Structure, bonding and magnetism in cobalt clusters

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The structural, electronic and magnetic properties of Co\(_n\) clusters (\(n=2\)–20) have been investigated using density functional theory within the pseudopotential plane wave method. An unusual hexagonal growth pattern has been observed in the intermediate size range, \(n=15\)–20. The cobalt atoms are ferromagnetically ordered and the calculated magnetic moments are found to be higher than that of corresponding hcp bulk value, which are in good agreement with the recent Stern-Gerlach experiments. The average coordination number is found to dominate over the average bond length to determine the effective hybridization and consequently the cluster magnetic moment.

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I. INTRODUCTION

Study of finite size clusters is an important means of understanding how magnetic behavior evolves in reduced dimensionality. The 3d transition metal (TM) elements are characterized by their unfilled \(d\)-shell, which gives rise to their magnetism and many other interesting physical and chemical properties. Early transition metals are nonmagnetic in bulk solids, and only Fe, Co, and Ni are known to be ferromagnetic among the 3d metals. However, the small clusters of all the early transition metals are magnetic and those of late transition metals possess magnetic moments enhanced from their bulk values due to their spatial confinement. Local spin density based calculation\(^{1}\) showed that the face centered cubic (fcc) phase is the lowest energy state for bulk Co in the paramagnetic phase, whereas the magnetic order stabilizes the hexagonal close packed (hcp) phase as the ground state. This indicates a strong correlation between the stable structure and magnetism. Although, a metastable antiferromagnetic state exists for bulk Co, the ferromagnetic state is found to be the most stable for all crystal structures. This is unlike other 3d transition metals Cr, Mn, and Fe which have a stable antiferromagnetic structure in their fcc phase. This means that not only the crystal structure, but also the electronic configuration controls magnetism. In the present communication, we focus on Co\(_n\) clusters to understand this interplay.

The magnetic properties of bare Co\(_n\) clusters were first investigated via Stern-Gerlach (SG) molecular beam deflection experiment by Bloomfield and co-workers for Co\(_{20}\)–Co\(_{215}\) clusters\(^{2,3}\) and by de Heer and co-workers for Co\(_{30}\)–Co\(_{390}\) clusters.\(^{4,5}\) These studies showed that in the temperature range of 77–300 K, the Co\(_n\) clusters display high-field deflections, which are characteristic of superparamagnetic behavior. The superparamagnetic model for free clusters was recently revisited by Xu et al.\(^{6}\) and they proposed that adiabatic magnetization together with avoided Zeeman levels crossing in isolated clusters can lead to the same high-field beam deflection behavior as observed in the superparamagnetic spin relaxation. However, both the models predict the same high-temperature limiting form for magnetization as given by the Curie law\(^{7,8}\) \(\mathbf{M} = \mu^2 B / 3kT\), where \(\mu\) is the cluster magnetic moment, \(B\) is the magnetic field and \(T\) is the cluster temperature. The intrinsic per-atom magnetic moment for small Co\(_n\) clusters was found to be substantially larger than the bulk value\(^{2,3,4,5,6,7,8}\) and generally decreases with increasing cluster size, eventually reaching the bulk value at \(\sim 500\) atoms\(^{7}\). The enhancement in the magnetic moment in small clusters has been attributed to the lower coordination of the surface atoms resulting in a narrowing of the \(d\)-bands and hence greater spin polarization.

Information on the ground state geometry of the transition metal clusters is usually obtained from the experiments involving chemical probe methods and photoelectron spectroscopy, though, such studies for the Co\(_n\) clusters are very limited and not definitive. Reactions of Co\(_n\) clusters with ammonia and water\(^{9}\) indicate icosahedral structures for the bare and ammoniated clusters in the size range \(n = 50–120\) and nonicosahedral packing for small (around 19 atoms) Co\(_n\) clusters. Although the structures of ammoniated Fe\(_n\), Co\(_n\) and Ni\(_n\) clusters in the size range of \(n = 19–34\) atoms have been found to be polyicosahedral\(^{10}\), it has been mentioned that the bare clusters probably adopt a variety of structures. The photoionization experiment\(^{11}\) indicated icosahedral atomic shell structures for large Ni\(_n\) and Co\(_n\) clusters of 50–800 atoms. However, structures were not well identified for small Co\(_n\) clusters (\(n \leq 50\)) because atomic sub-shell closings in different symmetry based clusters occur in close sequences. These experimental results put together indicate that the icosahedral growth pattern for small sized Co\(_n\) clusters is less evident.

Theoretical works on cobalt clusters are limited and
the available results are contradictory. Li and Gne^13 performed first-principles calculation of small Co_n clusters (4 \leq n \leq 19) using spin-polarized discrete variational method within local density functional theory (DFT). However, they had not optimized the structures and considered only some special structures with lattice parameters same as the bulk Co. Guevara et al^13 used an unrestricted Hartree-Fock (HF) tight-binding formalism, starting from spd-bulk parameterization, but they only considered fixed body-centered cubic (bcc) and fcc geometries for a maximum of 177 atoms without structural relaxation. Andriotis and Menon^14 used a tight-binding molecular dynamics scheme to study cobalt clusters for some selected cluster sizes. Castro et al^15 performed all-electron density functional calculations using both local density and generalized gradient approximations. However, the size of the clusters were limited only up to 5 atoms. Recently, Lopez et al^16 studied Co_n clusters (4 \leq n \leq 60), where minimization was done using an evolutive algorithm based on a many-body Gupta potential^17 and magnetic properties have been studied by a spd-tight-binding method. As compared to ab-initio methods, the parameterized tight-binding Hamiltonian reduces the computational cost drastically, but its main problem is the lack of transferability of its parameters. In particular, because of the lack of DFT like self-consistency the charge transfer effects are not properly accounted for and hence magnetic moment results are not fully reliable.

