Possibility of many magnetic states in cluster systems: V and Cr clusters

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The possibilty of more than one magnetic state in cluster systems has been explored using the local spin density linear combination of Gaussian orbitals method. Fixed moment calculations were done and their converged states were used to determine input potentials to find as many stable states as possible for the V and Cr clusters having body-centered-cubic (bcc) symmetry. Several calculations were made at different atomic spacings for V_9 and Cr_9 clusters. It was found that for some atomic spacings, as many as four or five magnetic states exist for a cluster. In addition to the states reported previously with small average magnetic moments of $0.33\mu_B$ and $0.67\mu_B$ per atom, states with moments as large as $2.78\mu_B$ and $3.78\mu_B$ per atom are also found to be possible for V_9 and Cr_9 clusters, respectively, as well as intermediate-moment states in some cases. The Cr_{15} cluster is found to have a state with $0.80\mu_B$ per atom in addition to the $0.40\mu_B$ state reported previously. The local moments for the $0.80\mu_B$ state in Cr_{15} clusters are found to be very close to that which has been reported by other groups.

I. INTRODUCTION

Usually only one self-consistent-field solution of the Kohn-Sham equations for a system is obtained and this solution is independent of the choice of input potential used to start the calculation. But in the case of magnetic solid $3d$ transition metals, it has been found that more than one magnetic state is possible for a certain range of lattice spacings.[1,2] Although the solid $3d$ transition elements have only one magnetic state for very small and very large volumes, it was shown that, in some cases, there could be as many as three magnetic states which were classified as nonmagnetic, low-spin, and high-spin states in a limited range of atomic volumes.[1] Four different shapes of magnetic transitions were found for $3d$ elemental solids.[2]

A variety of possible magnetic states is also a possibility for free cluster sytems and because the cluster atoms could assume any magnetic arrangement relative to their neighboring atoms, there is a possiblity that cluster systems could have even richer magnetic properties. But the existence of many magnetic states has not been reported yet within our knowledge.

In an actual cluster, the possible magnetic states could be classified according to the eigenvalues of square of the total spin operator $\mathbf{S}$, which might assume large values, particularly in the limit of large atomic spacings. Some of these might have competing energies in a range of atomic spacings, and the spin of the ground state could also vary with atomic spacing.[3] Unfortunately the S^2 operator is not easily introduced into present day local spin density functional theory; instead one has only S_z. The characteristics of the results obtained from density functional theory calculations for clusters or solids may be classified into three different categories depending on the atomic spacing of a system. At small spacing, the cluster should be nonmagnetic, because large overlap of atomic wave functions causes large broadening of energy levels which in turn makes it costly for any level to be singly occupied. At large spacing, the individual atoms have to be magnetic, having local moments close to atomic moments. These moments can couple in various ways (such as ferromagnetic or antiferromagnetic), but the energy difference between different ordering arrangements should be small because the atomic spins are weakly coupled at large distances. At intermediate distances, there is a complicated transition region where the moments couple in many different ways with possibly large energy differences between them. If more than one solution is obtained due to such reasons, all but one of the solutions will be metastable for a given spacing, i.e., they can correspond only to local minima of a complicated function of total energy $E(a, \mu_s)$, where a is the atomic spacing and μ_s is the moment of a given shell of atoms.

We have recently reported the results of our calculations for some V and Cr clusters which show very good agreement of the magnetic moment with the experimentally observed small magnetic moments of these clusters.[4] Our calculated magnetic moments were small enough to explain the experimental results while the previously calculated moments of others were too large.[5–7] We have repeated the calculations of V and Cr cluster properties with varying starting potentials and have found that clusters could have many different magnetic moments, like the solid. Low- and high-spin states coexisted for a wide range of atomic spacings, and in some cases as many as four or five magnetic states were found to exist.

