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## Calculations on the magnetic properties of rhodium clusters

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**Abstract.** The electronic structures of rhodium clusters with sizes of 6, 9, 13, 19, and 43 are studied by first-principles spin-polarized calculations within the local-density-functional formalism. The bond lengths of all clusters are optimized by minimizing the binding energies. The magnetic moments of the clusters are presented and compared with experiments. The electronic structure of the Rh<sub>43</sub> cluster has almost the same features as bulk rhodium.

### 1. Introduction

Rhodium has specially interesting magnetic properties. It is non-magnetic in the bulk state. However, the rhodium monolayers on an iron substrate have a measured magnetic moment of  $0.82\mu_B$  per atom [1]. The rhodium clusters are also found to have magnetic order with finite magnetic moments both theoretically and experimentally [2, 3]. In the past few decades, atomic clusters have been the new prospects in the development of material science. Taking advantage of the characteristic behaviour of small particles, one expects to be able to tailor new materials for specific technological purposes, for example, for catalysis and magnetic recording.

Reddy and co-workers [2] recently calculated the magnetic moments for ruthenium, rhodium, and palladium 13-atom clusters with icosahedral and cubo-octahedral symmetry. They predicted moments of  $1.62\mu_B$  per atom for icosahedral Rh<sub>13</sub>,  $1.02\mu_B$  per atom for icosahedral Ru<sub>13</sub>, and  $0.12\mu_B$  for icosahedral Pd<sub>13</sub>. Indeed, Cox *et al* [3] observed experimentally giant magnetic moments in small Rh<sub>*n*</sub> clusters with  $n = 12$ –34. However, their observed value of the average magnetic moment per atom for Rh<sub>13</sub> is  $0.48\mu_B$ , only about one-third of the theoretical prediction of Reddy *et al*. They also found that the average moment per atom of the Rh clusters depends significantly on the cluster size. There are several sizes, Rh<sub>15</sub>, Rh<sub>16</sub>, and Rh<sub>19</sub> which have magnetic moments per atom that are significantly larger than those of adjacent cluster sizes. The average moment of the rhodium cluster decreases to the bulk value of zero as the cluster size increases. Yang Jinlong *et al* [4] have also performed first-principles studies on Rh<sub>*n*</sub> ( $n = 2$ –19) clusters, but they did not observe the magnetic transition from magnetic state to non-magnetic state as the cluster size increases, due to the small number of atoms in their studies.

In this paper, we report an extensive first-principles study on Rh<sub>*n*</sub> clusters with  $n = 6, 9, 13, 19, 43$  within the local-spin-density (LSD) approximation [6]. The bond lengths of all clusters have been optimized by minimizing the binding energies, and the electronic structures are discussed.

## 2. Method

Since the exact structures of  $Rh_n$  clusters are not available experimentally, we assume the structure models for them shown in figure 1.  $Rh_6$  is an octahedron,  $Rh_9$  is a cube,  $Rh_{13}$  is an icosahedron,  $Rh_{19}$  is a cubo-octahedron, and  $Rh_{43}$  consists of another shell of atoms surrounding an  $Rh_{19}$  cluster. Different inequivalent sites are labelled A–D. The structures of  $Rh_6$ ,  $Rh_{19}$  and  $Rh_{43}$  are portions of the FCC crystal of rhodium. However, the icosahedral growth sequence is suggested for the transition-metal clusters [5], so we use the icosahedral structure for the  $Rh_{13}$  cluster.