In this communication, we report the first-principles calculation of Co_n clusters (2 \leq n \leq 20). Without any symmetry constraints, we simultaneously relax the geometric and magnetic structure to find out the true ground state. Our main interest is to study the evolution of structural, bonding and magnetic properties as a function of cluster size. We would also point out how the average bond length and coordination number determine the effective hybridization and hence the cluster magnetism.

II. COMPUTATIONAL DETAILS

The calculations are performed using density functional theory, within the pseudopotential plane wave method. We have used projector augmented wave (PAW) method and Perdew-Bruke-Ernzerhof (PBE) exchange-correlation functional^21 for spin-polarized generalized gradient approximation (GGA). The 3d and 4s electrons are treated as valence electrons and the wave functions are expanded in the plane wave basis set with the kinetic energy cut-off of 335 eV. Reciprocal space integrations are carried out at the Γ point. Symmetry unrestricted geometry and spin optimizations are performed using conjugate gradient and quasi-Newtonian methods until all the force components are less than a threshold value of 0.005 eV/Å. Simple cubic super-cells are used with the periodic boundary conditions, where two neighboring clusters are kept separated by at least 12 Å vacuum space. This essentially makes the interaction between the cluster images negligible. For each size, several initial geometrical structures have been considered. To get the ground state magnetic moment we have explicitly considered all possible spin multiplicities for each geometrical structure. The binding energy per atom is calculated as,

\[ E_b(Co_n) = \frac{1}{n} \left( n \ E(\text{Co}) - E(Co_n) \right), \]

where \( n \) is the size of the cluster. \( E(\text{Co}) \) and \( E(Co_n) \) are the total energies of isolated Co-atom and \( n \)-atom Co_n cluster, respectively. In such a definition, a positive sign in \( E_b \) corresponds to binding.

III. RESULTS AND DISCUSSIONS

A. Small Clusters: Co_2–Co_{10}

Both experimental and theoretical predictions of the true ground state of the Co_2 dimer are controversial. The first experimental estimation of Co_2 dimer bond length and binding energy has been made by mass spectroscopy^22 which are 2.31 Å and 1.72 eV, respectively. However, more recent collision-induced dissociation (CID) experiment^23 has estimated an upper bound of 1.32 eV to the dimer dissociation energy. The present calculation gives dimer binding energy as 1.45 eV/atom and a bond length of 1.96 Å, which is 78% of the bulk hcp Co. The Co atoms in dimer have bonding configuration closer to 3d^84s^2 than that of the isolated Co atom, which is 3d^74s^2 and in addition to the highly delocalized 4s electrons, the more localized 3d electrons also contribute strongly to the bonding^24 which consequently, produces a shorter bond length for the dimer. Compared to the neutral Co dimer, the experimentally^23,25,26 predicted that the bonding in Co_2^+ dimer cation is much stronger, \( \sim 2.73 \pm 0.27 \) eV, which is formed by combining a neutral Co (3d^74s^2) atom with a Co^+ (3d^8) cation in their respective ground state. Therefore, no promotional energy is required to form the cationic dimer. In fact, the bonding in Co_2^+ is relatively strong compared with other first-row transition metal dimer cations. On the other hand, the formation of neutral Co_2 dimer requires 3d^74s^2 \rightarrow 3d^84s^1 promotion^27 for both the Co atoms, which is 0.42 eV^22. We found that Co_2 dimer has a total magnetic moment of 4 \( \mu_B \), which is also consistent with mass spectroscopic measurement^22. Our estimates agree with the previous first-principles calculations^15,29,30,31.

In Fig. we show the geometrical structures of Co_n clusters for the ground state and the first isomer for \( n = 2–10 \) and the calculated binding energy, relative energy to the ground state and magnetic moment are given in the Table for the entire size range, \( n = 2–20 \).

For Co_3 cluster, we have studied both the linear and the triangular structures. An isosceles triangle with total magnetic moment 5 \( \mu_B \) is found to be the ground
state with binding energy 1.78 eV/atom. Each of the two equal sides has length of 2.19 Å and another one has 2.10 Å length. Another isosceles triangle with two long and one short bond lengths of 2.25 and 2.06 Å, respectively, is found to be nearly degenerate with the ground state structure (energy difference is only 3 meV). According to the present calculation, the linear structure lies much higher in energy. The optimal linear structure has a total magnetic moment of 7 μB and lies 0.43 eV higher than the ground state. Present result is consistent with the spin resonance spectra of Co$_3$ in Ar/Kr matrix, which indicated a triangular structure with a total moment of 5 or 7 μB to be the ground state.$^{22}$ The bonding in Co$_3^+$ cation is stronger than the neutral Co$_3$ as it is the case for dimer.$^{23}$ Yoshida et al.$^{33}$ reported that Co$_4^-$ has a linear structure with bond distance of 2.25–2.50 Å based on their photoelectron spectroscopic study. In agreement, previous all-electron (AE) density functional calculation$^{15}$ predicted an isosceles triangle (2.12, 2.12, 2.24 Å) with a magnetic moment of 1.7 μB/atom as the ground state for Co$_4$. This is also consistent with the tight-binding study$^{14}$ but they predicted much higher bond lengths and magnetic moment.

Three different initial geometries have been considered for Co$_4$ cluster: tetrahedral, rectangular and linear. A distorted tetrahedron with a total magnetic moment of 10 μB appears to be the most stable structure. It has 2.27 eV/atom energy and has an average bond length of 2.34 Å. Among the six sides of this tetrahedral ground state, two pairs have equal lengths of 2.14 Å, while the third pair is much larger, 2.72 Å. There is no experimental result available on the structure of neutral tetramer. However, Yoshida et al.$^{33}$ predicted a tetrahedral structure with a bond length of 2.25 ± 0.2 Å as the ground state for Co$_4^-$ anion. The initial rectangular structure becomes a rhombus after optimization, which also has 10 μB magnetic moment and lies 0.11 eV higher in energy from the ground state. It is the next energetically favorable state, which has sides of length 2.14 Å and two diagonals of 2.67 Å and 3.35 Å. Our results for Co$_4$ are consistent with previous calculations.$^{12,13,14,15,16}$ Castro et al.$^{15}$ predicted a strong Jahn-Teller distorted tetrahedral ground state with bond lengths almost equal to the present values. The distorted tetrahedral ground state structure is accomplished by a reduction of some inter-atomic distances (and the enlargement of other bonds) until some short equilibrium bond length result for which there is a more effective participation of the (short-range) 3d-electrons in the bonds. In fact, in the distorted tetrahedron, there are some bonds (these are always on opposite TM–TM sides), which have lengths close to that of the dimer. These short bonds have high 3d contributions and they are, therefore, the major source of increase of the bonding in the distorted structure. For both the ground state and the first isomer, the magnetic moment is found to be 2.5 μB/atom. The optimal linear structure is at a much higher energy than the ground state.

