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Size Dependence of the Effective Potentials and the Effective Magnetic Moments of Transition Metal Clusters

Manickam Mahendran
Department of Physics, Thiagarajar College of Engineering, Madurai 625015, INDIA, and
The Graduate School of Natural Science and Techinology, Okayama University, Okayama 700-8530, JAPAN
Fax: +91-452-248-3427, email: mmahend@rediffmail.com

The electronic structure of transition metal clusters such as Iron and Cobalt are computed self-consistently using the Density Functional Theory (DFT) scheme applied to the spherical jellium background model (SJBM) and using the superparamagnetic model, respectively. The effective potential, the energy eigenvalues and the radius of the cluster as a function of cluster size, *N*, containing upto 18 atoms have been investigated. The effective magnetic moments of these clusters having upto 700 atoms have been studied. It is observed that the magnetic moments are decreased with increasing the size, temperature and magnetic field of the clusters. The energy eigenvalues changes discontinuously as a function of the cluster size at the shell closing numbers. The effective potentials are smooth within the jellium spheres of the LDA. We have observed that if the radius of the cluster in a uniformly charged sphere is smaller the effective potential for the electrons inside the sphere is deeper. More experiments can throw light on the generation of experimental data to test this model and enlighten our understanding of the metal clusters. Our theoretical results are compared with the experimental data.

Key words: DFT, LDA, Effective Potential, Superparamagnetic Relaxation, Effective Magnetic Moment,

1. INTRODUCTION

The magnetism of transition metal clusters is of great interest in cluster Physics originated from the main investigation that their properties are very different from the bulk solid [1]. The nanometer world keeps on focusing the new technologically oriented magnetic properties, both in the potential applications in magnetic read head industry and in the understanding of basic and applied research [2]. A new technology is developed from the subject solid-state magnetism where the magnetic properties of clusters with various size ranges and temperature are obtained. The size dependence of the magnetic moment of Fe, Co and Ni clusters has been investigated using a molecular beam deflected with a Stern-Gerlach magnet [2,3]. This experiment reveals that when the size of the clusters increases their magnetic moment decreases pertaining to the bulk value with small oscillations. Dorantes-Davila and Pastor [4] have studied the magnetic anisotropy energy of 3d transition metal wires self-consistently using DFT A series of ionization potential of Fe, Co and Ni clusters has been measured using the laser photo ionization method combined with the time-of -flight mass Spectrometry [5]. The miniaturized devices are developed from the cluster magnetism containing few atoms to hundreds to thousand. This is because the large portion of the atoms in a cluster forming a surface, which is one of the important parameters to study the magnetic properties of transition metal clusters. It is observed that the smaller coordination number produces large magnetic moments in ferromagnetic clusters such as Fe, Co, and Ni. Fujima and Yamaguchi [6] calculated the magnetic properties of cobalt clusters using the local spin density functional method. They observed the fluctuations in the magnetic moment per atom of Co clusters with increasing the size of the cluster having atoms upto 147. Khanna and Linderoth [1] have proposed the superparamagnetic model for the first time to study the magnetic moments of ferromagnetic clusters. This model paves the way to the experimental side to work on the ferromagnetic clusters. It has been investigated that as the cluster size increases the magnetic moment of both Fe and Co decreases and reaches the bulk values. Experiments showed some oscillations in the magnetic moments of ferromagnetic clusters such as Fe, Co, Ni as a function of the cluster size ranging from 50 to 750 atoms [2,3,7].

The effects of electron correlation in transition metal clusters play a major role in magnetic moment because of the involvement of the d shell-giving rise to the ground state properties. The energy eigenvalues of Fe, Co and Ni clusters were computed by Perdew and Zunger [9]. Castro et al [28] have studied the structure and magnetism of Fe, Co and Ni clusters with less than or equal to 5 atoms using the DFT scheme. Since much work has not been devoted to transition metal clusters using LDA of Kohn-Sham density functional theory applied to the SJBM. This is due to less accuracy in applying LDA to strong-correlation regime. Therefore, we focus our attention only on the relative change of electronic structures of medium size Fe, Co and Ni clusters containing upto 18 atoms. We then apply the superparamagnetic model upto 700 atoms to analyze the magnetic properties of clusters. In this paper, we report our systematic investigation of the electronic structure of these clusters. The Spherical Jellium Background Model (SJBM) is chosen because; it is a prime tool to study the electronic structure of transition metal clusters. Though this is an old fashioned but well respected tool, we attempted to investigate the effective potential, the

energy eigenvalues, the radius of the clusters of Fe and Co clusters with upto 18 atoms self-consistently. In section 2, the details of the theoretical model adopted in this computation are discussed. Our results are presented and discussed in section 3, and section 4 presents the conclusion.

