Anomalous symmetry dependence of Rh_{13} magnetism

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Electronic structures of 13-atom Rh clusters with three possible high-symmetry geometries are studied using the discrete variational local-spin-density-functional method. An anomalous symmetry dependence of the cluster magnetism is found: the total magnetic moment of the icosahedral Rh_{13} cluster is smaller than that of the other two lower-symmetry clusters in a wide range of interatomic spacings. An energy difference is identified to explain this anomalous relationship, which is found to be also useful for judging whether some techniques can or must be used in the local-spin-density-functional calculations. The calculated results are compared and discussed with those of previous theory and a recent experiment. The real geometry of the Rh_{13} cluster is suggested to be a distorted icosahedron.

Transition-metal (TM) clusters have been the subject of widespread investigations in recent years because of their promising practical applications in developing new magnetic materials with large moments.[1,2] As is well known, all $3d$, $4d$, and $5d$ TM atoms have a finite magnetic moment due to the Hund's-rule coupling in their unfilled d shells, and only $3d$ Fe, Co, and Ni atoms are able to retain these moments at a much reduced level in the bulk environment. On the other hand, small TM clusters, as a different state of the materials, may have magnetic properties different from their bulk phases and atoms. For free Fe, Co, and Ni clusters, theoretical calculations[3–5] and experimental measurements[6–8] have shown they have magnetic moments per atom that are bigger than the corresponding bulk values. For the other TM clusters, however, we know little about their magnetic properties. Sometimes the conclusions from experiments contradict predictions from theories. Theoretical calculations[9,10] usually predict large moments for small clusters, while experimental measurements[11] give nonmagnetic results in the limits of experimental resolution. Whether these clusters can be magnetic was a question until recently, when Cox *et al.*[12] observed experimentally that clusters of $4d$ nonmagnetic solid Rh exhibit a permanent magnetic moment. This moment can be as large as $0.8\mu_B$/atom. This experiment confirmed the theoretical prediction by Reddy *et al.*[13] that 13-atom clusters of $4d$ Pd, Rh, and Ru all have nonzero magnetic moments. Carefully comparing the results of Cox *et al.* and of Reddy *et al.*, however, one can find a quantitative discrepancy between experiment and theory.[14] The average moment per atom for Rh_{13} was measured to be $0.48\mu_B$, only about one-third of the $1.62\mu_B$ predicted by theory.

In this paper, we have performed a first-principles study of the electronic structures of Rh_{13} clusters with three possible high-symmetry geometries. We find an anomalous relationship between the cluster symmetry and the magnetism of Rh_{13} clusters, i.e., the total moment of the icosahedral Rh_{13} cluster is smaller than that of the other two lower-symmetry clusters in a wide range of interatomic spacings. This is particularly remarkable because it has always been believed that the magnetic moment of a cluster is a consequence of the reduced dimensionality and increased symmetry. We will rationalize this anomalous relationship in terms of an energy difference which turns out to be useful also for judging whether some techniques can or must be used in a local-spin-density-functional (LSD) calculation. Although it is smaller than that of Reddy *et al.*,[13] our calculated average moment per atom for the icosahedral Rh_{13} cluster is still bigger than the experimental one. We will give some possible explanations for these discrepancies between theories and between theory and experiment.

The three possible high symmetries we chose for Rh_{13} clusters are I_h, O_h, and D_{3h} respectively. The I_h point group, being that of an icosahedron, is too highly symmetric for any crystal. The O_h structure is a cuboctahedron, which is a compact portion of the fcc crystal lattice. The D_{3h} structure is obtained from the O_h cluster by rotating any triad of nearest-neighbor surface atoms by 60° about their center. This third cluster is a compact portion of the hcp lattice.

The binding energy and electronic structure of clusters were calculated using the discrete-variational (DV)

LSD method. It is a kind of molecular orbital calculation method and its theoretical foundation is LSD theory. Since it has been described in detail elsewhere,[15,16] we do not give a further description here.