We took trigonal bi-pyramid, square pyramid and two planar structures: two triangles connected through a vertex and a pentagon as the initial structures for Co$_6$ cluster. The trigonal bi-pyramid with total magnetic moment 13 μB is found to be the most stable structure. This structure has 2.55 eV/atom binding energy and 2.34 Å average bond length. In this ground state (Fig.1), there are two types of bond lengths: all the sides of the upper and lower triangular pyramids are of same length and are smaller (2.18 Å), while those of the interfacing planar triangle are much larger, 2.65 Å. Another triangular bi-pyramid and a square pyramid with an equal magnetic moment of 11 μB are found to be the degenerate first isomer. They lie 125 meV higher in energy. The optimal planar pentagon with 11 μB magnetic moment lies much, 1.04 eV, higher and the double triangle structure lies even higher in energy from the ground state. Present results are in agreement with the previous AE-GGA calculation.$^{15}$ where they predicted the same geometric structure with 2.28 Å average bond length and 2 μB/atom magnetic moment as the ground state. On the other hand, the prediction$^{16}$ of average bond length and magnetic moment using Gupta potential is much higher, though it predicted the same geometry.

We have studied the capped trigonal bi-pyramid, octahedron and pentagonal pyramid to search the ground state for Co$_6$ cluster. From now on for the larger clusters, the planar structures have been discarded by intuition. An octahedral structure with 14 μB total magnetic moment is found to be the ground state. An initial capped triangular bi-pyramidal structure relaxes to the octahedral ground state. Each side of this octahedral ground state is about 2.27 Å and has a binding energy of 2.93 eV/atom. Another slightly distorted octahedron with 12 μB moment appears as the first isomer. However, it is 0.87 eV higher compared to the ground state. In the present calculation, the optimal pentagonal pyramid lies much higher (1.7 eV) in energy compared to the ground state and also has 12 μB magnetic moment. Present result is in agreement with previous theoretical studies.$^{12,16,30,34}$ and the octahedral structure is generally accepted as the most stable structure for Co$_6$ cluster. However, photoelectron spectroscopic study$^{33}$ predicted a pentagonal pyramid with bond distances ~ 2.75 ± 0.1 Å to be the most probable structure for Co$_6^-$ anion cluster, i.e., the geometrical structure might strongly be correlated with the charged state of the cluster.

For Co$_7$ cluster, we considered capped octahedron, pentagonal bi-pyramid and bi-capped triangular bi-pyramid. After simultaneous relaxation of both geometrical and magnetic structure, the capped octahedron with 15 μB magnetic moment appears as the most stable structure. This structure has an average bond length of 2.29 Å and has 2.97 eV/atom binding energy. The experimentally measured magnetic moment, 2.36 ± 0.25 μB/atom$^{8}$, is little higher than our result. The optimal pentagonal bi-pyramid, which is a building block of icosahedral structure, has a total magnetic moment of 15 μB, which lies 0.19 eV higher in energy from the ground
state. This is the first isomer and it has an average bond length of 2.32 Å. The optimal bi-capped triangular bi-pyramid has a total magnetic moment of 15 µB and lies 0.42 eV higher. However, using Gupta potential, Lopez et al. predicted a pentagonal bi-pyramidal structure as the ground state, and a capped octahedra as the first isomer.

We have studied three different geometries for Co$_8$ cluster: bi-capped octahedron, capped pentagonal bi-pyramid and tri-capped triangular bi-pyramid. The bi-capped octahedron with 16 µB magnetic moment is found to be the most stable structure. This ground state has 3.07 eV/atom binding energy and an average bond length of 2.30 Å. The experimentally measured magnetic moment, 2.51 $\pm$ 0.15 µB/atom, is higher than the present value. The optimal tri-capped triangular bi-pyramid and the optimal capped pentagonal bi-pyramid have an equal magnetic moment of 16 µB but lie 0.4 and 0.48 eV higher in energy respectively. They are the first and second isomers (see Fig.1).

For the Co$_9$ cluster, we considered tri-capped octahedron and bi-capped pentagonal bi-pyramid as initial configurations. A distorted tri-capped octahedron is found to be the most stable structure with 3.14 eV/atom binding energy. This ground state structure has 17 µB total magnetic moment, which is smaller than the experimental value of 2.38 $\pm$ 0.11 µB/atom. The optimal bi-capped pentagonal bi-pyramid has 17 µB magnetic moment and lies 0.53 eV higher in energy. This structure is found to the first isomer. The present results are not in good agreement with the semi-empirical predictions where they predicted the bi-capped pentagonal bi-pyramid as the ground state with a relatively high magnetic moment.

Different tri-capped pentagonal bi-pyramid (TCPBP) structures along with different tetra-capped octahedral structures were taken as initial structures for Co$_{10}$ cluster. A TCPBP structure with 18 µB total magnetic moment is found to be the ground state. The calculated magnetic moment in the ground state is smaller as compared to the neighboring sizes, which is indeed the case in experiment (cf. Fig. and will be discussed later). This is because of the fact that TCPBP is an icosahe-dral fragment based on pentagonal bi-pyramid. This is different from the structural growth seen for Co$_6$–Co$_9$ clusters, where the ground state structures are all octahedral based. For this TCPBP ground state, average coordination and average bond lengths are slightly higher and the competing effect of these two makes the magnetic moment smaller than its neighboring clusters. Another TCPBP with total magnetic moment 20 µB lies 0.08 eV higher in energy compared to ground state is found to be the first isomer. The experimental magnetic moment (2.07 $\pm$ 0.10 µB/atom) is larger compared to the predicted ground state but very close to the first isomer, which is energetically very close to the ground state. Lopez et al. predicted the same TCPBP structure, but with much higher, 2.45 µB/atom, magnetic moment as the ground state, whereas Guevara et al. predicted a fcc ground state with comparable, 2 µB/atom, magnetic moment.

