | 223 |         |
| IrPt  | PW91        | 2.294 | 4.44    | 4 | 242       |

Table 1. Bond length R, binding energy E_b, spin multiplicity S, and vibrational frequency Ω of the equilibrium structures of dimers.

*Present work.
*Ref. [29].
*Ref. [30].
*Ref. [31].
*Ref. [32].
*Ref. [33].
*Ref. [34].
*Ref. [35].
Table 2. The point-group symmetry, average bond length $R$, binding energy per atom $E_B$, and magnetic moment per atom $M$ of both Ir$_8$ and Pt$_8$ clusters.

| Cluster | Symmetry | $R$ (Å) | $E_B$ (eV/atom) | $M$ ($\mu_B$/atom) |
|---------|----------|---------|-----------------|-------------------|
| Ir$_8$  | $^\ast$Oh | 2.37    | 5.11            | 0                 |
|         | $^\ast$Oh | 2.37    | 4.90            | 0                 |
| Pt$_8$  | $^\ast$D$_{2h}$ | 2.53  | 3.42            | 1                 |
|         | $^\ast$D$_{2h}$ | 2.54  | 3.34            | 1                 |

$^\ast$Present work.
$^a$Ref. [37].
$^b$Ref. [38].

By comparing with the theoretical results of Xiao and Wang [38], our results show excellent agreement with theirs, further indicating the validity of the present computational approach.

For Pt$_{8-n}$Ir$_n$ clusters, we have optimised numbers of initial structures and then picked out four most stable isomers, i.e. the ground-state and three low-lying isomers. Structural geometries, total magnetic moments, average binding energies and relative energies of four isomers all over the clusters are provided in Table S1 from Supplemental data. Most of geometric structures are three-dimensional while low-lying behaviour could also be exhibited in the planar structure, such as the tetra-capped distorted rhombus. Most clusters are the distorted prismatic structures (see Table S1 and Figure S1 in Supplemental data), such as a Y-type prism, bicapped trigonal prism and so on. The distorted cubic and rhombic prismatic structures display the low-lying feature when the number of Ir is larger than that of Pt in the isomers.

In particular, the orthogonal distorted prismatic configuration is energetically favoured by the low-lying isomers for nearly all the composition. The distorted cubic configuration for the PtIr$_7$ cluster is approximately 1.0 eV in energy, more stable than other metastable isomers, and the cubic structure of the Ir$_8$ cluster is more stable within the range from 1.76 to 2.14 eV than other isomers. However, the other low-lying isomers lie above the minimum energy structures in the corresponding clusters ranging from 0.04 to 0.40 eV. Therefore, it can be seen that cubic conformation shows its relatively high stability for both PtIr$_7$ and Ir$_8$ clusters.

The ground-state structures with all possible compositions of Pt$_{8-n}$Ir$_n$ clusters are depicted in Figure 1. The orthogonal prism was the lowest energy structure of the Pt$_8$ cluster with C$_2$v symmetry. Single-iridium substitution (Pt$_7$Ir) adopts the distorted bicapped trigonal prism owning a five-coordinated Ir atom. Pt$_8$Ir$_2$ reveals the Y-type prismatic structure. The putative global minima structure of the Pt$_7$Ir$_3$ cluster still remains this Y-type prism configuration. When the atomic ratio of iridium to platinum is 1:1, the cluster exhibits the similar geometry with the Pt$_8$ cluster. Yet, for Ir-rich clusters, we found that the distorted cubic configuration is favoured for the global minimum of these clusters. Similarly, Davis et al. [39] have investigated that cube is the global minimum structural configurations of Ir$_8$, Ir$_7$Pd and Ir$_6$Pd$_2$ clusters. Therefore, the cubic structure may be the effective structural motif for Ir-rich clusters.

Energetic stability of clusters could be described by average binding energy, which is given by

$$E_b\text{(Pt}_{8-n}\text{Ir}_n) = [(8 - n)E\text{(Pt)} + nE\text{(Ir)} - E\text{(Pt}_{8-n}\text{Ir}_n)]/8,$$

where $E\text{(Pt)}$ and $E\text{(Ir)}$ represent the energy of single Pt and Ir atoms, respectively, and $E\text{(Pt}_{8-n}\text{Ir}_n)$ is the total energy of Pt$_{8-n}$Ir$_n$ clusters.

As seen in Figure 2, the average binding energy of all the clusters shows the linear increment trend with iridium atoms. This improvement in bonding could be attributed to the strong interaction between Ir atoms. Consequently,
The number of Ir atoms

Figure 2. Average binding energy as a function of the number of iridium atoms all over the clusters. The equation of straight line of best fit can be written as $y = 0.194x + 3.487$, where $x$, $y$ represent the number of iridium atoms and average binding energy, respectively.