There are two computational schemes within the DV method. In the first one, the exact cluster charge density $\varrho(\mathbf{r})$ is replaced approximately by a model density, which is a superposition of radial densities centered on cluster atoms via diagonal-weighted Mulliken populations.[17] In the second, a multipolar, multicenter model density is used to fit $\varrho(\mathbf{r})$ with a least-squares error-minimization procedure.[15] One of the methods used by Reddy *et al.* is the DV method: unfortunately they did not specify which scheme they used. In our calculations we adopted the second scheme which leads to a true self-consistent solution and therefore to the more precise results compatible with the method. Our calculations differ from those of Reddy *et al.* in three important respects: (a) We expanded the basis set to include the Rh $5p$ orbital and roughly optimized the Rh $4d^{8+x}5s^{1-(x+y)}5p^{y}$ ($0 \leq x \leq 1$ and $0 \leq x+y \leq 1$) configurations for the atomic basic functions in order to minimize the calculated cluster energy. The optimal basis set was found to be the numerical atomic basic functions of the Rh $4d^{8}5s^{0.9}5p^{0.1}$ configuration. (b) We dropped the Lorentzian broadening for determining the occupation number near the Fermi energy (E_F). This ensures that our results are the real solutions of the Kohn-Sham equations. The price to be paid is a slower convergence. (c) For each electronic structure calculation, we used several input potentials and started the calculations from configurations with various magnetic moments. For most cases, we obtained only one self-consistent solution. In certain interatomic spacings, however, more than one self-consistent solution can exist. These solutions correspond to local minima of the cluster energy as a function of the cluster moment. For these cases, the one which gives the largest cluster binding energy was chosen as our final solution. In addition, we used the two different forms of the exchange-correlation potential proposed by von Barth and Hedin[18] and by Perdew and Zunger.[19] The calculated results are found to be independent of the form of the exchange-correlation potential.

The binding-energy curves versus the distance r between the central and surface atoms are plotted in Fig. 1 for all the clusters. From Fig. 1, we can determine the equilibrium configuration of a cluster, as presented in Table I. The ground state is found to correspond to the I_h cluster, which is more stable than the D_{3h} and O_h clusters by 0.45 eV, and 1.35 eV, respectively. In the I_h cluster, the binding energy per atom is 4.01 eV, about 30% smaller than the bulk cohesive energy which is 5.75 eV. Compared to the bulk interatomic spacing of 5.1 a.u., one may find small bond-length contractions ($< 5\%$) in all clusters. Such a contraction effect was observed by extended x-ray-absorption fine structure measurements in Cu and Ni clusters and the contraction ratio was found to be proportional to the surface-to-volume ratio of the cluster,[20] so it is believed to be a consequence of surface effects. Table I also lists the results of Reddy *et al.*[13] The bond lengths in the two calculations are almost the same, but the binding energies have large differences. We believe that the smaller binding energies of Reddy *et al.* are a result of the smaller basis set used.

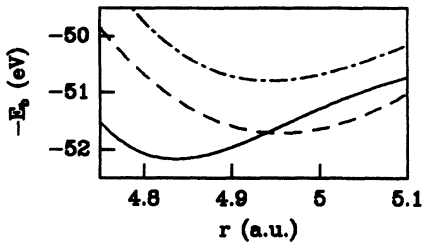

FIG. 1. Binding energies of the I_h (solid line), O_h (dot-dashed line), and D_{3h} (dashed line) Rh_{13} clusters vs the distance r between the central and surface atoms.

Figure 2 presents the cluster moment as a function of r for the three clusters. The O_h and D_{3h} clusters carry the same moment ($19\mu_B$), which remains unaltered over the range of r spanned in this figure. O_h and D_{3h} clusters are expected to exhibit similar magnetic properties since each surface atom of the two clusters has an identical nearest-neighbor environment. The total moment of the I_h cluster increases from $15\mu_B$ to $17\mu_B$ to $21\mu_B$ with the increase of r. In a wide range of r (r <5.0 a.u.), the total moment of the I_h cluster is smaller than that of the O_h and D_{3h} clusters. This result obviously contradicts the rule[3] for clusters of iron-group atoms occupying equivalent volumes: the higher the order of the group, the larger the cluster moment. From Fig. 2, we see that the I_h cluster does have the largest total moment when r >5.0 a.u., and obeys the above rule.

Why does the I_h cluster reduce its moment rapidly with the decrease of r while O_h and D_{3h} clusters do not? We found the answer by analyzing the one-electron energy levels around E_F. First, we define an energy difference ΔE.

For a cluster whose highest occupied molecular orbital (HOMO) is partially occupied, ΔE is the energy difference between the HOMO and its closest-in-energy spin-opposite molecular orbital (CSMO) which can be either occupied or unoccupied. If the HOMO is fully occupied, then ΔE is either the energy difference between the HOMO and its unoccupied CSMO or that between the lowest unoccupied molecular orbital (LUMO) and its occupied CSMO, depending on which one is the smaller.

TABLE I. The equilibrium bond lengths and binding energies for Rh_{13} clusters (r is the distance between the center and surface atoms).

Symmetry	r (a.u.)		E_b (eV)	
	Our work	Reddy *et al.* (Ref. 13)	Our work	Reddy *et al.* (Ref.[13])
I_h	4.84	4.84	52.16	42.6
O_h	4.95	4.90	50.81	41.3
D_{3h}	4.96		51.71	

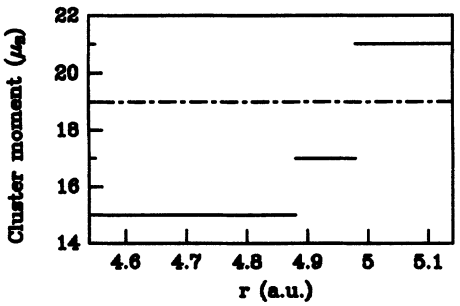

FIG. 2. The cluster moment as a function of r for the I_h Rh_{13} cluster (solid line), and for the O_h and D_{3h} Rh_{13} clusters (dot-dashed line).

