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Electronic-structure calculations of cobalt clusters

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The electric structure and magnetic properties of small cobalt clusters ($4 \leq n \leq 19$) have been studied using the spin-polarized discrete variational method within the local-density-functional theory. The results show that the magnetic moment of the Co_{13} cluster converges to that of the bulk, the average moment of the cluster is in agreement with the experiment. The Co_{13} cluster with icosahedral symmetry has the highest magnetic moment among the 13-atom isomers. The atomic magnetic moments of cobalt clusters have been discussed, in particular, with reference to changing cluster size and interatomic distances. The cluster symmetry is an important factor for determining the magnetic moments of the clusters.

The electronic structure of small atomic clusters has been studied with considerable interest.[1] In the past, small clusters were mainly used as models for calculating surface or bulk electronic properties. However, the studies on clusters themselves have developed very rapidly, and have provided an important means for a better understanding of the physical properties of low-dimensional materials.

Cox *et al.*[2] performed magnetic-deflection experiments on free-iron clusters. They observed that the average magnetic moment per atom of Fe clusters ($n \leq 17$) is larger than that of the bulk. Recently, small clusters of iron[3] and cobalt[4] have been produced in molecular beams, and their magnetic properties have been studied. The measured magnetic moment per atom $\bar{\mu}$ increases with applied magnetic field and cluster size but decreases with increasing temperature, consistent with superparamagnetic behavior. However, the measured $\bar{\mu}$ is much smaller than the theoretical value. Khanna and Linderoth[5] proposed that the direction of the magnetic moment fluctuates rapidly under thermal agitation and the clusters' internal temperatures are high enough to permit their magnetic moment to orient independently and result in the reduced average magnetic moment. A very interesting result[4] is that the deflection profiles of 55–66-atom clusters showed two maxima, indicating the coexistence of two isomers of different structure and magnetic moment, because a 55-atom cluster corresponds to a closed shell of both cubo-octahedral and icosahedral structures.

Many theoretical studies have been conducted to calculate the electronic structure of small transition-metal clusters. Some semiempirical calculations have been performed[6] and have obtained many results in agreement with first-principles calculations, but some uncertain parameters are needed in the calculation. First-principles calculations based on the local-density-functional theory provided very precise and reliable results,[7–11] but require much computational effort. Thus, most calculations were limited to small clusters ($n \leq 40$). Dunlap[8] has studied the effect of symmetry on the magnetic moment of 13-atom iron clusters by a Gaussian-type orbital method. No systematic calculations on the electronic structure of cobalt clusters have been reported to our knowledge.

In this paper, we present first-principles calculations on cobalt clusters ($4 \leq n \leq 19$) using the self-consistent-field molecular-orbital theory and local-density approximation. Emphasis is placed on the effects of cluster symmetry and the development of atomic magnetic moments of the clusters with increasing cluster size and interatomic distance. Recent experiments on the magnetic properties of small transition-metal clusters motivated this study.

The electronic structure of the clusters was calculated using the discrete variational method[12,13] within the local-density-functional theory.[14] In the effective one-particle Schrödinger equation, the nonlocal Hartree-Fock exchange potential is replaced by an exchange-correlation potential depending only on the local spin density $\rho_\sigma(\mathbf{r})$. The Kohn-Sham form for the exchange-correlation potential[14] was used in the calculations. Recent electronic structure calculations using the nonlocal density approximation (NLDA) have obtained excellent results for the binding energies of molecules and solids[15,16] but no improvements on the magnetic moment of iron,[17] as compared with experiments, have been made. In this paper we have not considered the NLDA corrections. The matrix elements of the Hamiltonian and overlap are obtained by a weighted summation over a set of discrete sample Diophantine points[14] $\mathbf{r}_k$,

TABLE I. Magnetic moment of cobalt clusters in each shell in units of μ_B. $\bar{\mu}$ is the average moment.

