Anomalous magnetic properties of Rh\textsubscript{13} clusters

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Abstract

Electronic structures of 13-atom Rh clusters with three possible high-symmetry geometries are studied using the discrete-variational local-spin-density-functional method. The ground state is found to be the icosahedral structure, and a total magnetic moment of 15\(\mu_B\) is obtained for the cluster. This value is anomalously smaller than those for clusters with lower symmetries, but in agreement with recent experiments. The magnetic interactions between the central and surface atoms of the cluster are not fully ferromagnetic, and a small amount of antiferromagnetic interactions is found to be mixed in. An energy parameter is introduced to explain the anomalous magnetic properties, which is found to be also useful for judging whether some techniques can or must be used in the local-spin-density-functional calculations.
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.\cite{1,2} As it is well-known, all 3$d$, 4$d$ and 5$d$ TM atoms have a finite magnetic moment due to the Hund’s-rule coupling in their unfilled $d$ shells, and only 3$d$ 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 new state of materials, may have magnetic properties different from their bulk phase and atoms. For free Fe, Co and Ni clusters, theoretical calculations\cite{3–5} and experimental measurements\cite{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 a little about their magnetic properties. Sometimes the conclusions from experiments contradict predictions from theories. Theoretical calculations\cite{9,10} usually predict large moments for small clusters, while experimental measurements\cite{11} give nonmagnetic results in the experimental resolution limits. Whether these clusters can be magnetic was a question until recently, when Cox et al.\cite{12} observed experimentally that clusters of 4$d$ nonmagnetic solid Rh exhibit a permanent magnetic moment. This moment can be as large as $1.1\mu_B$/atom. This experiment confirmed the theoretical prediction by Reddy et al.\cite{13} that 13-atom clusters of 4$d$ 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.\cite{14} The total moment of Rh$_{13}$ was measured to be $11.5\mu_B$, just above half the $21\mu_B$ predicted by theory. Moreover, theory gives a full ferromagnetic (FM)-interaction picture for the cluster, while experiment suggests a more complicated picture in which not all spins are parallel.

Motivated by the discrepancy mentioned above, we have performed a first-principles study on the electronic structures of Rh$_{13}$ clusters with three possible high-symmetry geometries. Our results have removed the discrepancy between experiment and theory, and are in agreement with the experimental measurement. Furthermore, we found 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 lower-symmetry...
clusters in a wide range of interatomic spacings. This is particularly remarkable because it is always 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 parameter 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.

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 $\rho(r)$ 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 $\rho(r)$ 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 two important respects: (a) we expanded the basis set to include Rh 5$p$ orbital and roughly optimized the Rh 4$d^{8+x}5s^{1-(x+y)}5p^y$ ($0 < x < 1$ and $0 < x + y < 1$) 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, and (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.

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 on 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 bondlength 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 bondlengths in the two calculations are almost 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.

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 sees 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 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 rapidly its moment 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 parameter $\Delta E$.

For a cluster whose highest occupied molecular orbital (HOMO) is partially occupied, $\Delta E$ 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 $\Delta E$ is either the energy difference between the HOMO and its unoccupied CSMO or between the lowest unoccupied molecular orbital (LUMO) and its occupied CSMO, depending on which one is the smaller. 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 $\Delta E$ is small, and this will result in the change of the cluster magnetic moment. The $I_h$ cluster is a case. We found that $\Delta E$ 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 $\Delta E$ 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 in good agreement with the experimental one ($0.88\pm0.16\mu_B$). Compared to our total moment
of 15µB, Reddy et al. [13] obtained a larger moment of 21µB. 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 Ih cluster ΔE is also about 0.05 eV. Since the broadening parameter is of the same order of magnitude of 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.

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, we found two self-consistent solutions for the Ih cluster with r=4.84 a.u.: the total moment of the first is 15µB while in the second it is 21µB. The two solutions correspond to two local minima of the cluster energy as a function of the cluster moment. The cluster binding energy of the former was calculated to be larger than that of the latter by 0.35 eV. So, the solution we discussed above is the global minimum while the solution obtained by Reddy et al. is only a local minimum.

When should one look for multiple solutions in a LSD calculation? Again, we link the answer to our energy parameter 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.

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, in agreement with the experimental suggestion. [12] The magnetic interactions between the central and surface atoms are mainly FM, but a small amount of
antiferromagnetic (AFM) interactions is found to be mixed in: the local moments of the central Rh 5s and 5p align in an opposite direction to those of the central Rh 4d and surface atoms. Such a small amount of AFM interactions can not be neglected because it may affect the temperature and external magnetic field dependences of the magnetic properties of the cluster. 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 polarizations 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, and discussed their anomalous magnetic properties. The ground state is found to exhibit the icosahedral structure, and has total magnetic moment of 15\( \mu \)B. This value is anomalously smaller than those for clusters with lower symmetries, but in agreement with recent experiments. The magnetic interactions between the central and surface atoms of the cluster are not fully FM, and a small amount of AFM interactions is found to be mixed in. The anomalous magnetic properties are explained in terms of an energy parameter, 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.
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FIGURES

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.

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).

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.

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.
TABLES

TABLE I. The equilibrium bondlengths and binding energies for Rh$_{13}$ clusters ($r$: the distance between the center and surface atoms).

| Symmetry | $r$ (a.u.) | $E_b$ (eV) |
|----------|-----------|-----------|
|          | Our work  | Reddy et al. [13] | Our work  | Reddy et al. [13] |
| $I_h$    | 4.84      | 4.84      | 51.16     | 42.6       |
| $O_h$    | 4.95      | 4.90      | 49.81     | 41.3       |
| $D_{3h}$ | 4.96      |           | 50.71     |            |

TABLE II. The local and total magnetic moments ($\mu_B$) of Rh$_{13}$ clusters at the equilibrium configurations.

| Symmetry | Orbital | Local moment | Total |
|----------|---------|--------------|-------|
|          | Center atom | surface atom | moment |
| $I_h$    | $4d$  | 1.323        | 0.993 | 15   |
|          | 5$s$  | -0.004       | 0.095 |      |
|          | 5$p$  | -0.195       | 0.068 |      |
|          | total | 1.123        | 1.156 |      |
| $O_h$    | $4d$  | 1.284        | 1.313 | 19   |
|          | 5$s$  | -0.015       | 0.105 |      |
|          | 5$p$  | -0.230       | 0.079 |      |
|          | total | 1.038        | 1.497 |      |
| $D_{3h}$ | $4d$  | 1.283        | 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|