Calculations leading to a self-consistent solution start using an initial potential which is usually the superposition of atomic potentials. However, in the case of V or Cr, the individual atoms have large magnetic moments in accordance with the Hund rule but their moments are

substantially suppressed in the bulk phase. Therefore, a choice of starting potential becomes a bit ambiguous for such elements. A cluster system is expected to have properties which are intermediate between an atom and a solid. In the previous calculation, we have chosen an almost paramagnetic potential, with a very small initial spin polarization as the starting potential and allowed the system to develop its own magnetic moment as the iterative calculations converge to a self-consistent solution. Through this procedure, we could obtain cluster magnetic moments which are in good agreement with the experiment.[4,5]

But, as has been mentioned, there is a possibility that a cluster system may have more than one magnetic state for a certain range of atomic spacings. We have tried a very large moment input potential to check the consistency of calculation and in some cases the converged state was found to be a very different state from what we obtained in previous calculations. With a larger moment input potential, the system was generally found to converge to a larger magnetic moment state rather than converging to the small moment state reported earlier.[4] Such a large moment was comparable in magnitude to the moments reported by other authors which were obtained using different methods from ours.[6,7]

But how many magnetic states are possible for a cluster with a fixed atomic spacing? To search for as many states as possible, we have carried out fixed moment self-consistent calculations. The fixed moment procedure was introduced by Moruzzi *et al.* in their study of magnetic properties of solid $3d$ transition metals.[1] In this procedure the system is forced to have a fixed magnetic moment, defying the ordinary Fermi occupation rule. This results in different Fermi levels for the majority and minority spin electrons, and the system could converge into a solution with very unnatural occupancy of single particle levels. With such forced artificial occupancy calculations, different possible stable solutions of a system could be identified from the minima of the fixed moment total energy curves.[1]

We have performed similar fixed moment calculations for V and Cr clusters and tried to find all possible magnetic states from the fixed moment total energy curves. We found that our calculated results are helpful in determining the possible magnetic states of the cluster system, but our results were found to be not very reliable in determining which states are the possible stable solutions. We found that the local minimum points in the curves were not always related to stable solutions although generally this was the case. For this reason, we have repeated relaxation calculations to determine what are the stable states without the fixed moment constraint, using the results of these fixed moment solutions to define the starting potential. Through this procedure we found that for some lattice spacings, there are as many as four or five stable magnetic states. These states are stable in the sense that if the spin densities are changed slightly, the iterative solution process will return to the same spin density (somewhat analogous to a fixed point in renormalization group theory). However, these solutions have different total energies, so all but one should be considered to be metastable. We have made calculations for V_9 and Cr_9 clusters for a wide range of atomic spacings around that characteristic of the bulk lattice. For the larger V_{15} and Cr_{15} clusters, we have considered only the lattice spacing of the solid at 0 K.

II. RESULT AND DISCUSSION

A. V clusters

We have performed calculations for six different lattice spacings ranging from 4.57 a.u to 6.85 a.u. for V_9 clusters having bcc symmetry. The 0 K bulk lattice spacing of V is 5.54 a.u. The calculational procedure was described in detail in a previous paper and will not be discussed again here.[8] The Gaussian orbital basis set and the local density functional parameters for the exchange correlation potential used in this calculation are the same as those used in our previous calculations.[4] The number of grid points used in this calculation was slightly smaller than the previously used number of points to handle large numbers of calculations.[9]

Fixed moments of about $0.8\mu_B$ intervals were chosen from around $0.0\mu_B$ to $5.0\mu_B$ initially to obtain fixed moment converged solutions. This range covers all the possible magnetic moments for $3d$ transition element atoms. After the fixed moment solutions were obtained, relaxation calculations have been repeated to determine the stable states which are obtained without the fixed moment constraint. If the fixed moment solution has a natural occupation of single particle levels in accordance with Fermi statistics, the solution remains unchanged after the relaxation. But if the solution has unnatural forced occupancy, it may relax into a state with a different moment. When the cluster moments of the relaxed stable solutions were different from each other for neighboring fixed moment solutions, intermediate fixed moments were tried again to determine whether any other possible moments are possible. Therefore the number of fixed moment calculations performed was at least five and more than ten in some cases for a single atomic spacing.

