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First-Principles Study of Ir\(_n\) (\(n = 3–5\)) Clusters Adsorbed on Graphene and Hexagonal Boron Nitride: Structural and Magnetic Properties

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Abstract: Magnetic clusters have attracted great attention and interest due to their novel electronic properties, and they have potential applications in nanoscale information storage devices and spintronics. The interaction between magnetic clusters and substrates is still one of the challenging research focuses. Here, by using the density functional theory (DFT), we study the structural stability and magnetic properties of iridium clusters (Ir\(_n\), \(n = 3–5\)) adsorbed on two-dimensional (2D) substrates, such as graphene and hexagonal boron nitride (hBN). We find that the most favorable configurations of free Ir\(_n\) clusters change when adsorbed on 2D substrates. In the meantime, the magnetic moments of the most stable Ir\(_n\) reduce to 53\% (graphene) and 23.6\% (hBN) compared with those of the free-standing ones. Interestingly, about 12-times enlargement on the magnetic anisotropy energy can be found on hBN substrates. These theoretical results indicate that the cluster–substrate interaction has vital effects on the properties of Ir\(_n\) clusters.

Keywords: clusters; graphene; hexagonal boron nitride; substrate effect; magnetic property

1. Introduction

Owing to unexpected electronic and magnetic properties, atomic clusters are promising candidates for technological applications such as catalysis and magnetic storage. They have been becoming gradually more and more attractive in interdisciplinary fields since the 1990s \([1–3]\). The size and atomic structure-dependent properties of clusters present a huge opportunity for designing cluster-assembled materials and devices. Therefore, determining the ground state structure of a cluster directly by combining experimental and theoretical techniques is vital \([1,4]\).

Magnetic clusters have attracted special attention, especially those composed of transition metals (TM) \([5]\). Because of the strong spin–orbital coupling (SOC), it is expected that nanostructures containing TM atoms will possess possibly greater magnetic anisotropy energy (MAE), which is a key parameter in nano-information storage devices. Generally, with the increase in the atom number \(n\), the geometric structure of clusters will undergo a transition from line models \((n = 2–3)\) to planar models \((n = 3–5)\) and then to three-dimensional configurations (such as a pyramid, octahedron, icosahedron, cube or core-shell model) \([6–13]\). For instance, owing to the \(s(p)-d\) hybrid, there is a predominantly icosahedral growth for Fe\(_{13}\) and Pd\(_{13}\) clusters \([14,15]\). The electronic and magnetic properties of magnetic clusters highly depend on the atomic size. As the cluster size increases, an odd–even oscillation of vertical ionization potentials occurs in Ir\(_n\) \((n < 8)\) and Rh\(_n\) \((n < 13)\) clusters \([16,17]\). The strongly quenched orbital magnetic moment in size-dependent Fe\(_n\) \((n = 3–20)\) clusters is
obtained experimentally [14] and then confirmed by DFT calculations [18]. Furthermore, the size effects on magnetic moments have also been observed in Ni\(_n\) (\(n = 10–15\)) [19,20], Rh\(_n\) (\(n = 2–13\)) [3,16], Pd\(_n\) (\(n = 2–23, 55, 147\)) [15], Pt\(_n\) (\(n = 2–20\)) [21] and Ir\(_n\) (\(n = 1–13\)) clusters [22].