**FIG. 1:** (Color online) Equilibrium geometries of the two energetically lowest isomers of Co$_n$ clusters for $n = 2-10$ (except $n = 8$, for which three consecutive isomers have been shown). Numbers in the parenthesis represent number of atoms in the cluster, relative energy to the respective ground state and total magnetic moment, respectively.
TABLE I: Binding energy, relative energy to the theoretically computed minimum energy state ($\Delta E = E - E_{\text{min}}$) and magnetic moment for Co<sub>n</sub> ($n = 2-20$) clusters. Recent SG experimental results<sup>7,35-36</sup> of the magnetic moment are shown for comparison.

| Cluster | $E_b$ (eV/atom) | $\Delta E$ (eV) | Magnetic Moment ($\mu_B$/atom) | Cluster | $E_b$ (eV/atom) | $\Delta E$ (eV) | Magnetic Moment ($\mu_B$/atom) |
|---------|----------------|----------------|------------------------------|---------|----------------|----------------|------------------------------|
|         | Theory         | SG Exp.        |                              |         | Theory         | SG Exp.        |                              |
| Co<sub>2</sub> | 1.452         | 0.000          | 2.00                         | Co<sub>15</sub> | 3.397         | 0.000          | 2.07                         | 3.38±0.03<sup>a</sup> (2.09±0.04)<sup>b</sup> |
| Co<sub>3</sub> | 1.783         | 0.000          | 1.67                         | Co<sub>16</sub> | 3.393         | 0.046          | 1.93                         |
|         | 1.783         | 0.000          | 2.33                         |         | 3.393         | 0.046          | 1.93                         |
| Co<sub>4</sub> | 2.274         | 0.000          | 2.50                         | Co<sub>17</sub> | 3.388         | 0.125          | 2.20                         |
|         | 2.248         | 0.106          | 2.50                         |         | 3.388         | 0.125          | 2.20                         |
| Co<sub>5</sub> | 2.553         | 0.000          | 2.60                         | Co<sub>18</sub> | 3.385         | 0.169          | 1.80                         |
|         | 2.528         | 0.125          | 2.60                         |         | 3.385         | 0.169          | 1.80                         |
| Co<sub>6</sub> | 2.929         | 0.000          | 2.33                         | Co<sub>19</sub> | 3.385         | 0.171          | 1.93                         |
|         | 2.784         | 0.869          | 2.00                         |         | 3.385         | 0.171          | 1.93                         |
| Co<sub>7</sub> | 2.971         | 0.000          | 2.14                         | Co<sub>17</sub> | 3.458         | 0.000          | 2.13                         | 2.53±0.04<sup>a</sup> (3.23±0.01)<sup>b</sup> |
|         | 2.944         | 0.192          | 2.14                         |         | 3.458         | 0.000          | 2.13                         | 2.53±0.04<sup>a</sup> (3.23±0.01)<sup>b</sup> |
| Co<sub>8</sub> | 3.074         | 0.000          | 2.00                         | Co<sub>18</sub> | 3.506         | 0.123          | 2.18                         |
|         | 3.024         | 0.400          | 2.00                         |         | 3.506         | 0.123          | 2.18                         |
| Co<sub>9</sub> | 3.143         | 0.000          | 1.89                         | Co<sub>19</sub> | 3.504         | 0.167          | 1.94                         |
|         | 3.084         | 0.527          | 1.89                         |         | 3.504         | 0.167          | 1.94                         |
| Co<sub>10</sub> | 3.137       | 0.000          | 1.80                         | Co<sub>19</sub> | 3.490         | 0.407          | 1.82                         |
|         | 3.128         | 0.085          | 2.00                         |         | 3.490         | 0.407          | 1.82                         |
| Co<sub>11</sub> | 3.205       | 0.000          | 1.91                         | Co<sub>19</sub> | 3.555         | 0.812          | 2.06                         |
|         | 3.203         | 0.016          | 1.91                         |         | 3.555         | 0.812          | 2.06                         |
| Co<sub>12</sub> | 3.252       | 0.000          | 2.00                         | Co<sub>19</sub> | 3.554         | 0.024          | 2.11                         |
|         | 3.243         | 0.103          | 1.89                         |         | 3.554         | 0.024          | 2.11                         |
| Co<sub>13</sub> | 3.279       | 0.000          | 1.92                         | Co<sub>19</sub> | 3.546         | 1.158          | 2.16                         |
|         | 3.268         | 0.140          | 2.08                         |         | 3.546         | 1.158          | 2.16                         |
| Co<sub>14</sub> | 3.323       | 0.000          | 2.00                         | Co<sub>19</sub> | 3.542         | 1.220          | 1.95                         |
|         | 3.322         | 0.004          | 2.00                         |         | 3.542         | 1.220          | 1.95                         |
| Co<sub>15</sub> | 3.322       | 0.005          | 1.71                         | Co<sub>19</sub> | 3.588         | 0.634          | 1.80                         |
|         | 3.322         | 0.007          | 1.86                         |         | 3.588         | 0.634          | 1.80                         |
| Co<sub>16</sub> | 3.320       | 0.008          | 2.14                         | Co<sub>19</sub> | 3.576         | 0.891          | 2.10                         |
|         | 3.320         | 0.008          | 2.14                         |         | 3.576         | 0.891          | 2.10                         |

<sup>a</sup>From Knickelbein (Ref.8 and Ref.35)
<sup>b</sup>From Xu et al. (Ref.7 and Ref.36)