The variation of the calculated total energy for some fixed moments is plotted in Fig. 1 for four different lattice

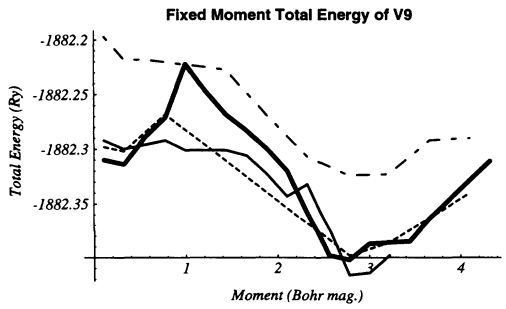

FIG. 1. Fixed moment total energy curves for the V_9 cluster. The thin line curve is for $a = 5.14$ a.u., the thick line curve is for $a = 5.71$ a.u., the dotted curve is for $a = 6.28$ a.u., and the dash-dotted curve is for $a = 6.85$ a.u.

spacing cases. The lines were drawn between data points to identify data points belonging to the same lattice spacing cluster. Converged solutions were hard to obtain in certain cases. Calculations were performed only at given moment intervals and no attempt was made to find the exact location of the minimum energy point. There is a small difference in the magnitude of total energy from the values reported in the previous paper because we used a smaller number of grid points near the nuclear sites to evaluate the matrix elements of the exchange correlation potential in the present calculation. Such reduction in grid points was found to lower the total energy by about 0.1 Ry consistently but did not affect any essential features of the calculated result.

As could be seen from Fig. 1, the fixed moment total energy curves we obtained for cluster systems were found to be less systematic in shape than those obtained for bulk systems.[1] For the bulk the curves showed very systematic variation for different lattice spacings, but they are intermixed for our cluster system. The two typical moments obtained in our calculation for the V_9 cluster were $0.33\mu_B$ and $2.78\mu_B$. One can see that the two typical stable solutions of $0.33\mu_B$ and $2.78\mu_B$ cluster moments are generally represented by the shallow and deep minimum features around the $0.33\mu_B$ and $2.78\mu_B$ regions in the curves, respectively. The shallow minimum at the $0.33\mu_B$ region disappears as the lattice spacing reaches 6.85 a.u. and only the $2.78\mu_B$ minimum point remains in the curve. We also find that, at the lattice spacing of $a =$ 5.14 a.u., the total energy curve has a very complicated shape which seems to allow many metastable solutions. But we found that the local minimum point in the graph does not always remain a stable converged state when the fixed moment constraint was removed in the calculation. We found that many states which might look like metastable states had very unnatural occupancy of energy levels. As a result, as soon as the sytem was allowed to relax by removing the fixed moment constraint, it converged to a different state which has a natural occupancy in levels with possibly a higher energy. Such behavior was more pronounced at the smallest lattice spacing of 4.57 a.u. There were wild variations in the curve shape which implies many metastable states, although there was just one stable solution. Some symptoms of such wild variations are already visible in the $a = 5.14$ a.u. curve.

We believe such behavior has occurred due to inaccuracy of our total energy calculation. For example, the variational charge fitting method adopted in our calculation uses a set of auxiliary fitting basis functions and the quality of fitting may not be consistent for different magnetic state charge configurations.[8] In a cluster system, the energy levels are discrete in contrast to band levels of the bulk, and a slight change in the occupation of levels could result in a big difference in the charge and spin density distributions. Therefore, if these distributions are not fitted with very good accuracy, inaccuracy of the total energy contribution coming from the Coulomb energy part could be large enough to forbid exact analysis based on the total energy. There is also a possibility that the fixed moment states we obtained belong to different values of the square of the total spin. The total spin of a cluster cannot be determined from present local density functional theory. If there is a big difference in total energy for different values of the total spin, as has been found to be the case for the Fe_2 molecule,[3] there could be unexpected variations in total energy.

Also, because the magnetic transitional region in the cluster system is very wide compared to the bulk case, the adequacy of a single basis set used to expand the wave function may not be consistent for all cases. In the bulk solids studied in Ref. 1, the magnetic transition region was small and located at larger volume relative to equilibrium.[1] But in our cluster, the transition domain is much wider than in the bulk and ranges from below to above the spacing characteristic of bulk equilibrium.