Generally, clusters can be experimentally prepared by several methods, such as magnetron sputtering [23], laser vaporization [24–26] and chemical vapor deposition (CVD) [27]. Normally, a substrate is necessary for many applications of the clusters. The interaction between the cluster and substrate can affect both the geometric structure and physical properties of a cluster. For instance, under the influence of the cluster–substrate interaction, Fe\(_n\) (\(n = 2–7\)), (Mn\(_n\) (\(n = 2–7\) and Si\(_n\) (\(n = 2–6, 10\))) clusters on graphene prefer different growth modes and various orientations [28,29]. Additionally, the electronic and magnetic properties of the substrate can be effectively modulated by the adsorption of clusters [30–33]. When the Mn\(_5\) cluster is absorbed on graphene, the magnetic moment of the Mn\(_5\) cluster is enhanced by 186% because of the electron redistribution [29]. On the contrary, for Fe\(_n\) (\(n = 1, 4–6\)) clusters, the magnetic moment is reduced by 2–4 \(\mu_B\) [28]. Furthermore, magnetic clusters can turn into stable nonmagnetic clusters when adsorbed on 2D substrates [33]. Interestingly, a large MAE can be achieved by absorbing clusters on substrates. Among them, Ir\(_2\) is a suitable candidate for nano-information storage devices and has been investigated extensively. Hu et al. [34] put an Ir\(_2\) dimer on the double vacancy site of 2D hexagonal boron nitride (hBN) and obtained an enlargement in MAE (~126 meV) [35]. Meanwhile, we have also investigated the substrate effect on MAE of Ir\(_2\) and found that MAE depends on the adsorption site and density [36]. However, from our limited knowledge, the interactions between magnetic clusters and substrates are still far from well known, especially on the MAE of larger clusters.

In this paper, by using first-principles calculations, we systematically study the interactions between Ir\(_n\) (\(n = 3–5\)) clusters and 2D substrates (graphene, hBN and germanene) [37]. Different ground state geometric structures of Ir\(_n\) and absorption sites of substrates are considered. We first investigate the geometric structures and stabilities with the help of cohesive and detachment energies. Then, we discuss the magnetic properties, including the magnetic moments and MAE, and explore the physics picture with the help of the local density of states and perturbation theory analysis. The present theoretical studies will provide insight into the substrate effect on larger magnetic clusters.

2. Materials and Methods

The structural, magnetic and electronic properties of Ir\(_n\) (\(n = 3–5\)) clusters adsorbed on 2D materials were studied by first-principles calculations, as implemented in the Vienna Ab-initio Simulation Package (VASP) code [38]. The ion–electron interaction was treated with the projector-augmented plane wave (PAW) potentials [39], and the exchange-correlation potential was described by generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) functional [40]. The wave functions were expanded in a plane wave basis set with an energy cut-off of 500 eV. The 2D substrates were chosen as \(7 \times 7\) graphene, \(7 \times 7\) hBN and \(4 \times 4\) germanene supercells, respectively. To avoid the interaction between two neighboring layers, a vacuum space of 40 Å was added along the Z-direction. A \(k\)-mesh of \(3 \times 3 \times 1\) was used for the Brillouin zone. The atomic structures were fully relaxed without any symmetric constraints, with total energy and force convergence criteria of \(10^{-4}\) eV and 0.01 eV/Å, respectively. For the calculations of the magnetic and electronic properties, the convergence criterion for the total energy was set to \(10^{-6}\) eV, and the SOC effects were considered.

We employed binding energy (\(E_b\), eV), cohesive energy (\(E_{coh}\), eV/atom) and detachment energy (\(E_{det}\), eV) to determine the most energetically favorable configuration of Ir\(_n\)/2D. \(E_b\) can be used to evaluate the interaction between the Ir\(_n\) cluster and the 2D substrate, which is defined as:

\[
E_b = E_{Ir_n} + E_{2D} - E_{Ir_n/2D}
\]
where \( E_{\text{Ir},n} \), \( E_{2\text{D}} \) and \( E_{\text{Ir},n/2\text{D}} \) are the total energies of the free—standing \( \text{Ir}_n \) cluster, 2D substrate (graphene or \( h\text{BN} \)) and \( \text{Ir}_n/2\text{D} \) hybrid system, respectively. A larger \( E_{\text{Ir}} \) means a stronger interaction between \( \text{Ir}_n \) and the 2D materials. \( E_{\text{coh}} \) is the energy gain when isolated Ir atoms are assembled into the \( \text{Ir}_n \) cluster, which is defined as:

\[
E_{\text{coh}} = (n \times E_{\text{Ir}} - E_{\text{Ir}_n})/n \quad \text{or} \quad E_{\text{coh}} = (E_{2\text{D}} + n \times E_{\text{Ir}} - E_{\text{Ir}_n/2\text{D}})/n
\]

(2)