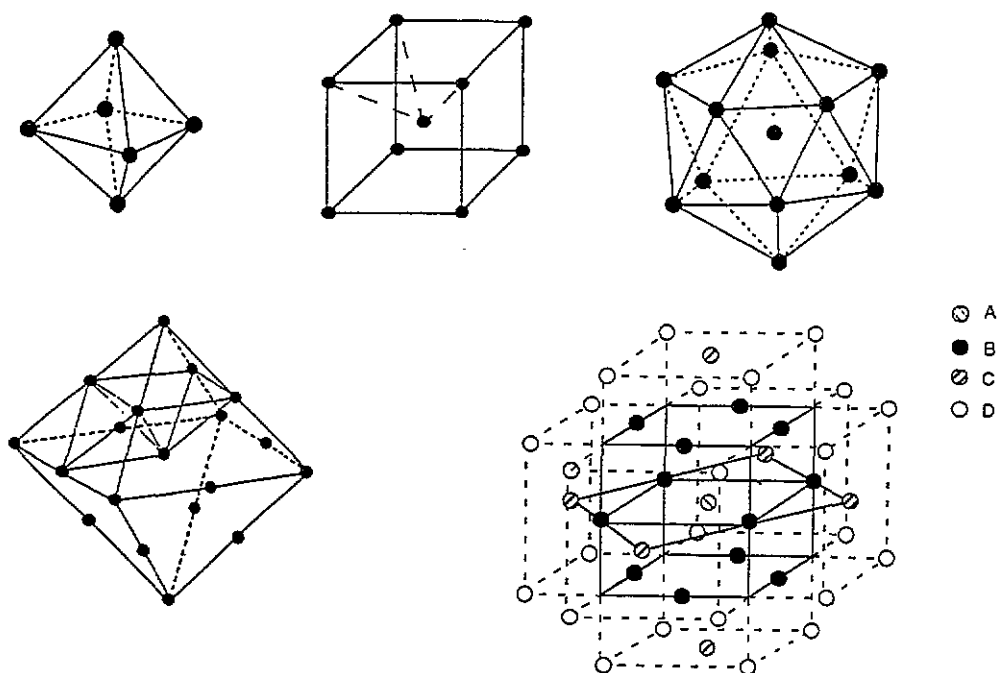


Figure 1. Structures of rhodium clusters.

The electronic structures of the clusters are calculated with the first-principles discrete variational method (DVM) [8]. The same method has already been employed in several other studies on metal clusters [9, 10], and described in detail elsewhere [12]. In brief, the numerical atomic orbitals are used in the construction of molecular orbitals. In the present work, atomic-orbital configurations composed of  $4d^8$  and  $5s^1$  for Rh atoms are employed to generate the valence orbitals. The secular equation  $(\mathbf{H}-\mathbf{E}\mathbf{S})\mathbf{C} = \mathbf{0}$  is then solved self-consistently using the matrix elements obtained via three-dimensional numerical integrations on a grid of random points by the Diophantine method. About 900 sampling points around each Rh site are employed. These points were found to be sufficient for convergence of the electronic spectrum within 0.01 eV [9]. The self-consistent-charge (SCC) scheme [11] and the von Barth–Hedin [7] exchange–correlation function are used in the calculations.

## 3. Results and discussion

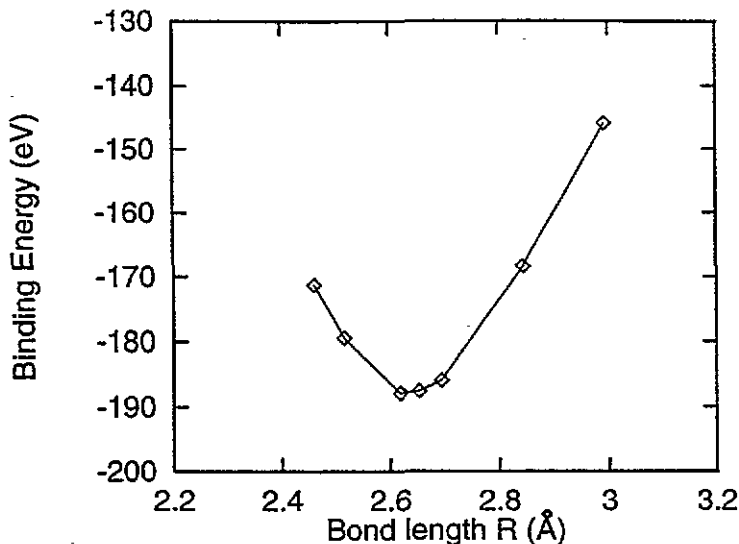
We discuss our results in three different steps. First, we optimize the bond lengths for all clusters by minimizing the binding energies. Second, the electronic configurations and the

magnetic moments of each cluster calculated at the optimized bond length are presented. This is followed by the discussion on the density of states (DOS).