Because the minimum points in the fixed moment total energy curve did not necessarily remain as self-consistent solutions in relaxed conditions in our calculation, we carried out relaxation process calculations again after the fixed moment solution was obtained. From such calculations, we could obtain as many as four fully self-consistent solutions at the lattice spacing of $a = 5.71$ a.u., which is the room temperature bulk lattice spacing, although there were just one or two solutions in all other cases. The total energies, total and local magnetic moments, and the contact spin densities (the spin density at the nucleus site) of the V_9 cluster are summarized in Table I. The local magnetic moment listed in the table was obtained by integrating the local moments within each Wigner-Seitz like cell around the atomic site.[10] The cell shape was revised to have a better spherical shape compared to the crude cubic shape used in our previous calculation. Such elaboration resulted in the reduction of interstitial moment but produced little change in the local moment.

TABLE I. Possible magnetic moments and the total energy of the V_9 cluster. a is the lattice spacing parameter. μ indicates the average magnetic moment per atom in μ_B units. μ_1, μ_2, and $\mu_{\rm int}$ indicate the local moments for center, first shell atom, and the interstitial moments, respectively. SD1 and SD2 are the contact spin densities at the center and first shell atom nucleus positions, respectively. The total energy per atom of the cluster is also shown (in Ry).

a	μ	$E_{\rm total}$	μ_1	μ_2	$\mu_{\rm int}$	SD1	SD2
4.57	0.33	-1882.262	-0.02	0.23	1.15	-0.04	-0.07
5.14	0.33	-1882.300	-0.08	0.28	0.81	-0.05	-0.09
5.14	2.78	-1882.416	-0.42	2.41	5.62	-0.47	-0.04
5.54	0.33	-1882.313	-0.17	0.32	0.54	-0.05	-0.10
5.54	2.78	-1882.406	-0.68	2.60	4.33	-0.46	-0.10
5.71	0.33	-1882.314	-0.15	0.29	0.50	-0.04	-0.08
5.71	1.00	-1882.222	-0.65	1.13	0.43	-0.22	-0.32
5.71	1.44	-1882.268	-0.68	1.61	0.54	-0.28	-0.47
5.71	2.78	-1882.402	-0.86	2.69	3.81	-0.45	-0.11
6.28	0.33	-1882.302	-0.81	0.45	0.16	-0.05	-0.11
6.28	2.78	-1882.398	-1.71	2.93	2.78	-0.49	0.18
6.85	2.78	-1882.324	-2.57	3.17	1.70	-0.57	0.27
6.85	3.22	-1882.323	2.21	3.11	1.35	-0.68	-0.05
Ref. 6	2.89		-1.38	3.42			
Expt.[a]	< 0.59						

[a]Reference 5.

The possible magnetic moments for each lattice spacing are shown graphically in Fig. 2. As can be seen in the figure, at $a = 4.57$ a.u., only the $0.33\mu_B$ state is possible and, at $a = 6.85$ a.u., the $2.78\mu_B$ and $3.22\mu_B$ states are the only possible solutions. Because the $3.22\mu_B$ state has almost the same total energy as the $2.78\mu_B$ state, some calculations converged to the $3.22\mu_B$ state rather than to the $2.78\mu_B$ state at $a = 6.85$ a.u. At the lattice spacings between these, two cluster moments of $0.33\mu_B$ and $2.78\mu_B$ were possible, although at $a = 5.71$ a.u. even $1.00\mu_B$ and $1.44\mu_B$ states were also found to be possible. From Table I, it can be seen that the high-spin state of $2.78\mu_B$ has lower energy than the low-spin state of $0.33\mu_B$ in all cases. Therefore the high-spin state is found to be the ground state and the low-spin state is the metastable state if our total energy is considered to be accurate. The cluster magnetic moment obtained by the discrete variational method was $2.89\mu_B$,[6] and the experimentally determined upper limit of this cluster's magnetic moment was $0.59\mu_B$.[5] As can be seen in Fig. 2, the coexistence region of high- and low-spin states is very wide in our cluster system compared to the bulk system. In our cluster, the range of such a magnetic transition region seems to be extended to at least 20% around the bulk lattice spacing.

The fixed moment total energy calculations were done for the V_{15} cluster also but only at a single lattice spacing of $a = 5.54$ a.u., which is the 0 K bulk lattice spacing. The self-consistent solutions were obtained at five fixed moment positions and were allowed to relax after convergence was reached as was done for the V_9 cluster. In all cases, the final stable state after the relaxation was the same $0.07\mu_B$ state which was reported in the previous paper.[4] The result of converged fixed moment calculations as well as the characteristics of the only stable state with an average moment of $0.07\mu_B$ are summarized in Table II. The results of other calculations are also included in the table for comparison.[6,11] The local moments presented here are improved numbers compared to the previously reported moments, since more spherically shaped volumes were used for integrating the spin density. We find that, at least at $a = 5.54$ a.u., the V_{15} cluster has only one possible magnetic moment. Considering that the V_9 cluster at this lattice spacing had two possible magnetic states, this may indicate that as the system grows larger the magnetic properties become simpler.