2. COMPUTATIONAL METHODS

i) Effective Potentials of Fe and Co Clusters

In the LDA applied to the SJBM of a system of electrons, the external potential is of the form [10],

$$V_{ext}(r) = \begin{cases} -\dfrac{NZ}{r}, & r > R \\ -\dfrac{3}{2}\dfrac{NZ}{R^3}\left[R^2 - \dfrac{r^2}{3}\right], & r \le R \end{cases} \quad \text{---- (1)}$$

where N is the number of atoms forming the cluster. The electronic charge density ρ(r) is given by

$$\rho(r) = \sum_{i=1}^{N} \left| \psi_i(r) \right|^2 . \quad \text{----(2)}$$

The energy eigen values are obtained by solving the Kohn-Sham equation self-consistently and is given by

$$\left[-\frac{1}{2}\nabla^2 + V_{eff}(r, \rho(r))\right]\psi_i(r) = \epsilon_i \psi_i(r), \quad \text{----(3)}$$

where the modified effective potential V_{eff} is [10]

$$V_{eff}(r,\rho(r)) = V_{ext}(r) + \int \frac{\rho(r') - \rho_i(r')}{|r - r'|} d^3r' - 3\alpha\left[\left(\frac{3}{4\pi}\right)\rho(r)\right]^{1/3}, \quad \text{----(4)}$$

where α = 0.71151, 0.71018 and 0.70896 for Fe, Co and Ni respectively.

The calculations have been carried out self-consistently. The computed V_{eff} forms the new input for the system of equation (4) and the procedure is repeated until the iterated Ψ_i , ϵ_i and the charge density have converged. All the calculations have been carried out in units of a.u. (1a.u. of energy =27.2 eV).

ii) Effective Magnetic Moments of Fe, Co and Ni Clusters

The magnetic properties of these clusters are depending upon the size and temperature, which favors the equal filling up of the spin states. The Heisenberg Hamiltonian of the system is given by

$$H = -\frac{1}{2}\sum_{i,j} J_{ij} \boldsymbol{S}_i \cdot \boldsymbol{S}_j , \quad \text{-----(5)}$$

where the summation is over the nearest neighbor spins, i and j are the spin sites, J_{ij} are the exchange interaction of the system, S_i and S_j are the spins at the sites i and j respectively. The internal magnetic field at each spin site (j) is given by [11]

$$H_j = \sum_{j'} J(j - j')\langle Sz_{j'} \rangle, \quad \text{-----(6)}$$

where, $J(n)$ is the spin-spin interaction with its n^{th} neighbor. $Sz_{j'}$ is the thermally averaged mean value of the spin component for the magnetic ions in the j^{th} site. The spins of the atoms of the cluster interact with the nearest neighbor spins. The average magnetic moments of the clusters are assumed to be in the field H_j with the temperature T. The average magnetic moment per atom of the single domain clusters having N atoms will have Nμ moment, where μ is the atomic magnetic moment. The values of μ for bulk are Fe=2.2μ_B, Co=1.7μ_B and Ni= 0.6μ_B. The effective magnetic moment per atom of the ferromagnetic clusters is given by the Brillouin function and is calculated using the relation [1]

$$\mu_{eff} = \mu B_J(x); \qquad x = \frac{N\mu H_{eff}}{k_B T}, \quad \text{------(7)}$$

where N is the number of atoms in the cluster, μ is the magnetic moment of the atom in the cluster. The surface effects through a geometrical dependent empirical relation is included in the above expression and is

$$N_{eff} = \frac{N}{2}\left[1 + \left(1 - \frac{N_s}{N}\right)\right], \quad \text{------(8)}$$

where N_{eff} is the effective number of atoms in the surface of the cluster and N_s is the number of atoms residing on the surface of the cluster.

3. RESULTS AND DISCUSSION

The results of the electronic and structural properties of the clusters as a function of N, the number of atoms forming a cluster and as a function of the radius of the cluster, r_s are presented for the transition metal clusters Iron and Cobalt. Our computed results exhibit enhancement of the electronic structure at the shell closing numbers. The enhancement of the structural energy eigenvalues, ϵ_i, between N and the effective potential, V_{eff}, and between radius of the cluster, r_s and V_{eff} , is due to the exchange-correlation effect. The enhancement in the electronic structure of transition metal clusters is associated within the spherical jellium of the LDA. The V_{eff} in the presence of the external potential V_{ext}(r) increases gradually with the increasing r_s . This gradual increase of the V_{eff} may be due to the use of the converged charge density ρ(r) . The ground state densities and the effective potential corresponding to the SJBM of the LDA are plotted in Figs. 1-4.