**Table 1.** Binding energies  $E_b$ , interatomic bond lengths  $R$  and magnetic moments of  $Rh_n$  clusters.

	$n = 6$	$n = 9$	$n = 13$	$n = 19$	$n = 43$	Bulk <sup>a</sup> [13]	Experiment
Symmetry	$O_h$	$O_h$	$I_h$	$O_h$	$O_h$	FCC	
$E_b$ (eV)	3.32	3.33	3.45	3.85	4.36	6.11	5.75
$R$ (Å)	2.63	2.64	2.66	2.65	2.65	2.69	2.69
Moment ( $\mu_B$ /atom)							
Present	0.0	0.556	0.692	0.427	0.016		
Experiment [3]		$0.8 \pm 0.2$	$0.48 \pm 0.13$	$0.61 \pm 0.08$	$0.16 \pm 0.13$		

<sup>a</sup> LDA calculation.



**Figure 2.** Binding energies against the bond length of the  $Rh_{43}$  cluster.

We optimize the bond length of  $Rh_n$  ( $n = 6, 9, 13, 19, 43$ ) clusters while maintaining the specific symmetry of these clusters. Figure 2 shows example curves of binding energies of the  $Rh_{43}$  cluster as a function of bond length. The results are tabulated in table 1. Comparing with the bulk interatomic spacing of 2.69 Å, it is clear that the bond lengths for all rhodium clusters are a little shorter. The optimized interatomic spacing for FCC  $Rh_{43}$  is 2.65 Å which is still smaller than that of the bulk, see table 1. It can be seen that the binding energy increases gradually as the cluster size increases (except for the  $Rh_9$  cluster; cubic structure may not be appropriate for this cluster since its binding energy is lower than that of the  $Rh_6$  cluster). However, the binding energy of  $Rh_{43}$  is also smaller than the bulk cohesive energy of 5.75 eV, because there are 24 surface atoms which are more weakly bonded than the atoms in the bulk. It should be pointed out that the binding energy calculated by the DVM depends on the variational basis set. Yang Jinlong *et al* [4] got a higher binding energy for the  $Rh_{13}$  cluster since they included 5p atomic orbitals in the basis set. The binding energy for the  $Rh_{13}$  cluster, in the present study, agrees well with that of Reddy *et al* [2]. We have also calculated the  $Rh_{13}$  cluster in the FCC structure.

and found that it is energetically unfavourable compared to the icosahedral structure. The cohesive energy and lattice spacing of FCC rhodium bulk have been calculated by Moruzzi *et al* [13] using the LDA method, and they obtained a cohesive energy of 6.11 eV, larger than the experimental value, which is ascribed to the overestimate of cohesive energy in LDA schemes. The lattice constant, however, is calculated accurately.

Table 2. Magnetic moments of  $Rh_n$  clusters at different sites A–D.

Cluster	A	B	C	D
Rh <sub>6</sub>	0.00			
Rh <sub>9</sub>	-0.073	0.634		
Rh <sub>13</sub>	1.595	0.634		
Rh <sub>19</sub>	0.059	0.588	0.165	
Rh <sub>43</sub>	0.001	0.130	0.037	0.006

Next we discuss the magnetic moments of the clusters, which are obtained by taking the difference between the spin-up and spin-down Mulliken populations and by counting the unpaired spins below the Fermi level. Table 2 presents the magnetic moments of  $Rh_n$  clusters at each inequivalent site calculated at the optimized interatomic distances. The calculated magnetic moments per atom are compared with the experimental results in table 1. It is noted from the table that the Rh<sub>6</sub> cluster is non-magnetic while Rh<sub>9</sub>, Rh<sub>13</sub>, and Rh<sub>19</sub> clusters exhibit finite magnetic moments of  $5\mu_B$ ,  $9\mu_B$ , and  $8\mu_B$  per cluster, respectively, and Rh<sub>43</sub> converges to the non-magnetic state of the bulk. Reddy *et al* [2] have reported a calculated magnetic moment for Rh<sub>13</sub> of  $1.62\mu_B$  which is almost three times larger than the experimental value of  $0.48\mu_B$ . The reason for this is that their solution for the Rh<sub>13</sub> cluster is not the realistic ground state.