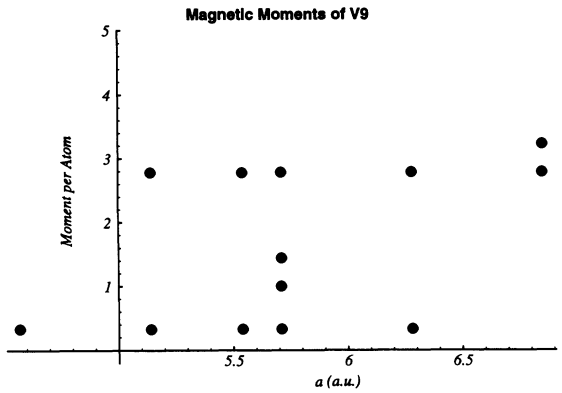

FIG. 2. Possible magnetic moments of the V_9 cluster depending on its lattice spacing parameters.

B. Cr clusters

We have performed calculations for six different lattice spacings ranging from 3.82 a.u. to 6.00 a.u. for Cr_9 clusters having bcc symmetry. The 0 K bulk lattice spacing of Cr is 5.30 a.u. The variation of the calculated total energy with the fixed moment is plotted in Fig. 3 for five different lattice spacings. The lines were drawn to connect data points belonging to the same lattice spacing cluster. As was the case for V, converged solutions were hard to obtain in certain cases also for this cluster. The fixed moment total energy curves we obtained for this cluster are also found to be less systematic in shape than those observed for bulk Cr.[1] The two typical moments obtained for the Cr_9 cluster were $0.67\mu_B$ and $3.78\mu_B$, although a $1.33\mu_B$ state has also been found at times. One can see that the large moment solution of $3.78\mu_B$ generally appears as the minimum above $3\mu_B$ in

TABLE II. Fixed magnetic moments and total energy of the V_{15} cluster. All states converged to the $0.07\mu_B$ state after relaxation. μ indicates the average magnetic moment per atom in μ_B units. μ_1, μ_2, μ_3, and μ_{int} indicate the local moments for center, first, second shell atom, and the interstitial moments, respectively. SD1, SD2, and SD3 are the contact spin densities at the center, first, and second shell atom nucleus positions, respectively. The total energy per atom of the cluster is also shown (in Ry).

μ	E_{total}	μ_1	μ_2	μ_3	μ_{int}	SD1	SD2	SD3
0.07 [a]		-0.02	+0.02	-0.03				
0.07 [b]		+0.1	-0.0	+0.2				
0.07	-1882.275	0.12	0.01	0.11	0.15	-0.02	-0.01	-0.01
0.87	-1882.264	0.07	0.47	1.00	2.92			
1.80	-1882.235	-0.31	1.02	2.15	5.72			
2.73	-1882.235	0.36	2.04	2.58	8.07			
3.67	-1882.312	0.17	2.95	3.13	1.54			
4.60	-1882.217	3.60	3.48	3.51	5.47			

[a]Reference 6.
[b]Reference 11.

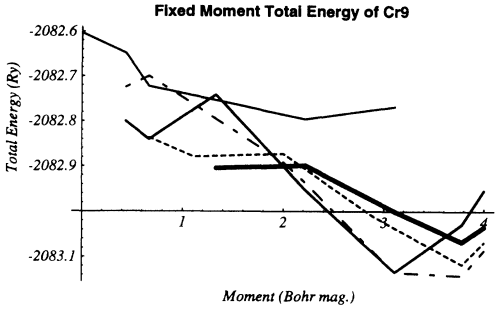

FIG. 3. Fixed moment total energy curves for the Cr_9 cluster. The thin line (upper) curve is for a = 3.82 a.u., the medium thick line (next lower) curve is for a = 4.36 a.u., the dash-dotted curve is for a = 4.90 a.u., the dotted curve is for a = 5.45 a.u., and the thick line curve is for a = 6.00 a.u.

the curves pertaining to clusters of large lattice spacing. The smaller moment solutions of $0.67\mu_B$ and $1.33\mu_B$ cannot be identified from the curve at all.

