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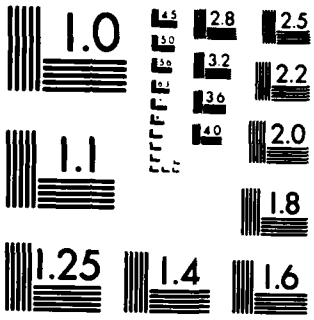

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Relationship between topological and magnetic order in small metal clusters

B. K. Rao* and P. Jena

Physics Department
Virginia Commonwealth University
Richmond, Virginia 23284

M. Manninen

Laboratory of Atomic and Solid State Physics
Cornell University, Ithaca, N.Y., 14853

PACS Index: 31.20Tz, 36.40+d

Permanent Address: Institute of Physics,
Bhubaneswar 751005, India

Abstract

The equilibrium geometries and ionization potentials have been calculated self-consistently for lithium clusters consisting of up to five atoms. The exchange interaction is treated exactly while the correlation effects are included perturbatively. The correlation contribution is found to have important influence on the magnetism of the cluster and its relationship with the topology.

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There has been a growing interest in the study of the electronic properties of small metal clusters in recent years. This is prompted not only because small metal particles may have technological importance but also because their study is interdisciplinary and bridges the gap in our knowledge of the electronic structures between atoms and solid state systems. Recent improvement in the experimental techniques [1-4] has enabled one to produce clusters of atoms ranging from 2 to 100 atoms per cluster. Three important features are noticed. (1) Conspicuously large peaks occur in the mass spectra of the clusters indicating that certain clusters of atoms are more abundant than others. (2) These "magic numbers" (i.e. the number of atoms in the more abundant clusters) are dependent not only on the type of atoms but also on experimental conditions. (3) The clusters containing even number of atoms are more abundant than those containing odd-number of atoms.

In a recent experiment on sodium clusters, Knight et. al.[1] found the magic numbers for N = 2, 8, 20, 40, 58, and 92 where N is the number of atoms in the cluster. While these results are somewhat different from that published earlier by Kappes et. al.[2], the remarkable aspect of the work of Knight et. al.[1] is that they could explain the occurrence of these magic numbers in terms of a simple one-electron shell model based on jellium calculations. This implies that the occurrence of above magic numbers should be a universal feature of all simple monovalent metals.

In this letter, we report three different calculations for lithium clusters. (1) We have carried out spin-polarized jellium cluster calculations based on local density approximation for N = 1 to 42. The second derivative of the total energy showed peaks at N = 2,8,20, and 40 in agreement with the calculations of Knight et. al.[1] These correspond to clusters with filled electron shells. In addition, we also observed additional peaks at N = 5, 13, 27, and 37 that are absent in the calculation of Knight, et. al.[1] These peaks originate from the half-filled shells and the filling of the orbital spin states follow Hund's rule. Thus, if the jellium model is correct, the results would imply that N = 13 cluster should be more abundant than the 12 and the 14 atom clusters. The experimental result[1] is just the opposite. (2) To resolve this issue and to try to understand the success of the original jellium model, we have carried out unrestricted Hartree-Fock (UHF) calculations for Li clusters consisting of one to five atoms. The total energy/atom decreases continuously as N increases from 1 to 5, thus revealing no tendency for N = 2 to be a magic number. When interatomic correlation was included, the total energy/atom for N = 2 did exhibit a dip compared to N = 1 or N = 3. This implies that correlation effects are crucial in studying the relative binding energy of small metal clusters. The equilibrium geometries of all our clusters in the calculations containing correlation are planar, in agreement with other observations[5-7]. These low symmetry planar geometries are a result of the Jahn-Teller effect[5]

which connects, via the Hellmann-Feynman theorem[5], the equilibrium nuclear positions with the electron density provided by the molecular orbitals. For the 4-atom clusters, we have considered two possible spin configurations, singlet and triplet. We find that the ground state is nonmagnetic (spin singlet). This is in contrast with the jellium calculation which predicts the triplet state to have lower energy. The source of this discrepancy is found to lie in the nature of preferred filling of the molecular orbitals as the cluster size increases.(3) The ionization potentials of these clusters have also been calculated. The UHF results for these decrease monotonically with the increase of cluster size. When correlation is included, structures similar to that observed in sodium clusters[8] appear. This reinforces our earlier claim that correlation effects are essential in understanding the electronic properties.