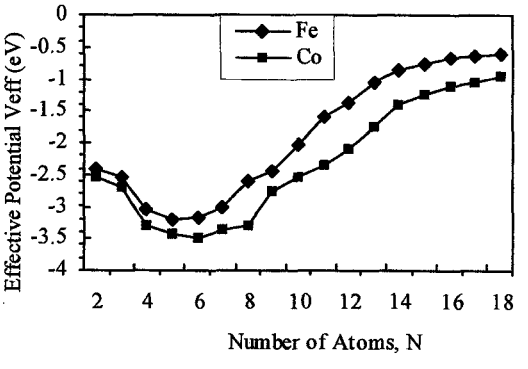

Fig.1 Computed effective potentials at the cluster surface, V_{eff} of Fe and Co clusters for the size, N=18 atoms. The V_{eff}s are given in eV. The lines are drawn to guide the guide

The potentials are smooth within the jellium spheres. It is interesting to note that the effective potential increases customarily with increasing N and r_s. The V_{eff} is almost saturated when we increase the value of r_s (Figs. 3 & 4) continuously. As r_s increases the potential decreases. This may be due to the fact that it behaves like $1/r$ for large r. An interesting, physical quantity which will expose the electronic structure of the clusters is the energy eigenvalue, ϵ_i. This quantity is calculated self-consistently while iterating the charge density. The total value ϵ_i for all occupied states as a function of the N for Fe and Co clusters is presented in Fig.2. For smaller number of atoms (N=upto 5) the clusters have shell-closing configuration, and hence the shell structure effects are systematically averaged out. It is clear from Fig. 2 that as the N in a cluster increases the total eigenvalues change show discontinuities. The discontinuities appear as the peaks of Fe and Co clusters. The electronic energy eigenvalues obtained from the DFT scheme have discontinuities whenever shells are completely filled. If the cluster radius of the uniformly charged sphere is smaller the effective potential for the electrons inside the sphere will be deeper. The physical significance of this is that it reveals how the properties of the bulk clusters can be determined.

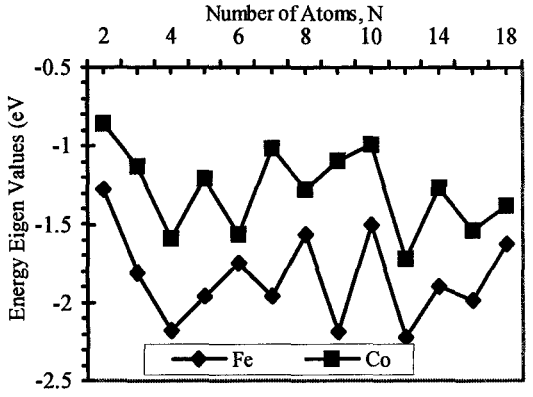

Fig.2 Computed energy eigenvalues of Fe and Co clusters for the size, N=18 atoms. The ϵ_i`s are given in eV. The lines are drawn to guide the guide.

Particles with smaller size of the order of nm exhibit superparamagnetic relaxation at varying temperatures. The observation of quantum size effect in basic research is important which results from the fact that the electronics states in smaller clusters affects the thermodynamic properties when the temperature of the cluster is reduced. Therefore, large metal clusters require higher temperatures to study the effective magnetic moments of transition metal clusters, which are computed using the superparamagnetic model.

The results of the effective magnetic moments are presented in Figs. 5, 6 and 7 for Fe, Co and Ni clusters respectively. The size of the cluster chosen for the computation is upto 700 atoms. Figure 5 shows the variation of effective magnetic moments in Fe clusters at T=200K and we fixed the T based on the assumption that μ is the same for all cluster sizes [1]. We have varied the size of the cluster by fixing the temperature to compute the effective magnetic moments of these clusters. It is interesting to note from the figures that the effective magnetic moments of these clusters give oscillations with the increase in size.

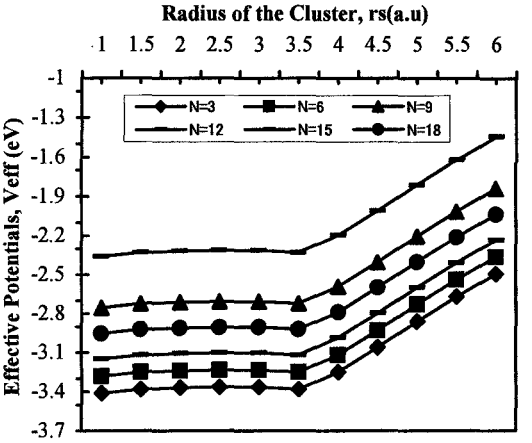

Fig.3 Computed effective potentials, V_{eff} of Fe clusters for the size, N=18 atoms against the radius of the clusters. The V_{eff}s are given in eV. The lines are drawn to guide the guide.