Iridium atoms play a dominant role in determining the stability of clusters. The result conforms to alloy bulk matter [10] and is in agreement with the computed results of Guo et al. [20].

Moreover, we have investigated the coordination atmosphere in combination with the bond characteristics. The average coordination number (ACN) of Pt and Ir atoms in 8-atom Pt–Ir cluster is defined as [40]

$$
\text{ACN(Pt)} = \frac{(2N_{\text{Pt-Pt}} + N_{\text{Ir-Pt}})}{(8 - n)} \quad \text{ACN(Ir)} = \frac{(2N_{\text{Ir-Ir}} + N_{\text{Ir-Pt}})}{n},
$$

(2)

where $N_{\text{Pt-Pt}}$, $N_{\text{Ir-Pt}}$, and $N_{\text{Ir-Ir}}$ represent the number of Pt–Pt, Ir–Pt and Ir–Ir bonds in clusters, respectively.

In general, the ACN of the iridium atom is larger than or equal to that of the platinum atom. The case of equal ACN between the Pt and Ir atoms appears in the cubic clusters, as depicted in Figure 3. As shown in Table 1, the bond length for PtIr is 2.294 Å, between 2.211 Å for Ir$_2$ and 2.334 Å for Pt$_2$. The binding energy per atom of Pt$_2$, PtIr and Ir$_2$ are 1.92, 2.22 and 2.76 eV, respectively. Hence, it is clear to understand the bonding strength order for the dimers, which follows this rule, namely, Ir–Ir > Ir–Pt > Pt–Pt. The preference of a lower ACN for Pt and a higher ACN for Ir in binary clusters originates from the bonding strength order.

To get a further insight into the bonding nature of binary clusters, we calculated deformation density, which is interpreted as the total charge density of the cluster with the density of free atoms subtracted. For the Pt$_4$Ir$_4$ cluster shown in Figure 4, the electrons are delocalised on platinum atoms and dominantly localised on the regions between iridium atoms. It is noteworthy that stronger covalent behaviour is shown between the iridium atoms than platinum atoms, indicating that the interaction of the Ir–Ir bond is the strongest in comparison with both Ir–Pt and Pt–Pt. Therefore, the geometries with a larger number of the Ir–Ir bond and with a lower number of the Ir–Pt and Pt–Pt bonds must be more energetically favourable in the clusters.

In addition, the ranges of average bond length for three different bond types are shown like this: 2.34–2.37 Å for the Ir–Ir bond, 2.44–2.49 Å for the Ir–Pt bond and 2.56–2.59 Å for the Pt–Pt bond, respectively. Moreover, the average bond length of Ir–Pt is 4% larger than the Ir–Ir bond, and the same with the case between the Pt–Pt bond and the Ir–Pt bond. Beyond our expectation, for the Pt$_4$Ir$_4$ cluster, the average interatomic distance of Ir–Pt is much larger than that of Ir–Ir because the excess value of the Ir–Pt bond length is about 8% in comparison with the Ir–Ir bond, but the bond length of Pt–Pt is approximately equal to the Ir–Pt bond length (see Figure 5). In the case of the same structural configuration, when Pt atoms in the central plane are

Figure 3. Average coordination number as a function of the number of iridium atoms all over the clusters.

In the case of the same structural configuration, when Pt atoms in the central plane are
replaced by Ir atoms, the interatomic distances in the central plane would be distinctly shortened, and so are the distances of atoms in between the top and inner layers. However, the bond lengths of Pt–Pt in the top and bottom layers are elongated, evidently for atoms in the bottom layer, as depicted in Figure 5.

By performing Bader charge analysis, we obtained the atomic charge population numbers for clusters. It is apparent that tiny charge transfers from iridium to platinum (see Table S2 in Supplemental data), owing to larger Pauling electronegativity of platinum (2.28) compared with iridium (2.20) [41]. As seen in Figure 6, the number of electrons transferring to platinum atoms is the largest for Pt$_4$Ir$_4$, followed by PtIr$_7$. For Pt$_8$, slight charge transfers from atoms in the central plane to those atoms in top and bottom layers, as shown in Figure 5. By comparing Pt$_4$Ir$_4$ with Pt$_8$ on the atomic charge distribution, one can see that there is more charge transferring from Ir in the central plane to Pt in the Pt$_4$Ir$_4$ cluster. Moreover, four iridium atoms prefer to occupy the central plane and build the square unit which is the structural motif of cube. It may be a foretaste that Ir-rich clusters would favour the cubic structure.