Here, \( n \) is the number of Ir atoms of the \( \text{Ir}_n \) cluster, \( E_{\text{Ir}} \) is the energy of an isolated Ir atom, \( E_{\text{Ir}_n} \) is the total energy of the free—standing \( \text{Ir}_n \) cluster and \( E_{2\text{D}} \) is the total energy of the 2D substrate, respectively. \( E_{\text{det}} \) is the energy gain when the \( \text{Ir}_{n-1} \) cluster is transformed to \( \text{Ir}_n \) by adding one more Ir atom, which can be used to determine the most favorable cluster size \( n \). For the free—standing cluster \( \text{Ir}_n \) or that on the 2D substrate, the detachment energy can be defined as:

\[
E_{\text{det}} = E_{\text{Ir}_{n-1}} + E_{\text{Ir}} - E_{\text{Ir}_n} \quad \text{or} \quad E_{\text{det}} = E_{\text{Ir}_{n-1}/2\text{D}} + E_{\text{Ir}/2\text{D}} - E_{\text{Ir}_n/2\text{D}} - E_{2\text{D}}
\]

(3)

where \( E_{\text{Ir}_{n-1}/2\text{D}} \) and \( E_{\text{Ir}/2\text{D}} \) are the total energies of the \( \text{Ir}_{n-1}/2\text{D} \) and \( \text{Ir}/2\text{D} \) hybrid systems, respectively.

3. Results

3.1. Structural Properties

We investigated the structural, electronic and magnetic properties of the magnetic \( \text{Ir}_n \) clusters on different 2D substrates and then compared them with the free—standing ones. For the \( \text{Ir}_n \) (\( n = 3, 4, 5 \)) clusters, we considered different isomers corresponding to the most stable configuration and the metastable ones. We then put the \( \text{Ir}_n \) cluster above three kinds of substrates: graphene, \( h\text{BN} \) and germanene, respectively. Owing to the stronger interaction between the Ir and Ge atoms, the \( \text{Ir}_n \) cluster will dissociate and embed into the monolayer germanene, which can induce defected germanene. Taking \( \text{Ir}_3 \) clusters as the examples, we show the optimized configurations of \( \text{Ir}_3 \) adsorbed on germanene (see Supplementary Figure S1). Therefore, differently from our previous work in which the favorite adsorption site for the \( \text{Ir}_2 \) cluster was the single vacancy of germanene [36], we mainly discussed the graphene and \( h\text{BN} \) substrates. Three kinds of adsorption sites have been considered: on the top of an atom (T), on the top of a C-C (B-N) bond (B) and on the top of a hexagonal-ring-center (H). Accordingly, the \( \text{Ir}_n \) cluster absorbed on the 2D substrate is named \( \text{Ir}_{nm}/2\text{D}-T \) (or B, H; see Figure 1), where \( n = 3, 4, 5 \) is the number of Ir atoms, \( m = a, b, c \) labels different isomers of free—standing \( \text{Ir}_n \) clusters, 2D is either graphene or \( h\text{BN} \) and T (or B, H) labels the absorption site of the nearest Ir atom.

As shown in Figure 1a,b, there are two relative stable configurations for the free—standing \( \text{Ir}_3 \) cluster: the line model (\( \text{Ir}_{3a} \)) and the triangle model (\( \text{Ir}_{3b} \)). Hereafter, we set the energy of the most stable configuration as zero and \( \Delta E \) as the energy difference between the most stable and metastable configuration, as listed in Table 1. \( \text{Ir}_{3a} \) is more stable than \( \text{Ir}_{3b} \), with an energy difference of 0.124 eV. \( \text{Ir}_{3a} \) has an average bond length of 2.181 Å. These results are consistent with most previous PBE calculations [22,41] and PW91 calculations [33]. However, when absorbed on graphene or the \( h\text{BN} \) substrate, the \( \text{Ir}_3 \) cluster prefers the triangle model because of the substrate effect (see Figure 1c–h), which is similar to the \( \text{Si}_3 \) cluster absorbed on the graphene substrate [42]. \( \Delta E \) is 0.159 eV (on graphene) and 0.268 eV (on \( h\text{BN} \)), respectively. For the graphene substrate, the most stable configuration is the \( \text{Ir}_{3b}/\text{graphene-}\text{H} \) (Figure 1c) hybrid system, in which the \( \text{Ir}_3 \) plane is perpendicular to the graphene sheet, the innermost Ir atom is located at the H site with a \( d \) (distance between the Ir atom and the substrate) of 1.771 Å and the other two Ir atoms are located at the B site. As opposed to \( \text{Ir}_{3b}/\text{graphene-}\text{H} \), the most stable configuration is \( \text{Ir}_{3b}/\text{hBN-TT} \) (Figure 1f), in which the plane of the \( \text{Ir}_3 \) cluster has a tilt angle of 76.5° with a horizontal \( h\text{BN} \) sheet. Compared with \( \text{Ir}_{3b}/\text{graphene-}\text{H} \), there is an inversion for the triangle model, in which two nearer absorbed Ir atoms form chemical bonds with N atoms.
with a $d$ of 2.248 Å. Owing to two Ir-N bonds, Ir$_{3b}$/hBN-TT has an $E_b$ of 5.583 eV, which is higher than that of Ir$_{3a}$/graphene-H (5.352 eV).