In our calculations, we always found partially occupied HOMO's. Generally speaking, the order of the HOMO (or LUMO) and its CSMO in a cluster can be altered by changing interatomic spacings, if the value of ΔE is small, and this will result in a change of the cluster magnetic moment. The I_h cluster is such a case. We found that ΔE in this cluster is very small (e.g., $\Delta E \approx 0.05$ eV for r near its equilibrium value). For O_h and D_{3h} clusters, however, the HOMO's are far from their CSMO's in energy and the values of ΔE are about 0.5 eV, so it is not easy to alter the order of the HOMO and its CSMO by simply changing the interatomic spacings of these clusters. This is the reason why the moments of the O_h and D_{3h} clusters remain unaltered over the range of r spanned in Fig. 2.

Table II lists the total magnetic moments of all the clusters at their equilibrium configurations. The moment per atom of the I_h cluster is calculated to be $1.15\mu_B$, which is smaller than that of Reddy *et al.*[13] The discrepancy, we believe, arises due to our modifications in the calculations. Since the effect of enlarging the basis set is obvious, we do not discuss it and focus our attention on other points. In their calculations, Reddy *et al.* used a 0.05 eV Lorentzian broadening to determine the occupation number near E_F. However, we have seen above that in the I_h cluster ΔE is also about 0.05 eV. Since the broadening parameter is of the same order of magnitude as ΔE, the occupation numbers are affected by its value. We note that the broadening technique is used to accelerate the iteration convergence in most LSD calculations.[3,5,9,10] Our result indicates that one must be very careful in choosing the value of the broadening parameter when ΔE is small.

TABLE II. The local and total magnetic moments (μ_B) of Rh_{13} clusters at the equilibrium configurations.

Symmetry		Local moment			Total
	Orbital	Center atom	Surface atom		moment
I_h	4*d*	1.323	0.993		15
	5*s*	-0.004	0.095		
	5*p*	-0.195	0.068		
	total	1.123	1.156		
O_h	4*d*	1.284	1.313		19
	5*s*	-0.015	0.105		
	5*p*	-0.230	0.079		
	total	1.038	1.497		
D_{3h}	4*d*	1.283	1.332	1.332	19
	5*s*	-0.014	0.098	0.095	
	5*p*	-0.207	0.051	0.092	
	total	1.062	1.481	1.509	

It is well known that the Kohn-Sham equations in the local-density-functional (LDF) scheme have a unique solution for a given system. In the LSD scheme, however, solving the equations—simultaneously optimizing the spin of the system—can yield more than one solution. This is to say, in LSD calculations the self-consistent solution may depend on the input potential. Actually, when $r \leq 4.94$ a.u., we found more than one self-consistent solution for the I_h cluster. Around the equilibrium distance $r = 4.84$ a.u. we find three: the total moment of the first is $7\mu_B$, while it is $15\mu_B$ and $21\mu_B$ in the second and third, respectively. The three solutions correspond to three local minima of the cluster energy as a function of the cluster moment. The cluster binding energy of the second was calculated to be larger than that of the first and third by 0.74 eV and by 0.35 eV, respectively. Thus, the solution we discussed above is the global minimum while the solution obtained by Reddy *et al.* is only a local minimum. The solution with total moment $7\mu_B$ exists for a wide range of $r \leq 4.94$ a.u., but its energy is always higher than that of other solutions, with higher magnetic moments. The solution with total moment $21\mu_B$ exists for any $r \geq 4.80$ a.u. and is the only solution for $r \geq 5.04$ a.u.

When should one look for multiple solutions in a LSD calculation? Again, we link the answer to our energy difference ΔE. We suggest that when one finds ΔE to be small, say, less than 0.1 eV, one should consider the possibility of multiple solutions in the calculation.

Although it is smaller than that of Reddy *et al.*[13], our calculated average moment per atom for the icosahedral Rh_{13} cluster is still bigger than the experimental one $(0.48 \pm 0.13)\mu_B$. A possible explanation of this discrepancy is that the real cluster geometry is not a perfect icosahedron, but is instead a distorted one, and that undergoing distortion decreases the total magnetic moment of the cluster. Such an expectation is reasonable for the following reasons. (a) In our calculations, the HOMO of the icosahedral Rh_{13} cluster is $h_u\downarrow$, which is partially occupied by one electron. This means that this cluster has a degenerate ground state. According to the Jahn-Teller theorem, it tends to distort further toward lower symmetry so as to lift the degeneracy of its ground state and lower its energy. (b) There is already a low-moment solution ($7\mu_B$) for the perfect icosahedral Rh_{13}, though it has not the lowest energy of this geometry.

