

First-Principles Study of the Magic Ar_6Fe^+ Cluster

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Complementary to the experimental studies on the magic Ar_6Fe^+ cluster [Bililign *et al.*, J. Chem. Phys. **108** (1998) 6312], the geometry, magnetic properties, dynamical stability, and magnetic stability are studied in detail by using *ab initio* molecular orbital calculations. The geometry expected by experimentalists is confirmed. When Ar_6 cluster is doped with Fe^+ , due to the charge transfer, the electronic shells in the Ar atoms are changed from closed to open, resulting in stronger interactions and producing a more compact structure. Because of orbital hybridizations, the Fe atom carries magnetic moment of only $3\mu_B$.

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1. Introduction

Clusters are finite aggregates of atoms or molecules that are bound by forces which may be metallic, covalent, ionic, hydrogen-bonded or Van der Waals in character and can contain from a few to tens of thousands of atoms (generally less than 10 nm). Clusters are usually detected experimentally via mass spectroscopy, where a common feature is the occurrence of a high abundance of clusters with a certain number of atoms, N , followed by a sharp dip in the intensity at $N + 1$. Such clusters of N atoms have been defined as magic. Among the magic clusters, the Ar cluster is a well-known example. Because of the localized character of the individual atomic orbitals, it can serve as a prototypes for a number of studies concerning structural, thermodynamic, and optical properties. In particular, the evolution of structure with respect to size is a very interesting topic, since it is well known that the Ar crystal possesses a face-centered-cubic (FCC) structure, while the clusters with sizes of less than 1000 atoms adopt an icosahedral structure. The icosahedral symmetry of Ar clusters has been verified experimentally by Farges *et al.* using electron diffraction methods.^{1,2)} It is clear that the high symmetry of icosahedral packing, in which the atoms arrange themselves in shell around a central atom, is reflected in the stability of the cluster. When the total number of atoms n is 13, 55, 147, . . . , shell-closing occurs, giving rise to very stable clusters with icosahedral geometry. Stable clusters are also observed for $n = 19, 23, 26, 29, 32, \dots$, where subshells are filled and the cluster geometry is characterized as poly-icosahedral.³⁾ The completion of shells and subshells takes place at a certain growth sequence, such that every additional atom occupies the position that offers the maximum number of neighbors or equivalently gives the maximum contribution to the total energy of the cluster. In recent years, with the advent of flexible and precise experimental techniques, well-controlled Ar clusters doped with metal atoms have become experimentally accessible, leading to the discovery that the Ar_6Fe^+ is magic,⁴⁾ which suggests that other new magic Ar clusters can be formed by doping with other metal atoms. Points of interest concerning this system include the geometry and stability of this cluster, how the doping changes the geometry and binding, how large the magnetic moment on

the Fe atom is, and how the charges are distributed among the atoms in this cluster. As far as we know, there is no paper published discussing these questions.

2. Theoretical Method

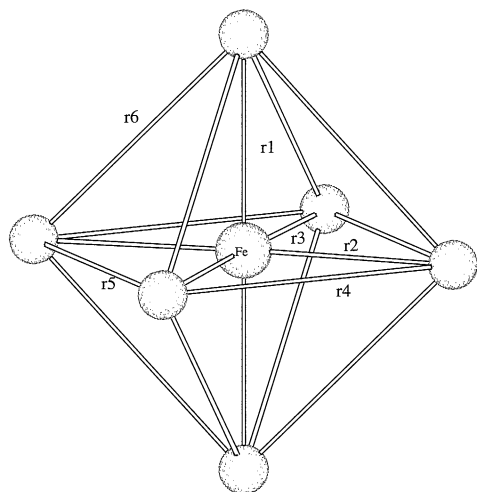
Ab initio methods based on density-functional theory (DFT) are well established tools to study structural properties of materials. We have used the molecular orbital theory in which the cluster wave function is represented by a linear combination of atomic orbitals centered at each atomic site. We used a series of basis sets to represent the atomic functions: Basis (1), the 6-311G basis set from Wachters and Hay^{5,6)} augmented with diffuse and polarization functions (6-311+G(d)) for both Fe and Ar; Basis (2), 6-311+G(d) for Fe and the LANL2DZ basis set,^{7,8)} incorporating effective core potentials, for Ar; Basis (3), 6-311+G(d) for Fe, and the SDD basis set,⁹⁾ also incorporating effective core potentials, for Ar; Basis (4), LANL2DZ for both Fe and Ar; and Basis (5), the DZVP polarized basis set^{10,11)} for both Fe and Ar. The B3LYP density functional,¹²⁾ which comprises Becke's hybrid exchange and Lee, Yang, and Parr's correlation,¹³⁾ was used. All calculations were performed with the Gaussian 98 package.¹⁴⁾ In our calculations, all the atomic positions of the cluster were relaxed without symmetry constraint, and the optimization was terminated when all the forces acting on the atoms were less than 0.00045 Hartree/Bohr. The energy convergence was 0.00003 eV. Due to the existence of the Fe ion in this cluster, the calculations were spin-polarized with 3 different spin multiplicities ($M = 2S + 1$) of 6, 4, and 2.