Because it was impossible to determine the stable converged states from the fixed moment total energy curve, we carried out relaxation process calculations again after the fixed moment solution was obtained, as was done for V_9 clusters. From such calculations, we could obtain as many as five fully self-consistent solutions at the lattice spacing of a = 4.90 a.u. This spacing is about 10% smaller than that of the room temperature bulk lattice, but at all other lattice spacings the number of solutions was just one or two. The total energies, total and local magnetic moments, and the contact spin densities of the Cr_9 cluster are summarized in Table III.

The possible magnetic moments for each lattice spacing cluster are again shown as a graph in Fig. 4. As can be seen in the Figure, even at the very small spacing of 3.82 a.u., the system has a small moment solution of $0.67\mu_B$ as well as the expected nonmagnetic solution. At a = 6.00 a.u., which is just about 10% larger than the room temperature lattice spacing, the $3.78\mu_B$ state is already the only possible solution. At a = 4.36 a.u., $0.67\mu_B$ as well as $1.33\mu_B$ are the possible moments, and at a = 5.30 a.u. and 5.45 a.u., which correspond to the 0 K and room temperature lattice spacing, respectively, the possible moments are $0.67\mu_B$ and $3.78\mu_B$. But at the lattice spacing of a = 4.90 a.u., $2.00\mu_B$ and $3.11\mu_B$ states are also found to be possible as well as the $0.67\mu_B$, $1.33\mu_B$, and $3.78\mu_B$ states. As in the case of the V_9 cluster, high-spin states have lower total energy than the low-spin states in general. The moment obtained from a parametrized Hamiltonian model of Pastor *et al.* was $3.89\mu_B$,[7] and the experimentally determined upper limit of this cluster's moment was $0.77\mu_B$.[5] The coexistence region of high- and low-spin states is also very wide in the cluster system compared to the bulk system.[1] For this cluster, the range of such a magnetic transition region is extended to as much as 30% below the bulk lattice spacing.

The fixed moment total energy calculations were done also for Cr_{15} clusters but at a single lattice spacing of a = 5.30 a.u. only, which is the 0 K bulk lattice spacing. The self-consistent solutions were obtained at five fixed moments of about $0.8\mu_B$ intervals from around $0.0\mu_B$ to $5.0\mu_B$ and were allowed to relax after convergence was reached. The result of fixed moment calculations as well as the self-consistent solutions after relaxation are summarized in Table IV. The results of other calculations are also included in the table for comparison. We have reported the magnetic moment per atom of $0.40\mu_B$ in our previous calculation, but the final converged state after the relaxation was found to be either $0.40\mu_B$ or $0.80\mu_B$ per atom in the present calculation. We have found that many fixed moment states have a tendency to relax to

TABLE III. Possible magnetic moments and the total energy of the Cr_9 cluster. a is the lattice spacing parameter. μ indicates the average magnetic moment per atom in μ_B units. μ_1, μ_2, and μ_{int} indicate the local moments for center, first shell atom, and the interstitial moments, respectively. SD1 and SD2 are the contact spin densities at the center and first shell atom nucleus positions, respectively. The total energy per atom of the cluster is also shown (in Ry).

a	μ	E_{total}	μ_1	μ_2	μ_{int}	SD1	SD2
3.82	0.00	-2082.603	0.00	0.00	0.00	0.00	0.00
3.82	0.67	-2082.723	-0.03	0.46	2.22	-0.21	0.12
4.36	0.67	-2082.841	-0.15	0.56	1.50	-0.19	-0.04
4.36	1.33	-2082.742	-0.22	1.10	3.17	-0.26	-0.11
4.90	0.67	-2082.700	-0.37	0.76	0.13	-0.14	-0.19
4.90	1.33	-2082.795	-0.57	1.28	2.04	-0.24	-0.19
4.90	2.00	-2082.892	-0.79	1.89	3.26	-0.39	-0.22
4.90	3.11	-2083.135	-0.70	2.85	5.30	-0.61	0.01
4.90	3.78	-2083.142	-0.95	3.53	6.07	-0.69	-0.10
5.30	0.67	-2082.819	-0.54	0.77	0.26	-0.13	-0.15
5.30	3.78	-2083.129	-1.50	3.77	4.64	-0.64	-0.13
5.45	0.67	-2082.837	-0.71	0.80	0.21	-0.13	-0.15
5.45	3.78	-2083.117	-1.76	3.86	4.16	-0.62	-0.12
6.00	3.78	-2083.065	-2.72	4.16	2.73	-0.59	-0.02
Ref. 7	3.89		-1.38	3.42			
Expt.[a]	< 0.77						

