Ab initio Study of Geometries and Magnetic Properties of Small Co Clusters

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Abstract. The lowest-energy geometric and isomers of freestanding Co clusters (n=2-13) and their corresponding magnetic moments have been systematically studied using the first principles (DMol method) based on the density-functional theory. The calculated results show that the Jahn-Teller effect plays an important role in the process because there are many isomers near the ground state. The difference of magnetic moment is in general very similar between the global minima and the second isomers. The second derivative of binding energy shows strong odd-even alternation and that the 6-, 10- and 12- atom cluster are all magic.

1. Introduction

Many theoretical studies have been conducted to calculate the electronic structure of small transition-metal clusters. Fortunately, the density-functional theory (DFT) [1,2] offers a computational alternative yet retaining the ab initio level. The first-principles calculations based on the local-density-functional theory provided very precise and reliable results.[3-4] Among transition atom systems the cobalt clusters have been much less studied than others from the first transition row of elements. Xie et al.[4] have successfully studied the electronic structures of small Ni (n3←2–13) clusters. Nayak et al.[5] have studied the structure of Ni7 using the DMol method together with molecular dynamics (MD) simulations.

In order to clarify the stable structures for Co clusters, we have performed a global minimization of the total energy using the first-principles cluster method. We have found that high symmetry clusters have heavy degeneracy and that the Jahn-Teller effect is prominent. To our knowledge, no systematic calculations on the electronic structure of small cobalt clusters have been reported. In this paper, we present our research results for the smallest Co (n3←2–13) clusters.

2. Computational details

The DMol cluster method can yield accurate and efficient self-consistent calculations using a rapidly convergent three-dimensional numerical integration scheme [6]. As is known, the basis sets and the exchange-correlation function used in the localized orbital method can affect the calculated results to some extent. It should also be noted that the BLYP functional has been applied successfully to several other systems. [3,4,7-9]. First of all, using several kinds of exchange-correlation functionals,
we have performed all-electron test calculations on Co₂ dimer. According to the results of test calculations summarized in Table I, we adopted the BLYP exchange-correlation functional in the present work.

**Table I.** Calculated binding energy $E_b$ (in eV) and atomic bond lengths (in Å) of the Co₂ dimer in the ground state.

|         | VWN  | PW91 | BP   | BLYP | PBE  | Expt. |
|---------|------|------|------|------|------|-------|
| $a_0$   | 1.946| 2.123| 2.127| 2.144| 2.127| 2.31  |
| $E_b$   | -5.89603| -5.48520| -5.39439| -5.07996| -5.36794| -2.75 ± 0.1 |

For accurate calculations, we chose an octupole scheme for the multipolar expansion of the charge density and Coulomb potential. In the optimizations, the energy gradient and atomic displacement converge to $1 \times 10^{-4}$ Hartree/Bohr and $1 \times 10^{-4}$ Å, respectively. The charge density in the self-consistent iterations converges to $1 \times 10^{-6}$ e/Å³, which corresponds to a total energy convergence of $1 \times 10^{-5}$ Hartree.

As the number of possible configurations increases very rapidly with the cluster size, it is obvious that one cannot explore all possible configurations. In general, clusters with higher symmetry and fewer low coordination surface atoms are expected to be more stable. The initial geometry was therefore constructed according to certain symmetry. We then examined almost all candidate configurations for up to 13 atoms appearing at present work. In order to determine the ground state of each cluster, by relaxation, starting from those configurations, we have employed Jahn-Teller theory [10], which states that an electronic system occupying an energy level with degeneracy is unstable and a structural distortion will occur to remove that degeneracy, especially in those systems whose highest occupied molecular orbital (HOMO) is not fully occupied.

3. **Results and Discussions**

The most stable structures obtained by us are summarized in Table 2 and their sketches are shown in Fig. 1.

**Table 2.** Calculated results for the most stable structures of Coₙ (n=3–13) clusters.

| N | Symbol | $E_b$ (eV) | HOMO | $\Delta E$ | n | $\mu_s$ ($\mu_B$) |
|---|--------|------------|------|-------------|---|------------------|
| 3 | d₄h    | -8.68428   | A2U.1| 0.851       | 1 | 7                |
| 4 | C₄n    | -12.45504  | AG.1 | 0.449       | 1 | 8                |
| 5 | C₅n    | -16.57775  | B2.1 | 0.603       | 1 | 11               |
| 6 | D₄h    | -21.39630  | B1G.1| 0.436       | 1 | 14               |
| 7 | C₆n    | -25.33536  | E.2  | 0.346       | 0.5| 15               |
| 8 | D₈d    | -29.79855  | E.2  | 0.412       | 1 | 16               |
| 9 | C₈n    | -33.96811  | B1.1 | 0.456       | 1 | 17               |
| 10| D₁₀    | -37.91272  | A.1  | 0.298       | 1 | 20               |
| 11| D₁₀    | -40.96087  | A.1  | 0.416       | 1 | 21               |
| 12| C₁₂n   | -46.30547  | E2.2 | 0.358       | 1 | 24               |
| 13| D₁₂h   | -50.00085  | B3G.1| 0.086       | 1 | 23               |

From the above results, it is clear that there are many low-lying states with very close-lying energies. The Jahn-Teller distortions, which lower the structural symmetry, help determine the ground states for Coₙ clusters for $n \leq 13$. In searching for the ground state, we find that the binding energy does not exhibit a smooth parabolic form when the cluster is expanded without changing the symmetry. This indicates that there are some false stable states very near the ground states for certain symmetries, which increases the difficulty of the calculation.
Figure 2 can be seen clearly that 6-[12], 10-[13] and 12-atom clusters are magic and should be abundant in the mass spectrum. The mean magnetic moment shows an oscillatory behavior in Fig. 3. The mean of the $n = 13$ cluster is very near the magnetic moment of the bulk of cobalt (1.72) [14].

4. Conclusions

In summary, we have obtained optimized geometries of a number of low-energy geometrical isomers of $\text{Co}_n (n = 2–13)$ clusters using the DMol method based on density functional theory. The Jahn-Teller effect is shown to play an important role in optimizing the ground states. Reduced symmetry can easily lift the degeneracy of the HOMO state and there are many isomers near the ground state. The magnetism is more sensitive to the symmetry relative to interatomic spacing when the change of interatomic spacing is in a small range. We indicate that the growth of Cobalt clusters is in an icosahedral pattern. The mean binding energy monotonously descends with the increase of atom number with the exception of $n = 11$ and the second derivative of binding energy indicates that 6-, 10- and 12-atom cluster are magic. The formation energy calculation further verifies this fact. All the above show strong odd–even alternation.

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