3. Results and Discussions

As for the geometry of Ar_6Fe^+ , an octahedron is expected by experimentalists,⁷⁾ which is used as the initial structure for the optimizations, as shown in Fig. 1. Tables 1 to 5 show the total energy, magnetic moment and charge on the Fe atom, as well as the spin gaps, which are defined as

$$\delta_1 = -(\epsilon_{\text{HOMO}}^+ - \epsilon_{\text{LUMO}}^-) \quad (1)$$

$$\delta_2 = -(\epsilon_{\text{HOMO}}^- - \epsilon_{\text{LUMO}}^+) \quad (2)$$

Fig. 1 Structure of Ar_6Fe^+ cluster.Table 1 Relative energy E (in eV), magnetic moment μ_{Fe} (in μ_{B}) and charge Q_{Fe} (in e) for the Fe atom as well as spin gaps δ_1 and δ_2 (in eV) obtained with Basis 1.

Quantity	$M = 6$	$M = 4$	$M = 2$
E	0.773	0.0	3.62
μ_{Fe}	4.8562	2.9338	0.9960
Q_{Fe}	0.5549	0.0198	0.0331
δ_1	1.3464	5.4590	2.0672
δ_2	9.7838	3.3728	0.6827

Table 2 Relative energy E (in eV), magnetic moment μ_{Fe} (in μ_{B}) and charge Q_{Fe} (in e) for the Fe atom as well as spin gaps δ_1 and δ_2 (in eV) obtained with Basis 2.

Quantity	$M = 6$	$M = 4$	$M = 2$
E	0.638	0.0	1.615
μ_{Fe}	4.9036	2.9786	0.9916
Q_{Fe}	0.5614	0.3677	0.2918
δ_1	1.3600	5.5297	3.9875
δ_2	8.4456	3.4381	2.9158

Table 3 Relative energy E (in eV), magnetic moment μ_{Fe} (in μ_{B}) and charge Q_{Fe} (in e) for the Fe atom as well as spin gaps δ_1 and δ_2 (in eV) obtained with Basis 3.

Quantity	$M = 6$	$M = 4$	$M = 2$
E	0.6990	0.0	1.5790
μ_{Fe}	4.9070	2.9793	0.9924
Q_{Fe}	0.5643	0.2805	0.1619
δ_1	1.3056	5.2714	4.0419
δ_2	8.4347	3.1606	2.9675

where + represents spin up and – spin down. The spin gap corresponds to the energy required to move an infinitesimal amount of charge from the HOMO of one spin to the LUMO of the other. Positive values for both spin gaps can guarantee that the system is stable magnetically and electronically.

Table 6 gives the geometry parameters obtained with the 5 different basis sets. The binding energies for the Fe ion in Ar_6 cluster are listed in Table 7.

Based on these data, the following conclusions can be ob-

Table 4 Relative energy E (in eV), magnetic moment μ_{Fe} (in μ_{B}) and charge Q_{Fe} (in e) for the Fe atom as well as spin gaps δ_1 and δ_2 (in eV) obtained with Basis 4.