[a]Reference 5.

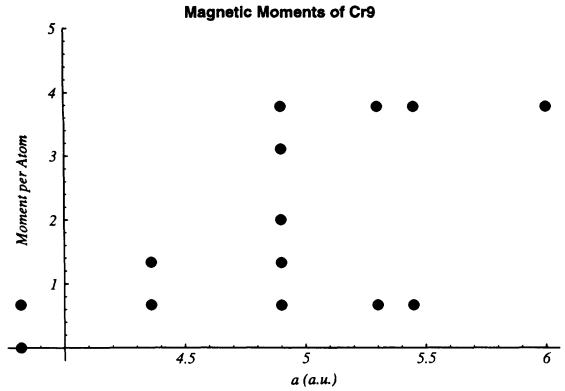

FIG. 4. Possible magnetic moments of the Cr_9 cluster depending on its lattice spacing parameters.

the $0.80\mu_B$ state but complete convergence was hard to reach. However the finally converged $0.80\mu_B$ per atom state was found to have a very high total energy of about 5 Ry, higher than an ordinary state. Such a large difference from the ordinary total energy values has not been observed in other cases.

Salahub and Messmer have obtained $0.8\mu_B$ per atom for the Cr_{15} cluster from their multiple scattering $X\alpha$ calculations (MS-$X\alpha$).[11] This moment is identical to our high moment result. We have also found that the calculated local moments of $-0.98\mu_B$, $2.72\mu_B$, and $-2.04\mu_B$ for the center, first, and second shell atoms respectively of our $0.80\mu_B$ state are reasonably close to their values of $-0.7\mu_B$, $4.1\mu_B$, and $-3.4\mu_B$. The local moments obtained by Pastor *et al.* using their empirical Hamiltonian were $-1.76\mu_B$, $+2.90\mu_B$, and $-2.74\mu_B$ which are also fairly close, although their magnetic moment per atom was only $0.33\mu_B$.[7] Such combinations of local moments indeed seem to be related to the antiferromagnetic nature of the bulk Cr. But, as has been argued in our previous paper,[4] one has to be very careful in regard to such an interpretation because the center atom in the transition metal cluster has often been found to have a negative moment. For example, the $0.40\mu_B$ per atom state has the local moments of $-0.15\mu_B$, $0.23\mu_B$, and $0.43\mu_B$ for the center, first, and second shell atoms respectively. It does not show symptoms of antiferromagnetism but the center atom has negative polarization.

What happens to the similarity of the density of states (DOS) between clusters and bulk if there are two possible cluster states? We have shown that there is a good similarity between the DOS of the $0.40\mu_B$ per atom cluster state and the bulk DOS in our previous calculation.[4] We have generated the DOS of the $0.80\mu_B$ per atom state using the same Gaussian broadening scheme described previously and compared it with the bulk and $0.40\mu_B$ state DOS's. In Fig. 5, the thick line, dotted, and thin line curves are for the bulk,[12] $0.80\mu_B$ state, and $0.40\mu_B$ state DOS respectively. As can be seen in the figure, the $0.80\mu_B$ state DOS matches with the bulk DOS very well also. Above the Fermi level region, our previous $0.40\mu_B$ state DOS did not match the bulk DOS well enough because the cluster levels were still thought to be in the process of developing broader bandwidths, i.e., a 15 atom cluster is not large enough to describe the extended nature of the orbitals for early $3d$ transition elements. But, defying such an argument, the $0.80\mu_B$ state DOS seems to have a comparable bandwidth with that of the bulk. The gross features of the $0.80\mu_B$ state DOS match very well the bulk DOS except that the DOS of the $0.80\mu_B$ state does not show a double peak structure just below the Fermi level as the $0.40\mu_B$ state does. But it seems clear that there exists a very good similarity between the bulk and cluster DOS's independent of the cluster states.