Cluster	Symmetry	Central	*NN*	*NNN*	$\bar{\mu}$
Co_4	T_d	2.202			2.202
Co_6	O_h	2.332			2.332
Co_{13}	D_{3d}	1.436	2.151	2.171	2.105
Co_{13}	O_h	1.522	2.159		2.110
Co_{13}	I_h	1.651	2.385		2.329
Co_{19}	O_h	1.615	2.160	2.210	2.147

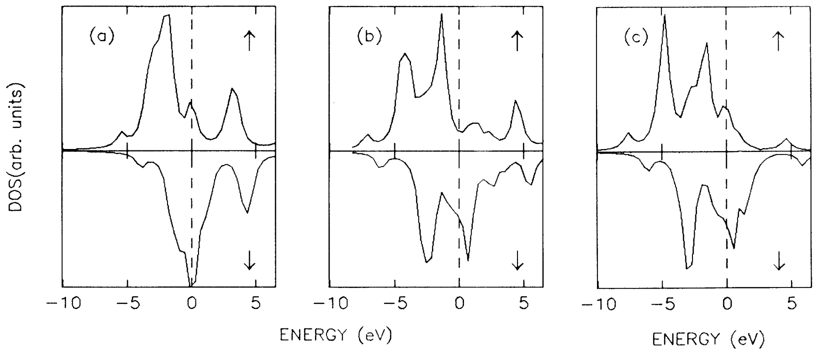

FIG. 1. Local density of states of (a) Co_4, (b) central atoms in Co_{19}, and (c) central atoms in a $\text{Co}_{13}(I_h)$ cluster. The dashed line represents the Fermi level.

$$H_{i\sigma,j\sigma'} = \sum \omega(\mathbf{r}_k)\chi^*_{i\sigma}(\mathbf{r}_k)H(\mathbf{r}_k)\chi_{j\sigma'}(\mathbf{r}_k) , \tag{1}$$

$$S_{i\sigma,j\sigma'} = \sum \omega(\mathbf{r}_k)\chi^*_{i\sigma}(\mathbf{r}_k)\chi_{j\sigma'}(\mathbf{r}_k) , \tag{2}$$

where $\omega(\mathbf{r}_k)$ is the integration weight.

In the self-consistent-charge (SCC) approximation, the actual electronic density is replaced by a model density $\rho_\sigma^{\text{SCC}}(\mathbf{r})$, which is a superposition of radial densities R_{nl}^v centered on cluster atoms via the diagonal-weighted Mulliken population f_{nl}^v,[18]

$$\rho_\sigma^{\text{SCC}}(\mathbf{r}) = \sum_{nl}\sum_{v} f_{nl}^v |R_{nl}(\mathbf{r}_v)|^2 . \tag{3}$$

The Co 3*d*, 4*s*, 4*p* atomic numerical functions were used as variational valence orbitals, while the inner orbitals were kept frozen in the calculations. The electrons of the cluster are filled successively into the cluster orbital Ψ_i according to the Fermi-Dirac statistic as

$$n_i = \frac{1}{e^{(\epsilon_i-\epsilon_F)\xi}+1} , \tag{4}$$

where n_i and ϵ_i are the occupation number and energy of the orbital Ψ_i, respectively, ϵ_F is the Fermi energy, and ξ, the Fermi distribution parameter, used to accelerate the iteration convergence, is 800 hartrees^{-1} which is close to room temperature. Dunlap and Rösch[19] have performed local-spin-density calculations on 13-atom iron clusters and found that the magnetic moment has converged with respect to the decreasing Fermi distribution parameter when this parameter is five times smaller than the value we used. Moreover, they have shown that the calculated total magnetic moment of the cluster is the same for both the Perdew-Zunger[20] and X_α (Ref. 21) exchange-correlation forms. Therefore, our results should essentially be the same for the choice of different Fermi distribution parameters and exchange-correlation functionals.

The goal of this study is to investigate the electronic structure and magnetic properties of real cobalt clusters. However, the actual geometries of small cobalt clusters are not available at present and we used the interatomic distance of the bulk for the clusters with the structure of tetrahedral Co_4, octahedral Co_6, fcc, hcp, and icosahedral Co_{13}, fcc Co_{19}.

The atomic magnetic moments of cobalt clusters, which were calculated by taking the difference of spin-up and spin-down Mulliken populations of 3*d*, 4*s*, and 4*p* orbitals, are tabulated in Table I and three local densities of states of the cobalt atoms in Co_4, Co_{19}, and $\text{Co}_{13}(I_h)$ clusters are shown in Fig. 1.

From Table I, we note that the average magnetic moment $\bar{\mu}$ of the 13-atom clusters is in good agreement with the extrapolated experimental value of $2.08\mu_B$ (Ref. 4) and that the magnetic moment of the central atom in the 13-atom clusters approaches the corresponding bulk value of about $1.6\mu_B$. This property is in remarkable contrast to that of iron and nickel clusters where the magnetic moment converges slowly to the bulk value with a much larger cluster.