The local magnetic moments of the three clusters at their equilibrium configurations are also shown in Table II. For all three clusters, the local moment of the central atom is smaller than that of surface atoms. This observation agrees with results for clusters of iron-group atoms.[2,5] From Table II, we found a complicated magnetic-interaction picture for all three clusters. The magnetic interactions between the central and surface atoms are mainly ferromagnetic, but a small amount of antiferromagnetic interaction is found to be mixed in: the local moments of the central Rh 5*s* and 5*p* align in an opposite direction to those of the central Rh 4*d* and

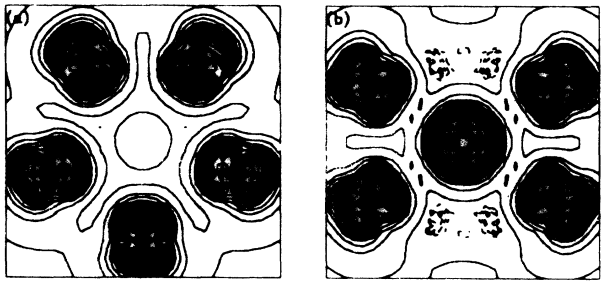

FIG. 3. Spin-density distribution of the I_h Rh_{13} cluster with r=4.84 a.u. (a) is plotted in the plane passing through the five surface atoms, (b) in the plane passing through the central and four surface atoms. Positive, zero, and negative values of the spin density are indicated by full, dotted, and dashed lines, respectively.

surface atoms. To substantiate our magnetic-interaction picture, we have prepared the spin-density distribution plots on two typical planes of the icosahedron (Fig. 3). In Fig. 3, a small amount of the negative polarization is apparent.

Figures 4(a) and 4(b) show the densities of states (DOS) for the majority- and minority-spin electrons in the I_h cluster with r=4.84 a.u. The DOS were obtained by a Lorentzian extension of the discrete energy levels and a summation over them. The broadening width parameter was chosen to be 0.4 eV. From Fig. 4, we can see that the central atom contributes mainly the DOS in the bottom region of the valence band, and the DOS around E_F are contributed mostly by the surface atoms. The total DOS in the valence-band region are dominantly of 4d character, but the compositions of 5s and 5p can be easily seen from the figures. E_F, which is −4.3 eV, is found to lie just at the peak of the minority-spin DOS. The valence band width is obtained to be 5.6 eV, 1.1 eV larger than that of Reddy *et al.*,[13] showing again the effect of enlarging the basis set. The exchange splitting is estimated to be 0.7 eV, compared to 0.9 eV of Reddy *et al.*

In conclusion, we have presented the electronic structure of 13-atom Rh clusters with three possible high-symmetry geometries. An anomalous symmetry dependence of the cluster magnetism is found: the total magnetic moment of the icosahedral Rh_{13} cluster is smaller than that of the other two lower-symmetry clusters in a wide range of interatomic spacings. An energy difference is identified to explain this anomalous relationship, which is found to be also useful for judging whether the broadening technique is correctly used and whether multiple input potentials must be used to reach the actual ground state in the LSD calculations. The calculated results are compared and discussed with those of previous theory and a recent experiment. The actual geometry of the Rh_{13} cluster is suggested to be a distorted icosahedron.

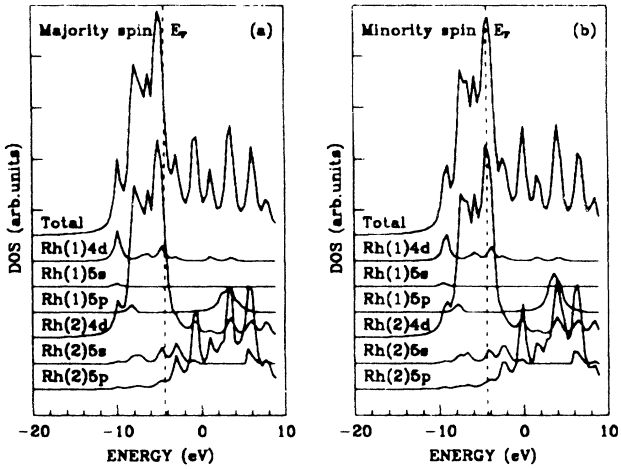

FIG. 4. DOS for the I_h Rh_{13} cluster with r=4.84 a.u.: (a) majority spin and (b) minority spin. Rh(1) and Rh(2) denote the central and surface atoms, respectively.

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