Figure 1. Atomic structures of the (a) Ir$_{3a}$ (line model) and (b) Ir$_{3b}$ (triangle model) clusters. Top and side view of the three relative stable atomic structures of the Ir$_3$ cluster adsorbed on the graphene (c–e) and hBN (f–h) substrate, respectively. The Ir, C, B and N atoms are labeled with golden, brown, green and gray balls, respectively.

Figure 2 shows three kinds of relative stable Ir$_4$ configurations for the free—standing clusters, and those absorbed onto the graphene and hBN substrates, respectively. For the free—standing Ir$_4$ clusters, the square planar (Ir$_{4a}$, Figure 2a) is the most favorable configuration and has an average bond length of 2.338 Å. The most stable configuration and structure parameters are consistent with those in the previous report [22]. Unlike the Ir$_3$ cluster, the most stable configurations of Ir$_{4a}$ remain unchanged on both the graphene and hBN substrate, along with a slight band angle deformation when they are adsorbed onto hBN. Figure 2e,h indicate that the metastable Ir$_4$ on either the graphene or hBN is still a square planar configuration. The difference is that that are two Ir atoms bonded with the substrate in the most stable configuration, but there is only one in the metastable structure. Therefore, $\Delta E$ decreases from 1.251 eV (free—standing Ir$_{4b}$) to 0.411 (Ir$_{4a}$/hBN-T) and 0.093 eV (Ir$_{4a}$/graphene-T), respectively. Similar to Ir$_{3b}$/hBN-TT, for Ir$_{4a}$/hBN-TT (Figure 2g), the Ir$_{4a}$ cluster plane has a tilt angle of 75.1° with the hBN sheet because of the strong Ir-N interactions. As shown in Table 1, Ir$_4$/hBN has a higher $E_b$ compared with Ir$_4$/graphene, which indicates a stronger interaction between the cluster and the substrate. Note that, because the configuration of the Ir$_n$ cluster in Ir$_n$-2D may be different, a higher $E_b$ indicates a stronger interaction between the cluster and the substrate and does not guarantee a higher stability. For example, as listed in Table 1, Ir$_{4c}$/hBN-TTT (Figure 2i) has a larger $E_b$, along with a higher total energy.
Table 1. The energy difference between the most stable configuration and its isomer (ΔE, eV), the binding energy (E_b, eV), the minimum distance between the cluster and the substrate (d, Å), the magnetic moment of the clusters (μ, μB) and the hybrid system (μ_{tot}, μB) and the transferred charge from the cluster to the 2D substrate (δ, e). The negative δ represents the electrons transferring from the cluster to the 2D substrate.