It is well known that the Kohn–Sham equations in the local-density-functional (LDF) scheme have a unique solution for a given system [4]. In the LSD scheme, however, solving the equations can yield more than one solution. Those solutions may correspond to local minima of the cluster energy as a function of the cluster spin. This means that with different input initial potentials for one system, sometimes the self-consistent results may be different, especially if the density of states near the Fermi level is very high. One should be cautious about the solutions of the LSD calculations and make sure that the solution is the true ground state of the system concerned. In the present study, we use a different input potential for each cluster and determine the ground state which has the lowest binding energy for the system if there are multiple solutions. Cox *et al* [3] have measured the deflections of  $Rh_n$  clusters with  $n = 12$ –100 in a gradient field, and deduced the cluster's internal magnetic moment per atom from their experimental moments per atom by assuming a superparamagnetic-cluster model. They found that the moments vary substantially with the cluster size, which is different from other transition-metal clusters [14]. From table 1, we can see that the theoretical results are in good agreement with the experiments.

It is interesting to compare the magnetic properties of 4d rhodium clusters to the 3d-element clusters. For iron and nickel clusters [12, 9], the calculated average moment is larger than the bulk value and the central atom in the cluster has a smaller magnetic moment while the surface atoms have larger ones due to the reduced coordination numbers. However, for rhodium clusters, the situation is not so uniform. For example, in the Rh<sub>19</sub> cluster, see table 2, the magnetic moments of the central atom, the nearest neighbours, and the next nearest neighbours are  $0.059\mu_B$ ,  $0.588\mu_B$ , and  $0.165\mu_B$ , respectively. The central atom in the cluster has a more bulk-like smaller moment.

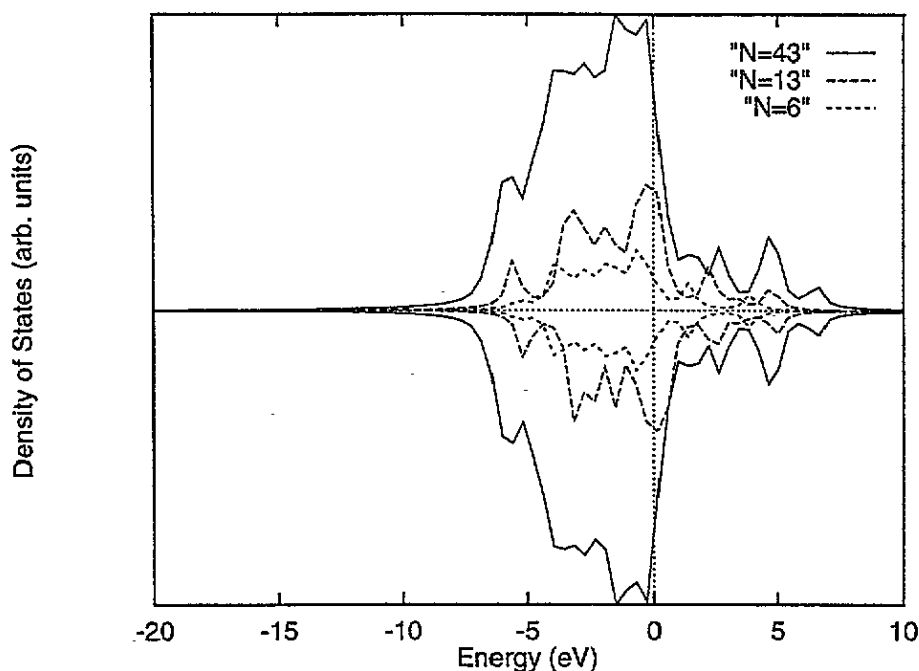


Figure 3. Total density of states of  $Rh_6$ ,  $Rh_{13}$ , and  $Rh_{43}$  clusters.