TABLE IV. Fixed magnetic moments and total energy of the Cr_{15} cluster. All states converged to either the 0.40 μ_B or the 0.80 μ_B state after relaxation. μ indicates the average magnetic moment per atom in μ_B units. μ_1, μ_2, μ_3, and μ_{int} indicate the local moments for center, first, second shell atom, and the interstitial moments, respectively. SD1, SD2, and SD3 are the contact spin densities at the center, first, and second shell atom nucleus positions, respectively. The total energy per atom of the cluster is also shown (in Ry).

μ	E_{total}	μ_1	μ_2	μ_3	μ_{int}	SD1	SD2	SD3
0.33[a]		-1.76	2.90	-2.74				
0.80[b]		-0.7	4.1	-3.4				
0.40	-2082.800	-0.15	0.23	0.43	1.67	-0.03	0.31	-0.08
0.80	-2078.182	-0.98	2.72	-2.04	3.32	0.26	0.44	0.09
1.87	-2082.867	-0.69	1.91	1.62	3.19			
2.80	-2082.873	-0.76	2.19	3.03	6.25			
3.73	-2082.847	2.09	2.88	3.44	9.24			

[a]Reference 7.
[b]Reference 11.

III. SUMMARY

We have done fixed moment calculations to find as many stable states as possible for V and Cr cluster systems. The fixed moment total energy curves were not very reliable in determining all possible stable states in the sense that they did not show a very systematic trend as has been the case in the bulk, and the local mini-

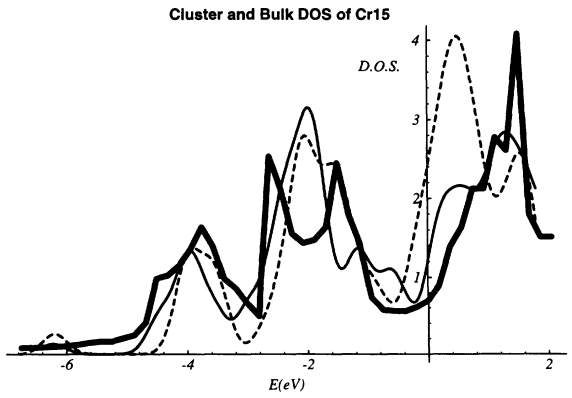

FIG. 5. Cluster and bulk DOS's of the Cr_{15} cluster. The thick line curve is a rough sketch of the bulk DOS, the dotted curve is for the $0.40\mu_B$ state, and the thin line curve is for the $0.80\mu_B$ state.

mum did not always correspond to a stable state in our case. To make sure of stability, relaxation calculations have been done for all fixed moment states and as many as four or five converged states were obtained in some cases. Because we have tried a limited number of fixed moment calculations, the possibility of even more stable states cannot be excluded. But for most cases there were just one or two possible states. The typical low- and high-spin moments were $0.33\mu_B$ and $2.78\mu_B$ for V clusters and $0.67\mu_B$ and $3.78\mu_B$ for Cr_9 clusters. The high-spin state has lower total energy than the low-spin state for most of the atomic spacings studied. The V_{15} cluster is found to have just one almost nonmagnetic $0.07\mu_B$ per atom state as has been found previously, but the Cr_{15} cluster is found to have a $0.80\mu_B$ state also in addition to the previously reported $0.40\mu_B$ state.

There are some factors in our calculational method which might not allow exact analysis based on the small variations in total energy. For example, the effectiveness of the fitting function may not be satisfactory enough to allow for exact analysis based on small variations in total energy. The total energy of the $0.80\mu_B$ state in Cr_{15} is exceedingly high compared to other ordinary solutions, as can be seen in Table II, and this may be due to unsatisfactory charge density fitting. For such reasons, it may not be proper to conclude definitely from our calculation which state is the ground state. But if our total energy is considered to be reliable, the high-spin states are the ground states for most cases studied and the small V_9 and Cr_9 clusters are expected to have large magnetic moments.

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