| Cluster | ΔE | E_b | d  | μ  | μ_{tot} | δ     |
|---------|----|-----|----|----|---------|-------|
| Ir_{5b}/graphene-H   | 0  | 5.352 | 1.771 | 1.408 | 1.287 | −0.163 |
| Ir_{5b}/graphene-BH  | 0.159 | 5.192 | 2.007 | 2.385 | 2.517 | −0.221 |
| Ir_{5a}/graphene-HH  | 0.278 | 4.950 | 1.714 | 1.017 | 1.083 | −0.269 |
| Ir_{5b}/hBN-TT       | 0   | 5.583 | 2.248 | 2.687 | 2.713 | −0.0305|
| Ir_{5b}/hBN-H        | 0.268 | 5.315 | 1.957 | 2.644 | 2.702 | 0.101  |
| Ir_{5a}/hBN-T        | 0.691 | 4.768 | 2.253 | 0.822 | 0.829 | 0.107  |
| Ir_{5a}/graphene-BB  | 0   | 4.818 | 2.662 | 4.929 | 4.973 | −0.245 |
| Ir_{5a}/graphene-T   | 0.093 | 4.725 | 2.080 | 4.943 | 4.941 | −0.104 |
| Ir_{5b}/graphene-H   | 0.462 | 5.607 | 1.895 | 0.548 | 0.259 | −0.037 |
| Ir_{5b}/hBN-TT       | 0   | 5.546 | 2.363 | 1.535 | 1.519 | −0.023 |
| Ir_{5a}/hBN-T        | 0.411 | 5.135 | 2.241 | 2.877 | 2.900 | 0.010  |
| Ir_{5a}/graphene-HH  | 0.938 | 6.722 | 2.075 | 0    | 0       | −0.133 |
| Ir_{5a}/graphene-T   | 0   | 5.434 | 1.989 | 4.516 | 4.539 | −0.173 |
| Ir_{5a}/graphene-BB  | 0.586 | 4.847 | 2.374 | 2.181 | 2.196 | −0.468 |
| Ir_{5b}/graphene-BB  | 0.645 | 5.029 | 2.595 | 2.452 | 2.452 | −0.170 |
| Ir_{5b}/hBN-H        | 0   | 5.554 | 1.736 | 3.861 | 3.844 | 0.093  |
| Ir_{5a}/hBN-T        | 0.103 | 6.567 | 2.298 | 2.377 | 2.358 | 0       |
| Ir_{5b}/hBN-H        | 0.172 | 5.622 | 1.742 | 3.940 | 3.933 | 0.067  |

Figure 2. Atomic structures of the (a) Ir_{4a} (square planar model), (b) Ir_{4b} (a triangle configuration adding the fourth atom attached with the vertex of the triangle) and (c) Ir_{4c} (tetrahedral model) clusters. Top and side view of the three relative stable atomic structures of the Ir_{4} cluster adsorbed on the graphene (d–f) and hBN (g–i) substrate, respectively.
The free-standing Ir$_5$ isomers are listed in Figure 3a–c, in which Ir$_{5a}$ (square pyramid model) is the most stable configuration, and the metastable ones are Ir$_{5b}$ (square adding a co-plane triangle model, with an $\Delta E$ of 0.24 eV) and Ir$_{5c}$ (triangular bipyramid model, with an $\Delta E$ of 1.117 eV), respectively. When it is absorbed on the 2D substrates, the square pyramid Ir$_{5a}$ is still the most stable. A previous theoretical calculation also suggested that the square pyramid model of Ir$_5$ is more stable for both free-standing clusters [22,33,41] or on the monolayer graphene [43]. As shown in Figure 3d,g, the bottommost Ir atom of the cluster is located at the H site of the graphene (hBN) with a $d$ of 1.989 (1.736) Å. Ir$_{5c}$/hBN-T is metastable owing to its higher $E_b$ (6.567 eV), which is larger than that of Ir$_{5b}$/hBN-H (5.622 eV).