B. Intermediate size clusters: Co<sub>11</sub>–Co<sub>20</sub>

With the increase in the number of atoms in the cluster, the determination of the ground state becomes a difficult task as the number of local minima in the potential energy surface increases very rapidly with the number of atoms in the cluster. In the search for the ground state structures, we have considered several possible geometrical structures as initial guess and we relax all of them for all possible spin multiplicities for each n-atom cluster. The predicted minimum energy structure along with an higher energetic isomer for each cluster in the size range n = 11–20 have been shown in Fig.2

The 13-atom hexagonal close packed structure consists of a hexagonal ring around a central atom and two triangular planes above and below it: 3,7,3 stacking, and the 13-atom close packed icosahedral structure has two pentagonal rings, two apex atoms and a central atom: 1,5,1,5,1 stacking. The initial structures for both the Co<sub>11</sub> and Co<sub>12</sub> clusters, have been derived from these 13-atom close packed structures by removing 1 or 2 atoms, respectively. As initial configurations for Co<sub>11</sub>, we considered three hcp derived structures (4,7; 3,5,3 and 1,7,3 stacking) and two icosahedral derived structures (5,1,5 and 1,5,1,4 stacking). On relaxation, all the structures distorted heavily. The distortion of the 4,7 hexagonal structure is such that one atom from the hexagonal ring comes out of the plane (Fig.2) and is the most stable configuration with binding energy 3.20 eV/atom. This structure has a total magnetic moment of 21 $\mu_B$, which is considerably smaller than that of the experimental value, 2.42 ± 0.09 $\mu_B$/atom. The initial 1,5,1,4 icosahedral structure is found to be the next isomer after relaxation. This structure lies just 16 meV higher in energy from the ground state and also has 21 $\mu_B$ magnetic moment.

For Co<sub>12</sub> cluster, we have considered two hcp structures: one with 3,6,3 stacking (without the central atom) and the other with 2,7,3 stacking (with the central atom) and two icosahedral structures: a closed icosahedra without one apex atom and a closed icosahedra without the
FIG. 2: (Color online) The ground state and a higher energy structure of Co$_n$ clusters ($n = 11-20$). For the size range $n = 13-20$, we show the optimal icosahedra-derived structures for comparison. The first entry within the parenthesis, $n.k$, indicates that the structure corresponds to the $k$-th isomer of Co$_n$ cluster, second and third entries give the relative energy to the ground state and magnetic moment per atom, respectively for the $k$-th isomer. $k = 0$ corresponds to the ground state.

central atom. After relaxation the initial hcp structures undergo a considerable rearrangement, which consists of a plane of 7 atoms coupled with another 5-atoms plane (see Fig.2). This structure having a total magnetic moment of 24 $\mu_B$ is the lowest energy state, which has 3.25 eV/atom binding energy. A structural rearrangement has also been seen for 1,5,5,1 icosahedral structure, which looks like a hcp fragment of 3,5,4 stacking after relaxation. This structure has a total magnetic moment of 22 $\mu_B$ and has 3.24 eV/atom binding energy. The icosahedral structure with 1,5,1,5 stacking does not lead to such rearrangement after relaxation. However, the relaxed structure lies much higher in energy compared to the minimum energy state. The calculated magnetic moment in the lowest energy structure, agrees with the recent SG experiments and the previous theoretical
We considered the icosahedral, hcp, cuboctahedral and fcc structures as initial structures for Co$_{13}$ cluster. A distorted hexagonal structure is found to be the minimum energy state and it looks like the most stable Co$_{11}$ structure along with two additional capped atoms (see Fig.2). This structure has a total magnetic moment of 25 $\mu_B$ and has 3.28 eV/atom energy. Knickelbein found the experimental magnetic moment to be $2.30 \pm 0.07$ $\mu_B$/atom, which is slightly higher than the present value, $1.92$ $\mu_B$/atom. However, this calculated value is in good agreement with another recent SG experiment by Xu et al.\cite{8} which predicted 2.00±0.06 $\mu_B$/atom energy. Another distorted hcp structure with total magnetic moment 27 $\mu_B$ is found to be the first isomer, which lies 0.14 eV higher in energy from the ground state. The optimal icosahedral structure has a comparatively large magnetic moment, $31 \mu_B$, and it lies 0.17 eV higher in energy being the second isomer. The optimal fcc and cuboctahedral structures are much higher in energy with respect to the minimum energy state. The present prediction of hcp structure as the minimum energy state is in agreement with the previous tight-binding prediction\cite{11}. However, there are some reports\cite{15,16} which favor the icosahedral structure as the ground state.

For Co$_{14}$ cluster, the trial structures are complete icosahedra with a single atom capping and a hexagonal structure with 3,7,4 stacking. The optimal icosahedral and the optimal hexagonal structures are found to be degenerate. The energy separation is only 4 meV. Both of these structures have equal (28 $\mu_B$) magnetic moment (see Fig.2). We also found several isomers which lie very close to these structures: An icosahedral structure (24 $\mu_B$), a hexagonal structure (26 $\mu_B$) and another icosahedra (30 $\mu_B$) lie only 5, 7 and 8 meV above the ground state, respectively (see Table I). The recent SG experimental predictions range magnetic moment from $2.11 \pm 0.02$ $\mu_B$/atom\cite{12} to $2.29 \pm 0.06$ $\mu_B$/atom\cite{12} for Co$_{14}$ cluster, which is in good agreement with the present result.

The Co$_{15}$ trial structure with lowest energy is the hexagonal structure with 4,7,4 atomic stacking. This structure has 31 $\mu_B$ magnetic moment, which is in agreement with the SG experiment of Xu et al., which is $2.09 \pm 0.04$ $\mu_B$/atom\cite{12}. However, Knickelbein predicted a larger value\cite{11}. The other hexagonal structures with total magnetic moments 29, 33 and 27 $\mu_B$ lie ~ 0.05, 0.12 and 0.17 eV higher than the minimum energy state, respectively. The optimal icosahedral structure of 1,5,1,5,1,2 stacking (with 29 $\mu_B$ magnetic moment) is the fourth isomer, which lies 0.17 eV above the lowest energy state.