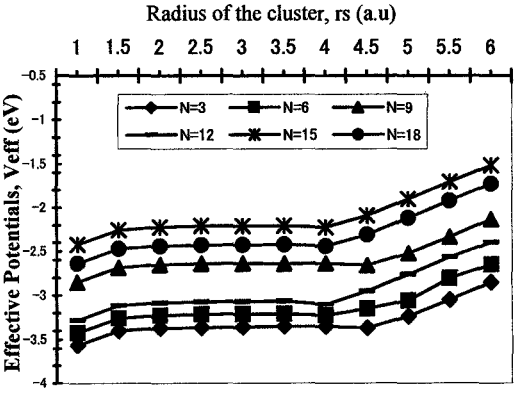

Fig.4 Computed effective potentials, V_{eff} of Co clusters for the size, N=18 atoms against the radius of the clusters. The V_{eff}s are given in eV. The lines are drawn to guide the guide.

Some of the interesting oscillatory peaks μ_{eff} are obtained. The peaks confirm the mean field theory approximation is suited for the estimation of effective magnetic moments of magnetic materials. When the size is increased the effective magnetic moment of the ferromagnetic clusters approaches the bulk value. The μ_{eff} obtained for Fe clusters have been compared with Stern-Gerlach experimental results [2]. The μ_{eff} of $3.3\mu_B$ attains the maxima at N=100-200 and gradually decreases. At about N=300-400 the μ_{eff} of $2.8\mu_B$ occurred, again goes to the maximum and after N=450 it is decreased smoothly till reaching the bulk value $2.2\mu_B$.

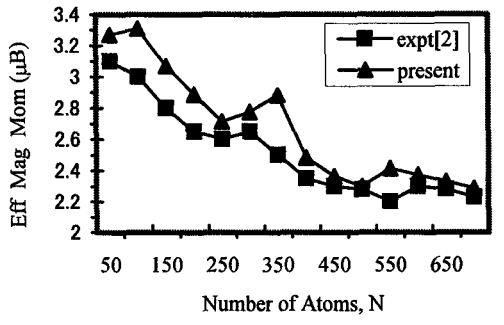

Fig. 5 Computed values of effective magnetic moments of Fe clusters having size N=700 atoms for T=200K .The lines are drawn to guide the guide.

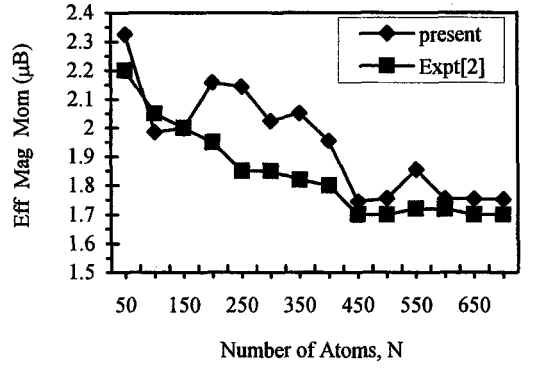

Fig. 6 Computed values of effective magnetic moments of Co clusters having size N=700 atoms for T=200K . The lines are drawn to guide the guide.

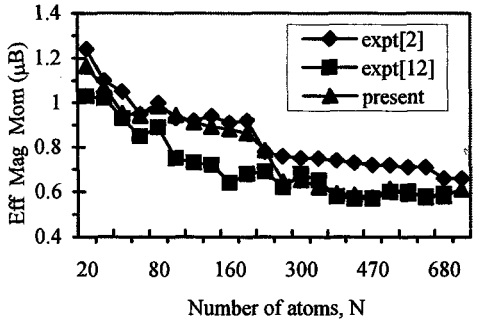

Fig.7 Computed values of effective magnetic moments of Ni clusters having size N=700 atoms for T=200K .The lines are drawn to guide the guide.

4. CONCLUSION

The effective potentials of Fe and Co clusters are analyzed using the LDA of DFT. It is observed that the they are decreased with the increasing the cluster size. The effective magnetic moments of these clusters have been computed based on the superparamagnetic model. It is found that they are decreasing with the cluster size, temperature, and magnetic field.

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