![Figure 3. Atomic structures of the three relative stable atomic structures of the Ir$_5$ clusters for the free-standing (a–c), graphene (d–f), top and side view) and hBN (g–i), top and side view) substrate, respectively.](image)

We employ $E_{\text{coh}}$ and $E_{\text{det}}$ to further discuss the favorable Ir$_n$ clusters on the substrates. As shown in Figure 4a, $E_{\text{coh}}$ increases with the number of cluster atoms (n) for both the free-standing Ir$_n$ [33] and Ir$_n$/2D hybrid systems. Compared with the free-standing Ir$_n$ cluster, Ir$_n$/2D possesses a higher $E_{\text{coh}}$, suggesting that the substrate effect can make the Ir$_n$ cluster energetically stable. The $E_{\text{coh}}$ of Ir$_5$ on graphene (hBN) is 5.19 (5.34) eV/atom, which is comparable with that from Ghazi’s works [43,44]. As plotted in Figure 4b, for free-standing clusters, that the maximum of $E_{\text{det}}$ belongs to the Ir$_4$ configuration indicates that Ir$_4$ is the favorite Ir$_n$ cluster. After being absorbed on the substrates (either graphene or hBN), Ir$_3$/2D turns out to be the most stable configuration due to it having the largest $E_{\text{det}}$.
3.2. Magnetic Properties

We next discuss the magnetic properties of Ir\(_n\) clusters on graphene and hBN. By setting different spin directions in Ir\(_n\), we can determine what the magnetic ground state (ferromagnetic or anti-ferromagnetic) is. For all the stable configurations, including the free—standing Ir\(_n\) and Ir\(_n\) on the substrates, the ferromagnetic ground state is more energetically favorable, as shown in Supplementary Table S1. The total magnetic moments of the free—standing Ir\(_3a\) and Ir\(_3b\) are 0.947 \(\mu_B\) and 2.654 \(\mu_B\), respectively. The total magnetic moments of Ir\(_4a\), Ir\(_4b\) and Ir\(_4c\) are 6.509 \(\mu_B\), 3.583 \(\mu_B\) and 0 \(\mu_B\), respectively. These results are consistent with the previous calculations [22,33]. Moreover, the total magnetic moments of Ir\(_5a\), Ir\(_5b\) and Ir\(_5c\) change to be 5.574 \(\mu_B\), 7.641 \(\mu_B\) and 7.562 \(\mu_B\), respectively. As listed in Table 1, except for Ir\(_3a\)/graphene-HH and Ir\(_3b\)/hBN-TT, the magnetic moments of the Ir\(_n\) clusters on the 2D substrates decrease more or less. Compared with the free—standing Ir\(_n\) cluster, the magnetic moments of the most stable Ir\(_n\) clusters adsorbed onto the substrates were reduced to 53\% (Ir\(_3b\)/graphene-H) and 23.6\% (Ir\(_4a\)/hBN-TT), respectively. Furthermore, for metastable Ir\(_4b\)/graphene-H, the magnetic moment of the Ir\(_4b\) cluster is only 0.548 \(\mu_B\) (84.7\% reduction). The variation of the magnetic moment caused by the substrate effect or adsorption site can be understood by the charge transfer between the cluster and the 2D sheet.

Table 1 lists the charge transfer (\(d\)) between Ir\(_n\) and the substrates from the Bader analysis [45]. Interface bonds may form between the Ir\(_n\) cluster and the substrate due to the electron transferring. Firstly, the magnitude of \(d\) on graphene is generally larger than that on hBN and relies on the absorption site. Secondly, for the considered Ir\(_n\)/graphene, electrons transfer from the Ir\(_n\) cluster to the graphene sheet, corresponding to a negative \(d\). On the contrary, the transfer direction depends on the bonded atom number when the clusters are absorbed onto the hBN substrate. Specifically, if one Ir atom is attached to the substrate, such as in Ir\(_3b\)/hBN-H (as shown in Figure 1), the charges transfer from hBN to Ir\(_n\) (\(d > 0\)). If two or more atoms are attached to the substrate, such as in Ir\(_3b\)/hBN-TT, the transfer direction is reversed (\(d < 0\)).