The same kind of structural growth is observed in the case of Co$_{16}$ cluster. The hexagonal structure with a total magnetic moment of 34 $\mu_B$ is found to be the lowest in energy. This structure has 4,7,5 stacking and 3.46 eV/atom binding energy. This structure is nearly degenerate (5 meV lower) with another hexagonal structure, which has 32 $\mu_B$ magnetic moment. The next two isomers are also of same hexagonal motif, which have 30 and 36 $\mu_B$ magnetic moment and they lie 0.21 and 0.31 eV higher in energy with respect to the lowest energy state, respectively. The optimal icosahedral structures with 1,5,1,5,1,3 stacking and with magnetic moments 30 and 32 $\mu_B$ lie 0.32 and 0.36 eV higher, respectively. The optimal hexagonal and icosahedral structures are shown in Fig.2. The other icosahedral structure with 5,1,5,4 stacking is found to be much higher in energy.

The hexagonal structure with total magnetic moment 35 $\mu_B$ is the lowest energy state for Co$_{17}$ cluster. This structure has 5,7,5 stacking and 3.5 eV/atom binding energy. The calculated magnetic moment, 2.06 $\mu_B$/atom, is slightly smaller than that of predicted by both the recent experiment\cite{18} (see Table I). The next three isomers also have hexagonal symmetry. They have 37, 33 and 31 $\mu_B$ magnetic moment and they lie 0.12, 0.17 and 0.41 eV higher than the lowest energy state, respectively. The optimal icosahedral structure (Fig.2) has 5,1,5,1,5 stacking and lies much higher in energy.

A 6,7,5-hcp trail structure (Fig.2), which has a total magnetic moment of 36 $\mu_B$ is found to be the lowest energy state for Co$_{18}$ cluster. This structure has a binding energy of 3.61 eV/atom. The magnetic moment is in agreement with Knickelbein, 2.07±0.04 $\mu_B$/atom.\cite{8,35} However, Xu et al. predicted a higher value, 2.37±0.07 $\mu_B$/atom.\cite{8,35} Another two hcp structures with total magnetic moments 38 and 34 $\mu_B$ lie 0.02 and 0.19 eV higher in energy, respectively and are the first and second isomers. The optimal icosahedral structure has a total magnetic moment of 36 $\mu_B$, which lies much higher (0.57 eV) in energy and is the third isomer.

For Co$_{19}$ cluster, we investigated a double icosahedral structure, a hcp structure with 6,7,6 stacking and a cuboctahedral structure. The hcp structure (Fig.2) with 39 $\mu_B$ magnetic moment appears as the most stable structure among all the trial structures. The calculated magnetic moment, 2.05 $\mu_B$/atom, is closer to the value of Knickelbein, 2.21±0.03 $\mu_B$/atom,\cite{8,35} than that of the value predicted by Xu et al., 2.48±0.04 $\mu_B$/atom.\cite{8,35} The next four isomers are also found to be of same hcp packing. These isomers with total magnetic moments 37, 35, 33 and 41 $\mu_B$ lie 0.17, 0.48, 0.90 and 1.16 eV higher than the minimum energy state, respectively. On the other hand, the optimal icosahedral structure (Fig.2) has 37 $\mu_B$ magnetic moment and lies 1.22 eV higher from the ground state. The fcc and hcp fragments have also been proposed as ground state structures in the previous theoretical calculations.\cite{12} Our results are in according with the predicted hcp structure. Also some calculations\cite{15,16} predicted icosahedral ground state for Co$_{19}$.

Among all the considered structures the capped 19-atom hexagonal structure (Fig.2) is found to be the lowest energy state for Co$_{20}$ cluster. The calculated magnetic moment is found to be 2 $\mu_B$/atom for this structure, which is in agreement with the value predicted by Knickelbein (2.04±0.05 $\mu_B$/atom). However, the mo-
ment predicted by Xu et al. is much higher (2.36±0.02 μB/atom). Similar to what we have seen for Co15–Co19 clusters, the next few isomers are also of hexagonal motif. The hcp structures with total magnetic moments 38, 36, and 42 μB, which are 0.26, 0.63 and 0.89 eV higher are found to be the first, second and third isomers, respectively. The optimal icosahedral structure has a total magnetic moment of 38 μB and appears as the forth isomer (Fig. 2). However, this structure lies much higher in energy.

C. Binding energy, stability and dissociation energy

Calculated binding energies are plotted in Fig. 3 for the ground states of Coₙ clusters in the size range n=2−20. Since the coordination number increases with the number of atoms in the cluster, the binding energy increases monotonically. The binding energy of the largest cluster studied here (Co₂₅) is 3.62 eV/atom, which is about 82% of the experimental bulk value, 4.4 eV/atom, for hcp Co. Upon extrapolation of the linear fit of the binding energy per atom data to n⁻¹/₃ → 0 (Fig. 3(a)), we can estimate the binding energy of the infinitely large cluster. This is found to be 5.0 eV/atom, which is larger than the experimental value for hcp bulk Co. However, within the same level of theory we found the hcp bulk cohesive energy to be 5.11 eV/atom, which is close to the extrapolated value but again larger than the experimental value. This overestimation is consistent with the DFT calculation. Calculated binding energies for the optimal hexagonal and optimal icosahedral structures (see Fig. 3 for the optimal geometries) and the corresponding energy difference (E₉) between them are plotted in Fig. 4 for the size range n=13–20. E₉ increases with cluster size.

FIG. 3: Plot of binding energy per atom as a function of cluster size n for the ground state structures of the entire size range 2 ≤ n ≤ 20. (a) Plot of binding energy per atom (B.E) as a function of n⁻¹/₃ for the clusters Coₙ, 6 ≤ n ≤ 20 and a linear fit (−3.90 n⁻¹/₃ + 5.00) to the data. (b) Plot of second difference in total energy (Δ²E), which represents the relative stability.