Quantity	$M = 6$	$M = 4$	$M = 2$
E	1.405	0.0	1.895
μ_{Fe}	4.9092	2.9864	0.9922
Q_{Fe}	0.5688	0.385465	0.2953
δ_1	0.3890	5.3530	4.1480
δ_2	9.4901	3.3755	3.1144

Table 5 Relative energy E (in eV), magnetic moment μ_{Fe} (in μ_{B}) and charge Q_{Fe} (in e) for the Fe atom as well as spin gaps δ_1 and δ_2 (in eV) obtained with Basis 5.

Quantity	$M = 6$	$M = 4$	$M = 2$
E	1.232	0.0	1.803
μ_{Fe}	4.9227	2.9880	0.9955
Q_{Fe}	0.6715	0.4105	0.2796
δ_1	0.1632	5.0674	4.2867
δ_2	9.7838	2.9594	3.1280

Table 6 The geometry parameters (in nm) for Ar_6Fe^+ cluster, calculated with different basis sets, where r1–r6 are designated in Fig. 1. The parameter r0 is edge length for the pure Ar_6 cluster with octahedron.

Parameter	Basis 1	Basis 2	Basis 3	Basis 4	Basis 5
r1	0.272	2.840	2.790	2.800	2.874
r2	0.273	2.819	2.799	2.800	2.828
r3	0.274	2.830	2.791	2.847	2.828
r4	0.387	3.994	3.953	3.993	4.032
r5	0.387	3.749	3.953	3.993	4.032
r6	0.386	4.072	3.947	3.993	4.032
r0	0.406	4.306	4.299	4.306	4.097

Table 7 The binding energy E_{B} for Fe^+ in Ar_6 cluster for the most stable spin-multiplicity ($M = 4$) calculated with different basis sets.

	Basis 1	Basis 2	Basis 3	Basis 4	Basis 5
E_{B}	0.4912	1.3937	1.3970	2.0615	1.6901

tained:

(1) Geometry and geometrical stability. After optimization, the skeleton of the octahedron is maintained. Due to the small size of Fe as compared to Ar, the bond length of Ar–Fe is much smaller than that of Ar–Ar. However, is this structure dynamically stable? *Conventional* geometry optimizations converge to a structure on the potential energy surface where the forces on the system are essentially zero and the structure may correspond to a minimum on the potential energy surface or it may represent a saddle point, which is a minimum with respect to some directions on the surface while a maximum in other direction(s). This ambiguity can be resolved by analyzing the dynamical properties of the system. In fact, in the case of saddle point, the system displays one or more imaginary vibrational frequencies, suggesting there are some geometry distortions for which the energy of the system is lower than for the current structure. In Ar_6Fe^+ , there are $3 \times 7 - 6 = 15$ vibrational modes. We found these modes to

be positive, suggesting the geometry is dynamically stable.

(2) Magnetic state and magnetic stability. Comparing the total energy for different spin states in Tables 1–5, we can see that the magnetic state with $M = 4$ is most stable. Due to orbital hybridizations between Ar and Fe, the magnetic moment of Fe atom is reduced to about $3.0\mu_B$. The magnetic stability for this state is confirmed by the spin gaps, as shown in Tables 1 to 5. The positive values for the spin gaps guarantee the stability for this magnetic configuration.

(3) Charge distributions. When Fe^+ is placed inside of the Ar_6 cluster, most of the positive charge is distributed among the Ar atoms in the cluster, which means that some electrons are transferred to Fe atom from the Ar atoms. When the Ar atoms lose electrons, the electronic shells change from closed to open, and the interactions become stronger, which shortens their bond lengths.

(4) Comparisons of different basis sets. Among the 5 basis sets used in the present calculations, basis 1 and basis 5 are all electrons, while other 3 basis sets include pseudopotential. Results using Basis 1 show a smaller Fe binding energy and a correspondingly small charge transfer for the lowest-energy structure, as well as a significantly larger energy difference between the $M = 4$ and $M = 2$ states. The other four basis sets give results similar to each other. Basis 1 is the most often used basis set for transition metals,⁴⁾ but it is difficult to conclude which result is most reliable here without comparison to experimental binding energies, which is not available at present. However, it is important to note that the general features concerning geometry, magnetism, and charge are similar for all the basis sets.

In conclusion, in this paper, we used *ab initio* molecular calculations with several different basis sets, the geometry, magnetic properties and stabilities for magic Ar_6Fe^+ cluster are studied.

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