The density of states (DOS) of the most stable free—standing Ir\(_n\) and Ir\(_n\)/2D hybrid systems is shown in Figure 5. Generally speaking, the DOS of the Ir\(_n\) cluster is perturbed due to the substrate effect. The substrate effect can be divided into two parts: energy level repulsion and charge transfer. From the DFT calculations, the projected DOS indicated that \(d_{xy}\) states are induced from the energy level repulsion between the \(d_{yz}\) states of Ir\(_n\) and the \(p_x\) of C (N) atoms. Meanwhile, the energy level repulsion shifts the states and increases or decreases the magnetic moments of Ir\(_n\). Taking Ir\(_3\) as an example, the magnetic moment of Ir\(_3\) (2.654 mB) is increased to 2.687 \(\mu_B\) on hBN but decreased to 1.408 \(\mu_B\) on graphene. Similar changes can also be found for the Ir\(_4\) and Ir\(_5\) clusters (see Table 1). The charge transfer can be quantitatively characterized by the Bader analysis (Table 1) and qualitatively characterized by the Charge Density Difference (CDD). The CDD in Figure 6 demonstrates that charge redistribution takes place at both the interface region and the

![Figure 4. \(E_{coh}\) (a) and \(E_{def}\) (b) of the most stable structure for the Ir\(_n\), Ir\(_n\)/graphene (hBN) clusters (\(n = 1–5\)).](image-url)
$\text{Ir}_n$ cluster. Note that, differently from other $\text{Ir}_n$/2D hybrid systems, the electrons in the $\text{Ir}_3$/hBN-H structure transfer from hBN to Ir atoms, as listed in Table 1. Accordingly, positive charge density dominates the interface region in Figure 6f.

Figure 5. DOS for free standing $\text{Ir}_n$ clusters (b,e,h) and $\text{Ir}_n$/graphene (a,d,g) and $\text{Ir}_n$/hBN (c,f,i) hybrid systems. Contributions of Ir, C, B and N atoms are highlighted in black, red, blue and cyan, respectively.

Figure 6. CDD of the most stable structure of $\text{Ir}_3$ to $\text{Ir}_5$ adsorbed on graphene (a–c) and hBN (d–f). Every figure shows the top and side views of CDD, respectively. Yellow and blue isosurfaces represent positive and negative charge densities. The isosurface is set at 0.005 e Å$^{-3}$. 
Finally, we discuss the substrate effect on the magnetic anisotropy energy (MAE) of the \( \text{Ir}_n \) clusters. MAE is defined as the energy difference between different easy axes (parallel (//) and perpendicular (⊥) to the 2D substrate) per Ir atom, i.e., MAE (in meV/Ir atom) = \( E_{//} - E_{\perp} \). The MAE values of the free—standing \( \text{Ir}_{3b} \), \( \text{Ir}_{4a} \) and \( \text{Ir}_{5a} \) are 11.57, 10.05 and 32.43 meV, respectively, which are consistent with previous theoretical calculations \[41\]. However, owing to the slight structural difference, the MAE of the free—standing \( \text{Ir}_{4b} \) (9.32 meV) is lower than that yielded from Ge’s calculation (40.26 meV) \[41\]. Figure 7 plots different MAE values, as discussed in reference \[46\].

Figure 8 shows the orbital-resolved MAE of the free—standing \( \text{Ir}_n \) cluster and \( \text{Ir}_n/\text{graphene} \) (\( \text{Ir}_n/h\text{BN} \)). As shown in Figure 8b, the main contribution of the free—standing \( \text{Ir}_{3b} \) cluster to the MAE comes from the matrix element difference between the \( d_{xz} \) and \( d_{yz} \) orbitals. However, Figure 8a,c indicate that the main contributions on the substrate changed to \( d_{xy} \) and \( d_{x^2−y^2} \) orbitals for both the \( h\text{BN} \) and graphene, owing to the \( d_{x^2−y^2} \)-to-\( d_{xy} \) orbitals transition, as discussed above. For \( \text{Ir}_{4a} \), Figure 8e (free—standing) and Figure 8f (\( \text{Ir}_{4a}/h\text{BN} \)) suggested that the interaction between \( d_{xz} \) and \( d_{xy} \) is the main contribution for MAE, which results in a smaller MAE. In \( \text{Ir}_{4b}/\text{graphene} \), we found that the \( d \) orbital is closer to the Fermi level, resulting in a higher MAE. Finally, the interactions between \( d_{x^2−y^2} \) and \( d_{xz} \) (\( d_{xy} \)) determine the MAEs of the free—standing (on substrates) \( \text{Ir}_{5a} \) clusters. The positive (negative) contributions given by the matrix element difference between different orbitals and coupling factors result in different MAE values, as discussed in reference \[46\].