FIG. 4: (color online) Plot of binding energy per atom (E₉) for optimal hexagonal and optimal icosahedral structures (left) and plot of total energy difference between these optimal structures, E₉ = |E(hexagonal) − E(icosahedral)|, (right) for the size range n=13–20. E₉ increases with cluster size.

FIG. 5: (color online) Plot of total energy as a function of cluster size n for Co13 (a), Co15 (b), Co17 (c) and Co19 (d) clusters. The • (■) represents icosahedral (hexagonal) structure. Insets represent magnification around the minima.
hexagonal minima around $\sim 2 \mu_B/\text{atom moment}$. We calculate the second difference in the total energy:

$$\Delta_2E(n) = E(n+1) + E(n-1) - 2E(n),$$

where $E(n)$ represents the total energy of an $n$-atom cluster. Calculated $\Delta_2E$ has been plotted in Fig3(b), where we see the peaks at $n = 6$ and 9, i.e., the clusters with 6 and 9 atoms are particularly more stable than their neighboring clusters. The stable structure for Co$_6$ is a octahedron and for Co$_9$, it is a distorted tri-capped octahedron. The CID experiment has also been indicated a maximum at $n = 6$ in the measured dissociation energy, which indicates a higher stability of the hexamer. The extra stability of hexamer indicates that the octahedral structure can act as a building block for larger size clusters and, indeed, for Co$_{15}$–Co$_{20}$ clusters, we have found a distinct hexagonal growth pattern and an octahedron is just a fragment of a hexagonal structure. The calculated stability (Fig3(b)) shows minima at $n = 3, 5, 7, 10$ and 14, which are related to their weak bonding. This can be further demonstrated by studying the dissociation energies as an $n$-atom cluster fragments into $m$ and $(n - m)$-atom clusters. The $m$-channel dissociation energy can be calculated as,

$$D_m(n) = E(m) + E(n - m) - E(n),$$

where $E(n), E(m)$ and $E(n - m)$ are the total energies of $n, m$ and $(n - m)$ atom clusters, respectively. We have plotted the calculated single channel ($D_1$) and dimer channel ($D_2$) dissociation energies in Fig4 and $D_1$ is compared with the CID experiment by Hales et al. However, they have estimated this dissociation energy through an indirect method: actually, they measured the single channel dissociation energy of Co$_n^+$ cation cluster and derived the same for the neutral one by using the ionization energies (IE) of the neutral clusters measured by Yang and Knickelbein and Parks et al., i.e.,

$$D_1^{\text{exp}} = D_1(\text{Co}_n^+) + IE(\text{Co}_n) - IE(\text{Co}_{n-1}).$$

The calculated single channel dissociation energy, $D_1$, shows a high peak at $n = 6$ and dips at $n = 5, 7$ and 10, which are consistent with our stability analysis. However, we do not find any dip in the calculated dissociation energy at $n = 14$, as has been seen in the CID experiment. Generally, the single channel dissociation energy is the most favorable except for $n = 4$, where the dimer dissociation (Co$_4$ $\rightarrow$ Co$_2$ + Co$_2$) is more favorable than the single channel (Co$_4$ $\rightarrow$ Co$_3$ + Co) dissociation. Table II shows the theoretically computed single channel bond dissociation energy compared to the experimentally measured values for the entire range of clusters having sizes 2 to 20.

![Diagram](image-url)

**FIG. 6:** (Color online) Plot of single channel, $D_1$ and dimer channel, $D_2$, dissociation energies as a function of cluster size $n$ for the GS configurations. We compare our calculated single channel dissociation with the CID experimental result.

| $n$ | Theory | CID Exp. | Theory | CID Exp. |
|-----|--------|----------|--------|----------|
| 2   | 2.90   | $\leq$ 1.32 | 12  | 3.77  | 3.41(0.28) |
| 3  | 2.45   | $\leq$ 1.45 | 13  | 3.61  | 3.68(0.31) |
| 4  | 3.75   | 2.41(0.21) | 14  | 3.89  | 3.12(0.36) |
| 5  | 3.67   | 2.84(0.28) | 15  | 4.33  | 3.84(0.39) |
| 6  | 4.81   | 3.31(0.29) | 16  | 4.38  | 3.82(0.39) |
| 7  | 3.22   | 2.65(0.24) | 17  | 4.40  | 3.44(0.44) |
| 8  | 3.79   | 2.93(0.22) | 18  | 4.26  | 3.84(0.56) |
| 9  | 3.70   | 2.89(0.17) | 19  | 4.54  |            |
| 10 | 3.08   | 3.05(0.16) | 20  | 3.88  |            |
| 11 | 3.89   | 3.12(0.26) |            |            |

**TABLE II:** Theoretically calculated single channel bond dissociation energies (BDE) compared with experimentally measured values for Co$_n$ ($n = 2$–20). Experimental uncertainties are within parentheses.

The average coordination number in a cluster is defined $\langle c \rangle = \frac{1}{n} \sum_{i>j} r_{ij}$, where $r_{ij}$ is the bond distance between the $j$-th and $i$-th atoms, and $n_b$ is the number of such bonds. Here we consider that two atoms are bonded if their inter atomic distance is within 2.91 Å, which is around the average of the first (2.51 Å) and second (3.54 Å) nearest-neighbor distances in bulk Co. The average coordination number in a cluster is defined as $\langle n_c \rangle = \frac{1}{n} \sum_k n_k$ where $n_k$ is the number of neighbors within the chosen cut-off of the $k$-th atom in the cluster of $n$ atoms. The convergence of the average bond length to the bulk value (2.51 Å) is much faster than the convergence of average coordination, which is far below the bulk value (12 for hcp Co). Dips at $n = 6$ and 9 in Fig. 3(a) indicate that the atoms in these clusters are closely spaced and strongly bonded compared to the neighbors, and therefore are more stable than the neighboring structures. While the peaks at $n = 5, 10$ and 14 in Fig. 3(a) and at $n = 10$ and 14 in Fig. 3(b) indicate that atoms in...
these clusters are far apart and slightly more coordinated than their neighbors, which results in a weak bonding in these clusters compared to their neighbors.