Previous theoretical calculations[9,10] concluded that the atomic magnetic moment increases as its coordination number decreases, and as the cluster size becomes larger the magnetic moment will reduce uniformly. Our results

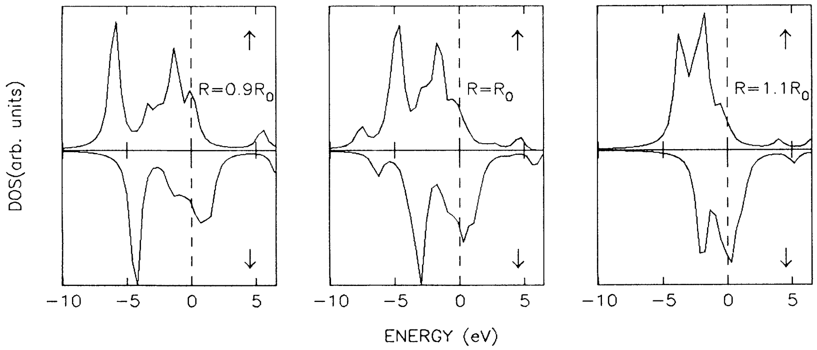

FIG. 2. 3*d* density of states of central Co in a $\text{Co}_{13}(O_h)$ cluster with different bond lengths. The dashed line represents the Fermi level. R_0 is the bond length of the bulk.

TABLE II. d charge distribution and d magnetic moments of central cobalt atoms in 13-atom clusters.

Symmetry	I_h		O_h				D_{3d}			
	$h_g^{\uparrow}$	$h_g^{\downarrow}$	$e_g^{\uparrow}$	$e_g^{\downarrow}$	$t_{2g}^{\uparrow}$	$t_{2g}^{\downarrow}$	$a_{1g}^{\uparrow}$	$a_{1g}^{\uparrow}$	$e_g^{\uparrow}$	$e_g^{\uparrow}$
d charge	4.870	3.025	1.878	1.316	2.913	1.805	0.975	0.593	3.817	1.539
μ_d (μ_B)	1.845		1.689				1.661			

are at odds with this assumption. First, $\bar{\mu}$ is oscillatory as the atom number goes from 4 to 19. Second, the $\bar{\mu}$ of Co_6 is larger than that of Co_4, although the reverse order of the coordination numbers holds for these two clusters; this is due to the cluster symmetry effect that we will discuss later. Third, both O_h and I_h 13-atom clusters have 12 bonds between the central atom and a surrounding atom. However, the O_h cluster has 24 bonds of the same length 4.74 a.u. between surface atoms while the I_h cluster has 30 bonds with a length of 4.98 a.u. Table I shows that the $\bar{\mu}$ of the I_h cluster is larger than that of the O_h cluster, which indicates that the interatomic spacing dominates over the coordination number in determining the magnetic moment. The changes of magnetic moment with bond length R can be seen from Fig. 2 which shows the $3d$ density of states of the central cobalt atom at different R. Obviously, the splitting of e_g-t_{2g} orbitals becomes narrower as R increases and thus results in the increase of the $3d$ magnetic moment.

It is interesting to note from Table I that the higher the cluster symmetry, the larger the $\bar{\mu}$; for example, $\bar{\mu}_{I_h} > \bar{\mu}_{O_h} > \bar{\mu}_{D_{3d}}$, which is in agreement with the results of iron clusters.[8] The maximal degeneracy of the irreducible representations (IR's) of I_h, O_h, and D_{3d} is 5, 3, and 2, respectively. The d orbitals do not split in the I_h crystal field and transform according to the fully h_g IR; thus, the five-d basis functions of the central atom have identical hybridizations with the surrounding atoms. However, in the O_h crystal field the d orbitals will split into e_g and t_{2g} orbitals. In Table II, we present the d charge distribution of the central atom in the I_h, O_h, and D_{3d} clusters. It is noted that the central atom in the I_h cluster is almost like a free cobalt atom with five spin-up electrons and three spin-down electrons. On the other hand, the e_g and t_{2g} orbitals in O_h have bonded considerably with the surrounding atoms which broadens the d-band width and thus reduces the magnetic moment. On the whole, the magnetic moment of a cluster is strongly affected by its symmetry. This effect may be stronger than that of interatomic spacing because even if we expand the interatomic distances (about 2% from the bulk parameters) of the D_{3d} cluster without changing the symmetry, $\bar{\mu}$ is $2.11\mu_B$ and is still smaller than that of the I_h cluster. Therefore the magnetic moments of clusters can be used to separate the isomers among the clusters as was done by Bucher, Douglass, and Bloomfield.[4]