Figure 3 shows the total density of states (DOS) for the majority- and minority-spin electrons in the  $Rh_n$  ( $n = 6, 13, 43$ ) clusters. The DOSs are obtained by a Lorentzian expansion of the discrete energy levels and a summation over them. The broadening width parameter is chosen to be 0.4 eV. It is noted that the Fermi energy lies near the top of the valence band. The majority- and minority-spin DOS for  $Rh_6$  and  $Rh_{43}$  clusters are identical, indicating that these clusters are non-magnetic. However, the DOS of the  $Rh_{13}$  cluster shows a little exchange splitting which gives rise to nine unpaired spins. The valence band width (VBW) increases as the cluster size increases, and the VBW of the  $Rh_{43}$  cluster is close to that of the bulk which was obtained by band-structure calculations. The total DOS of  $Rh_{43}$  has less structure compared with that of the bulk [13] because the DOS of the  $Rh_{43}$  cluster has significant contributions of the surface atoms which have fewer neighboring atoms, and so the overlaps of the molecular wavefunctions are not sufficient. In order to establish whether the electronic properties of  $Rh_{43}$  cluster converge to the bulk, we present the local DOS of the central atom of  $Rh_{43}$  and the DOS of the bulk in figures 4(b) and (a), respectively. It is obvious that the local DOS has almost the same features as that of the bulk. This is due to the fact that the central atom in the  $Rh_{43}$  cluster has complete coordination like that of the bulk atoms. This is similar to the calculations on iron and nickel clusters [9] as well as slab calculations [15] where the central layer of a five-layer film has bulk-like properties. The VBW of the local DOS of  $Rh_{43}$  is wider than that of the bulk, since the optimized lattice spacing of the  $Rh_{43}$  cluster is a little smaller than that used in the calculation of the bulk, see table 1.

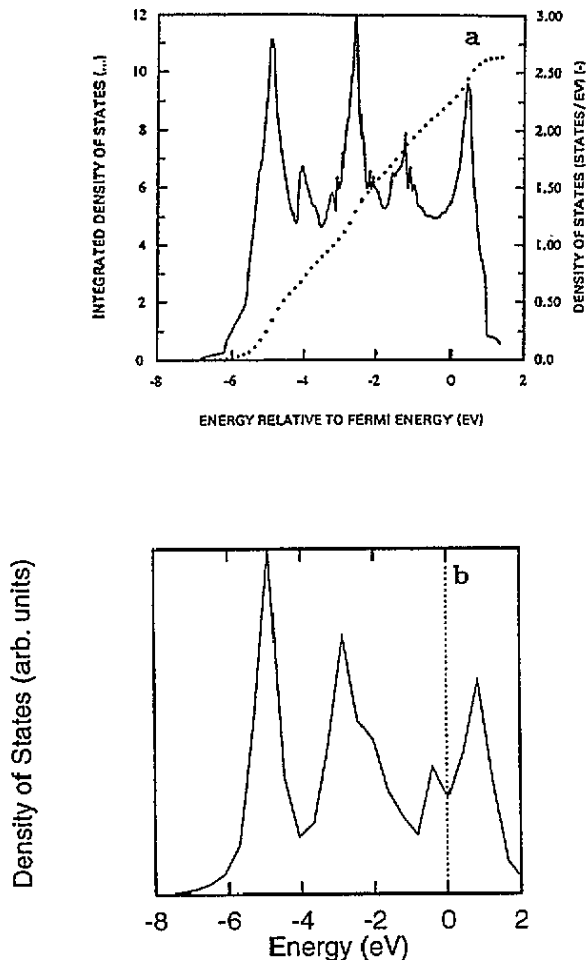


Figure 4. (a) Density of states of rhodium bulk. From [11]. (b) Local density of states of the central atom in the  $\text{Rh}_{43}$  cluster, only for the majority spin.

#### 4. Conclusions

The electronic structures of  $\text{Rh}_n$  ( $n = 6, 9, 13, 19, 43$ ) clusters have been studied by first-principles spin-polarized calculations. In summary, we find the following.

(a) The ground state of  $\text{Rh}_6$  is non-ferromagnetic, while  $\text{Rh}_9$ ,  $\text{Rh}_{13}$ , and  $\text{Rh}_{43}$  clusters have non-zero magnetic moments. The  $\text{Rh}_{43}$  cluster is non-magnetic as is the rhodium bulk.

(b) We obtain better magnetic moments for the  $\text{Rh}_{13}$  cluster than previous calculations compared with experiments.

(c) The optimized bond lengths for all clusters have small contractions compared with the bulk interatomic spacing.

(d) The calculated binding energies increase as the cluster size increases. However, the binding energy of the  $\text{Rh}_{43}$  cluster is still smaller than the cohesive energy of rhodium bulk. The local density of states of the central atom in the  $\text{Rh}_{43}$  cluster has similar features to the DOS of the bulk.

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