**Figure 7.** The MAE of the most stable free—standing \( \text{Ir}_n \) and \( \text{Ir}_n/2\text{D systems} (n = 3–5) \), respectively. The zero MAE is labeled by a dashed line.

MAE can be understood with the help of the second-order perturbation approach \[46\], which is defined as:

\[
\text{MAE} = \xi^2 \sum_{\text{O,U}} \left| \langle \text{O}|l_z|\text{U} \rangle \right|^2 - \left| \langle \text{O}|l_x|\text{U} \rangle \right|^2 \frac{E_{\text{O}} - E_{\text{U}}}{E_{\text{O}} - E_{\text{U}}}
\]

(4)

where \( \xi \) is the SOC constant, \( \text{O} \) (\( \text{U} \)) stands for the occupied (unoccupied) states, \( E_{\text{O}} \) (\( E_{\text{U}} \)) stands for the corresponding energy eigenvalues and \( l_z \) (\( l_x \)) is the orbital angular momentum operator. As described by Equation (4), the coupling spin orbital matrix element difference, i.e., \( \left| \langle \text{O}|l_z|\text{U} \rangle \right|^2 - \left| \langle \text{O}|l_x|\text{U} \rangle \right|^2 \), contributes to the value of MAE, including different coupling orbitals and various coupling factors. For \( \text{Ir}_{4a} \), Figure 8a,c indicate that the main contributions on the substrate changed to \( d_{xy} \) and \( d_{x^2−y^2} \) orbitals for both the \( h\text{BN} \) and graphene, owing to the \( d_{x^2−y^2} \)-to-\( d_{xy} \) orbitals transition, as discussed above. For \( \text{Ir}_{4a} \), Figure 8e (free—standing) and Figure 8f (\( \text{Ir}_{4a}/h\text{BN} \)) suggested that the interaction between \( d_{xz} \) and \( d_{xy} \) is the main contribution for MAE, which results in a smaller MAE. In \( \text{Ir}_{4b}/\text{graphene} \), we found that the \( d \) orbital is closer to the Fermi level, resulting in a higher MAE. Finally, the interactions between \( d_{x^2−y^2} \) and \( d_{xz} \) (\( d_{xy} \)) determine the MAEs of the free—standing (on substrates) \( \text{Ir}_{5a} \) clusters. The positive (negative) contributions given by the matrix element difference between different orbitals and coupling factors result in different MAE values, as discussed in reference \[46\].
Figure 8. The angular momentum operator matrix of the d orbital of the most stable structure: (a) Ir$_3$b/BN-H, (b) free-standing Ir$_3$b, (c) Ir$_3$b/hBN-TT, (d) Ir$_4$a/graphene-BB, (e) free-standing Ir$_4$a, (f) Ir$_4$a/hBN-TT, (g) Ir$_5$a/graphene-H, (h) free-standing Ir$_5$a and (i) Ir$_5$a/hBN-H. The units of the coordinates are eV.

4. Conclusions

In conclusion, the structural and magnetic properties of Ir$_n$ (n = 3–5) clusters adsorbed on 2D substrates (graphene and hBN) were systematically investigated using the DFT method. The calculated results show that, after the structure relaxation, the stability order of Ir$_n$ may change on 2D substrates. The detachment energies suggest that, for the free-standing Ir$_n$, the most favorite cluster is the one of n = 3. After being adsorbed on 2D substrates, the most stable cluster changes to n = 4. The magnetic moments of Ir$_n$ generally decrease owing to the charge transfer between the Ir$_n$ and the substrates, which depends on the substrate type and adsorption site. The MAE of the Ir$_n$ cluster can be enlarged by 12 times for Ir$_4$a/graphene, which is understood with the help of the second-order perturbation approach.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/nano12142436/s1. Figure S1: Three optimized configurations of Ir$_3$ on Germanene; Table S1: The relative energies (in meV) of ferromagnetic (FM) and antiferromagnetic (AFM) states for the free-standing Ir$_n$ and Ir$_n$ on graphene and hBN substrates. We set the energy of FM ($E_{FM}$) state as zero.

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