3.2. Magnetic properties

In this section, the magnetism of the lowest energy isomers of Pt$_8$–nIr$_n$ clusters should be discussed. As depicted in Figure 7, the range of magnetic moments of all the clusters is from 3.6 to 6.5 $\mu_B$, except for the Ir$_8$ cluster. It does not show magnetism for the Ir$_8$ cluster, as proposed in previous papers [36,37,42]. However, the PtIr$_7$ cluster presents magnetic moment with 4.5 $\mu_B$. For the cube, the magnetic moment shows increasing tendency after replacing an iridium atom by a platinum atom for two successive times. On the other hand, after doping an Ir atom, the value of the magnetic moment of the Pt$_7$Ir cluster slightly decreases by 0.75 $\mu_B$ in comparison with the Pt$_8$ cluster.

We further discuss their magnetic stability, which is interpreted by two spin gaps. Two spin gaps $\Delta_1$ and $\Delta_2$ can
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The total magnetic moments ($\mu_B$) can be calculated as [42]

$$\Delta_1 = E_{\text{LUMO}}^{\text{down}} - E_{\text{HOMO}}^{\text{up}},$$

$$\Delta_2 = E_{\text{LUMO}}^{\text{up}} - E_{\text{HOMO}}^{\text{down}},$$

where the energy of superscript ‘up’ (‘down’) represents the energy corresponding to the $\alpha$ ($\beta$) spin state. According to Figure 8, all the clusters are found to be magnetically stable because two spin gaps $\Delta_1$ and $\Delta_2$ for clusters of all the compositions are positive values. The Pt$_8$ cluster presents high values of two spin gaps, indicating that it is in the best magnetic stability, followed by Pt$_6$Ir$_2$ and Pt$_4$Ir$_4$.

The magnetic properties could be interpreted by the electronic structure of clusters. The density of states (DOS) of all the 8-atom clusters is shown in Figure 9. For the DOS of the Ir$_8$ cluster, the perfect mirror symmetry between the majority and the minority spin states indicates that the Ir$_8$ cluster is the zero magnetic moment. The sharp peaks in its DOS could be interpreted by the high degeneracy of energy level resulting from the high point-group symmetry. On the other hand, the spin-resolved DOS of the Pt$_8$ cluster is asymmetric and shows distinct exchange split between $\alpha$ and $\beta$ spin states, implying that it has a relatively large magnetic moment in comparison with Ir$_8$. The DOS of the Pt$_5$Ir$_3$ cluster presents the strongest shift between $\alpha$ and $\beta$ spin states, followed by Pt$_7$Ir$_6$, Pt$_5$Ir$_3$, and PtIr$_7$ clusters. This phenomenon is consistent with the behaviour of magnetism shown in Figure 7.

Furthermore, we have also calculated the local atomic magnetic moments in the PAW sphere of Pt and Ir atoms in the clusters for all possible compositions. The local magnetic moment $\mu(i)$ at atom $i$ can be calculated from [43],

$$\mu(i) = \int_0^R \left[ \rho_\uparrow(\mathbf{r}) - \rho_\downarrow(\mathbf{r}) \right] d\mathbf{r},$$

where $\rho_\uparrow(\mathbf{r})$ and $\rho_\downarrow(\mathbf{r})$ are spin-up and spin-down charge densities, respectively, and $R$ is the radius of the PAW sphere centred on the atom $i$ and its value is taken such that no two neighbouring spheres overlap. Figure 10 provided further insight on the specific magnetic moments distributions, showing that the contribution to total moments for the iridium atom is relatively larger than that for the platinum atom. By contrast with pure clusters, the monatomic impurity in clusters could enhance the magnetism. The Pt$_4$Ir$_4$ cluster shows its unique magnetic moment distribution, so we further focused our attention on the spin populations of Pt and Ir atoms and found that the unusual magnetism of the Pt$_4$Ir$_4$ cluster stems from the ferromagnetic coupling among Ir atoms and anti-ferromagnetic coupling among Pt atoms, as shown in Table 3. However, larger magnetic moments are exhibited in the inner layers than the top and bottom layers for both Pt$_8$ and Pt$_4$Ir$_4$. Moreover, the distance of two Pt atoms revealing the anti-ferromagnetic alignment (about $-0.148 \mu_B$) is the longest among all the atoms and its value is larger than that of another two Pt atoms, which means the bond length could affect the local magnetism of atoms.

The magnetic properties of clusters can be further explained by the spin density in conjugation with the DOS. For example, the spin-density surface of the Pt$_5$Ir$_3$ cluster is shown in Figure 11. The yellow region is localised on Ir atoms and another two Pt atoms and the blue is delocalised over the remaining two Pt atoms. The excess of spin-down electrons on two platinum atoms (Pt7 and Pt8, seen in Figure 5) results in negative magnetic moments, whereas more spin-up electrons localised on Ir atoms and two platinum atoms would give rise to positive magnetic moments (see Table 3). Thus, this phenomenon leads to the magnetic moment of $4.06 \mu_B$ in the Pt$_4$Ir$_4$ cluster, mainly resulting from the contribution of 5d electrons. In general, the magnetic moments of clusters are primarily caused by...
Figure 9. The spin-restricted density of states (DOS) of all the clusters. Positive (negative) value corresponds to majority (minority) spin state. A Lorentzian width $\lambda = 0.08$ eV. The Fermi level is shifted to zero and is presented as the vertical dashed line.