Recent experiments[22] indicated that the measured magnetic moments of clusters were much smaller than the theoretical value. For example, the calculated average magnetic moment of a V_9 cluster in an O_h symmetry is $2.89\mu_B$/atom.[9] On the other hand, the maximum experimental value is $0.59\mu_B$.[22] Though this may be partly due to the smaller bond length in the cluster, it may be mainly due to the lower symmetry of the cluster because for such a small cluster a lower symmetry structure may be more favorable. Pastor, Davila, and Bennemann[6] have pointed out that for Fe_n, Cr_n, and Ni_n ($n \geq 9$) clusters the contraction of bond length is not more than 2%. The measured magnetic moment reduction in the cluster therefore cannot be explained by such a change in bond length.

In summary, we have revealed through self-consistent calculations that the central atom in a 13-atom cobalt cluster has a magnetic moment close to that of the bulk. This small cluster therefore is a good model of the bulk cobalt as far as the electronic and magnetic properties are concerned. The interatomic spacing can affect the magnetic moment as a cluster through changing overlap of atomic integrals, but the cluster symmetry may also play an important role in determining the moment by splitting the d orbitals into different subsets.

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[1] See, for instance, Proceedings of the 6th International Meeting on Small Particles and Inorganic Clusters, Konstanz, 1990 [Z. Phys. D **19-20**, 1 (1991)].

[2] D. M. Cox, D. J. Trevor, R. L. Whetten, E. A. Rohlfing, and A. Kaldor, Phys. Rev. B **32**, 7290 (1985).

[3] W. A. de Heer, P. Milan, and A. Chatelain, Phys. Rev. Lett. **65**, 188 (1990).

[4] J. P. Bucher, D. C. Douglass, and L. A. Bloomfield, Phys. Rev. Lett. **66**, 3052 (1991).

[5] S. N. Khanna and S. Linderoth, Phys. Rev. Lett. **67**, 742 (1991).

[6] G. M. Pastor, J. D. Davila, and H. Bennemann, Phys. Rev. B **40**, 7642 (1989); Physica B **149**, 22 (1988).

[7] C. Y. Yang, K. H. Johnson, D. R. Salahub, J. K. Kaspar, and R. P. Messmer, Phys. Rev. B **24**, 5673 (1981).

[8] B. I. Dunlap, Phys. Rev. A **41**, 5691 (1990).

[9] F. Liu, S. N. Khanna, and P. Jena, Phys. Rev. B **43**, 8179 (1991).

[10] M. R. Press, F. Liu, S. N. Khanna, and P. Jena, Phys. Rev. B **40**, 399 (1989).

[11] K. Lee, J. Callaway, K. Kwong, R. Tong, and A. Ziegler, Phys. Rev. B **31**, 1796 (1985).

[12] D. E. Ellis, Int. J. Quantum Chem. Symp. **35**, 2 (1968); D. E. Ellis and G. P. Painter, Phys. Rev. B **2**, 2887 (1970).

[13] Z. Q. Li, H. L. Luo, W. Y. Lai, and Q. Q. Zheng, J. Phys. Condens. Matter **3**, 6649 (1991).

[14] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964); W. Kohn and L. J. Sham, *ibid.* **140**, A1133 (1965).

[15] J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Perdersion, D. J. Singh, and C. Fiolhais, Phys. Rev. B **46**, 6671 (1992).

[16] F. W. Kutzler and G. S. Painter, Phys. Rev. B **46**, 3236 (1992).

[17] D. J. Singh, W. E. Pickett, and H. Krakauer, Phys. Rev. B **43**, 11 628 (1991); J. Zhu, X. W. Wang, and S. G. Louie, *ibid.* **45**, 8887 (1992).

[18] R. S. Mulliken, J. Chem. Phys. **23**, 1833 (1955); **23**, 2338 (1955).

[19] B. I. Dunlap and N. Rösch, J. Chim. Phys. Phys. Chim. Biol. **86**, 671 (1989).

[20] J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).

[21] K. Schwarz, Phys. Rev. B **5**, 2466 (1972).

[22] D. C. Douglass, J. P. Bucher, and L. A. Bloomfield, Phys. Rev. B **45**, 6341 (1992).