D. Magnetic moment

The calculated magnetic moments are plotted in Fig. 8 as a function of cluster size \( n \). The Co–Co interaction is always ferromagnetic for the entire size range studied, as it is for hcp bulk Co. However, the magnetic moment (2–2.5 \( \mu_B/\text{atom} \)) is larger than the hcp bulk value, 1.72 \( \mu_B/\text{atom} \). This enhancement in moment for a few atom cluster can readily be understood from the more localized d-electrons resulting from the decrease in effective hybridization. The calculated magnetic moments are in fair agreement with the very recent SG experiments by Xu et al.\(^7\) and Knickelbein\(^8\) Fig. 8 shows a qualitative agreement between the calculated and the experimental values,\(^7,8,35,36\) though the calculated moments are always underestimated systematically. However, calculated moments are close to that of predicted by Xu et al.\(^7,36\) for the size range \( n = 13–17 \) and in the size range \( n = 18–20 \) they are close to the values predicted by Knickelbein.\(^8,36\) The underestimation of calculated moment may be due to the fact that we did not include spin-orbit interaction in the present calculation. Moreover, one should remember that the magnetic moments in a magnetic deflection measurement are always derived assuming a model, which may influence the outcome. For example, Knickelbein\(^8\) used either superparamagnetic or locked moment model, whether Xu et al.\(^7\) assumed an adiabatic magnetization model to derive the moments experimentally for cobalt clusters. It is important to note that both experiments show same size evolution in general but there are some systematic differences. However, this is not due to the adoption of different models to calculate the magnetic moment as both the models resemble with the same Curie law for magnetization,\(^2,8\) but may be due to differing isomer distribution in the SG beam.

The magnetic moment is strongly correlated with the effective hybridization, which is closely related to the average bond length \( \langle r \rangle \) and the average coordination number \( \langle n_c \rangle \). As \( \langle n_c \rangle \) decreases the magnetic moment should increase through the decrease in effective hybridization. On the other hand, the dependency of magnetic moment on \( \langle r \rangle \) is directly proportional: a decrease in \( \langle r \rangle \) results in decrease in magnetic moment through the enhancement in effective bonding. Fig. 7(a) and Fig. 7(b) show that as we go from \( n = 4 \) to \( n = 10 \), both \( \langle r \rangle \) and \( \langle n_c \rangle \) increase, whereas Fig. 8 shows that the magnetic moment per atom decreases. Therefore, between these two competing contributions (\( \langle r \rangle \) and \( \langle n_c \rangle \)) to the magnetic moment, the average coordination number dominates over the average bond length in the size range \( n = 4–10 \).

In the intermediate size range, \( n = 11–20 \), the variation of \( \langle r \rangle \) (Fig. 7b) and \( \langle n_c \rangle \) (Fig. 7b) is much slower with \( n \), and therefore, the magnetic moment per atom does not vary rapidly. It is around 2 \( \mu_B/\text{atom} \) for all the clusters in this size range. So, in this size range, it is hard to predict the dominant parameter for magnetism. To illustrate the effect of \( \langle r \rangle \) and \( \langle n_c \rangle \) on the magnetism in the intermediate size range we compare these two quantities for the optimal hcp and icosahedral structures (see insets (a) and (b) of Fig. 7). It is seen that for a hcp structure, both the \( \langle r \rangle \) and \( \langle n_c \rangle \) are smaller than those of corresponding icosahedral structure for a particular \( n \)-atom cluster. In addition the magnetic moments of optimal hcp clusters are always larger than or equal

![FIG. 7: Plot of (a) average bond length \( \langle r \rangle \) and (b) average coordination \( \langle n_c \rangle \), as function of cluster size \( n \) for the ground state geometries. Dots and squares represent the data points, while solid line through them is guide to eye.](image)

![FIG. 8: (Color online) Size dependent variation of magnetic moment of the corresponding ground states. Calculated magnetic moments of the first isomers have also been shown. Calculated magnetic moments are compared with experimental results (Ref. 8 and Ref. 7).](image)
to that of the corresponding optimal icosahedral clusters (see Fig. 9), which again demonstrates that in this intermediate size range also the coordination dominates over the average bond length in deciding magnetism.

IV. SUMMARY AND CONCLUSIONS

We have systematically studied the structure, bonding and magnetism in Co\(_n\) clusters in the size range \(n = 20\). In the intermediate size range, the clusters adopt hcp structural packing, which is different from the trend observed for the other 3d transition metal clusters.\(^{41,42}\) In the size range \(n = 15\sim 20\), the energy difference between the hexagonal minimum energy states and optimal icosahedral structures increases with cluster size making the icosahedral structures more and more unfavorable with increasing size. The calculated magnetic moments are in good agreement with both the recent SG experiments. It is found that the effect of average coordination number always dominates over the average bond length to determine the effective hybridization and therefore, the magnetic moment of the clusters.

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FIG. 9: (Color online) Comparison of magnetic moment between optimized hcp and optimized icosahedral structures for Co\(_n\) in the size range \(n = 15\sim 20\). The filled squares and filled circles correspond to results for hcp and icosahedral structures, respectively. The insets show the corresponding comparisons for (a) average bond length and (b) average coordination number.
The $3d^{7}4s^{2} \rightarrow 3d^{8}4s^{1}$ transition energy for a neutral cobalt atom is found to be 0.12 eV within our scheme of calculation.

For $n = 14$, two degenerate ground states have been observed: one with icosahedral symmetry and other has hexagonal symmetry. The icosahedral structure is just slightly lower in energy compared to hexagonal structure and for Fig. 7 we have taken this icosahedron as the ground state, for which both $\langle r \rangle$ and $\langle n_{c} \rangle$ are higher than the neighbouring hcp ground states.