5d-orbital electrons of platinum and iridium atoms (see Table S3 in Supplemental data). Meanwhile, Figure 12 shows that the spin exchange splitting effect of Ir atoms is a little stronger than that of Pt atoms. It indicates that the atomic magnetic moments of Pt are lower than that of Ir atoms, which is in line with the behaviour of the spin density of Pt$_4$Ir$_4$.

4. Summary

In the present work, first-principles calculations have been performed to study the geometries, stabilities, electronic structures and magnetic properties of 8-atom Pt–Ir clusters for all possible compositions. The most stable configurations were obtained after doing structural optimisation extensively, and Ir-rich clusters always show cubic structures.

By analysing clusters’ coordination environment and bonding nature, we found the average coordination numbers of iridium atoms in the clusters are always larger than or equal to that of platinum atoms, and the bonding strengths of three bond styles obey this rule, i.e. Ir–Ir $>$ Ir–Pt $>$ Pt–Pt. Iridium doped into Pt clusters could enhance the stability of clusters and Ir atoms play the major role in determining the
Table 3. The spin populations (units: μB) in the PAW sphere of Pt and Ir atoms in Pt₄Ir₄ and Pt₈ clusters are shown as follows.

| Clusters | Atom (no.) | s orbital | p orbital | d orbital | Total moments |
|----------|------------|-----------|-----------|-----------|---------------|
| Pt₄Ir₄   | Ir (1)     | 0.047     | 0.036     | 0.684     | 0.767         |
|          | Ir (2)     | 0.047     | 0.036     | 0.683     | 0.766         |
|          | Ir (3)     | 0.047     | 0.036     | 0.683     | 0.766         |
|          | Ir (4)     | 0.047     | 0.036     | 0.683     | 0.766         |
|          | Pt (5)     | 0.021     | 0.008     | 0.201     | 0.229         |
|          | Pt (6)     | 0.021     | 0.008     | 0.201     | 0.229         |
|          | Pt (7)     | −0.018    | −0.008    | −0.122    | −0.148        |
|          | Pt (8)     | −0.018    | −0.008    | −0.122    | −0.148        |
| Pt₈      | Pt (1)     | 0.048     | 0.024     | 0.477     | 0.549         |
|          | Pt (2)     | 0.048     | 0.024     | 0.477     | 0.549         |
|          | Pt (3)     | 0.048     | 0.024     | 0.477     | 0.549         |
|          | Pt (4)     | 0.048     | 0.024     | 0.477     | 0.549         |
|          | Pt (5)     | 0.018     | 0.009     | 0.172     | 0.198         |
|          | Pt (6)     | 0.018     | 0.009     | 0.172     | 0.198         |
|          | Pt (7)     | 0.018     | 0.009     | 0.172     | 0.198         |
|          | Pt (8)     | 0.018     | 0.009     | 0.172     | 0.198         |

Stability in the clusters because of stronger covalent bonding among Ir atoms than Pt atoms, which is evidently demonstrated by the analysis of bonding nature. Bader charge analysis shows that Ir atoms act as the electron donor and Pt atoms gain the electrons from Ir atoms in the clusters. Magnetic moments of all the clusters are dominantly contributed by 5d-orbital electrons. Generally, Ir atoms carry greater moments, and Ir-rich clusters have higher moments overall, than Pt atoms and Pt-rich clusters, with the exception of Ir₈ and PtIr₇. The magnetic moments of cubic clusters are enhanced by doping Pt atoms into a pure iridium cluster. In Pt₄Ir₄, all the iridium atoms and two platinum atoms exhibit ferromagnetic alignment, but two other platinum atoms show anti-ferromagnetic alignment. The unique magnetic property for Pt₄Ir₄ depends on its electronic structure.

Figure 11. The spin density surface of Pt₄Ir₄ cluster with an isovalue of 0.03 e/Å³. In colour coding scheme, yellow and blue regions represent the excess of spin-up (↑) and spin-down (↓) electrons, respectively.

Figure 12. The total, Ir-projected, and Pt-projected electronic density of states of Pt₄Ir₄ cluster. Positive (negative) values correspond to α (β) spin states. A Lorentzian width λ = 0.08 eV. The Fermi level is shifted to zero and is presented as the vertical dashed line.

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