We now present the details of our calculation. The jellium calculations were carried out by representing the external perturbation by a spherical distribution of homogeneous density of positive charge, namely,

$$n_{ext}(\vec{r}) = n_o \, \theta(\vec{R}-\vec{r}), \tag{1}$$

where $R = r_s N^{1/3}$ is the radius of the cluster. The electron radius r_s and electron density n_o are related through the equation $1/n_o = (4\pi/3) r_s^3$. The electronic structure of the cluster of N-atoms was calculated self-consistently by solving the density functional equation,

$$\left[-\nabla^2 + V^{\sigma}_{eff}(r)\right]\psi^{\sigma}_i(r) = \varepsilon^{\sigma}_i\,\psi^{\sigma}_i(r). \qquad (2)$$

The potential V^{σ}_{eff} is composed of electrostatic and exchange-correlation potential for spin σ in the local spin density approximation. ε^{σ}_i and ψ^{σ}_i are respectively the energy eigenvalue and wave function of the ith electron with spin σ. The total energies of the clusters E(N) for $1 \leq N \leq 42$ were calculated. In Fig. 1 we plot the second derivative of this quantity $E''(N) = E(N+1)-2E(N)+E(N-1)$ in order to fascilitate the comparison of our spin polarized calculation with the result of Knight et. al.[1] The peaks at N = 2,8,20,34, and 40 correspond to the filling of 1s,1s1p; 1s1p1d2s; 1s1p1d2s1f and 1s1p1d2s1f2p shells as in the work of Knight et.al.[1] We observe additional peaks at N = 5, 13,27, and 37 which correspond to half-filling of orbitals 1p, 1d, 1f, and 2p orbitals in keeping with Hund's rule coupling.

The UHF calculations were carried out by representing the molecular orbitals as a linear combination of the Gaussian-type atomic orbitals centered at the atomic sites. Interatomic correlation correction was introduced perturbatively[9] by including pair excitations of the valence electrons. The equilibrium geometries for both neutral and singly ionized clusters were obtained by calculating the Hellmann-Feynmann forces on every atom and following the path of steepest descent to the minimum energy configuration. The equilibrium geometries are given in Fig. 2, and the corresponding bond lengths are listed in Table 1. The energy/atom of the neutral cluster obtained from UHF as well as with correlation correction are given in Table 1. Note that in UHF calculation

the energy/atom decreases continuously unlike that in the jellium calculation. However, when correlation is introduced, the energy/atom for N = 2 cluster is distinctly lower than those for N = 1 and N = 3. Thus, purely on energy considerations, one would expect a dimer to be more abundant than either a monomer or a trimer. This establishes N = 2 as a magic number.

Using the optimized geometries of the neutral and the ionized clusters the ionization potentials were calculated. These are presented in Table 1. The experimental ionization potential[10] of lithium is 5.39 eV. For N = 2, the impact[11] and photo-ionization[12] appearance potentials are 4.8 eV and 5.1 eV respectively. For N = 3, the impact appearance potential is 4.3 eV. Experimental results for higher clusters are not yet available. However, the nature of variation of the ionization potential with cluster size obtained with correlation is consistent with that found in Sodium[8]. The equilibrium geometries and ionization potentials for $N \lesssim 3$ are in good agreement with previous calculations[13]. The fact that the small even clusters have larger ionization potentials than the odd ones suggests that they are less reactive than the odd clusters. This leads to the observed results that the even clusters are more abundant than the odd ones[1,4].

We now discuss the magnetism of the clusters. The minimum value of N where we can make a choice of spin populations is 4. In this cluster, one can either have ↑↓↑↑ (spin triplet) or ↑↓↑↓ (spin singlet) configuration for the valence electron spins. Taking the planar cluster obtained for the spin singlet case (shown in Fig. 2 (iii)) we reoptimized the bond lengths and angles for the triplet case. This energy was 0.0164 eV higher

than the singlet energy (including correlation). In the jellium calculation, however, the triplet was found to be the ground state. To see if this effect is associated with the dimensionality of the clusters (jellium is three-dimensional whereas Fig. 2 (iii) is planar) we calculated the energy for both spin configurations by optimizing the bond lengths of the N=4 cluster where the atoms are arranged in a bcc tetrahedron. The energy/atom of the tetrahedral cluster for the spin triplet is -202.4884 eV while for the spin singlet tetrahedral cluster, the energy/atom is -202.0729 eV. Thus, the three-dimensional N=4 cluster prefers to be magnetic. This is in agreement with the spherical jellium model calculations. We must remind the reader that the planar configuration (Fig. 2(iii) is the equilibrium geometry obtained by complete optimization. The preferred spin orientation and its relationship with the dimensionality of the cluster can be understood in the following way, An analysis of the populations of the molecular orbitals of the planar clusters reveals that the p_x-, p_y- and p_z-like states are filled in succession. For the N=4 cluster, p_y- and p_z-like states are empty. For the three-dimensional tetrahedral cluster, on the other hand, $p_{\bar{x}}$, $p_{\bar{y}}$, and $p_{\bar{z}}$ like states are filled simultaneously and hence energy can be lowered by maximizing spin due to exchange interaction. In addition, we want to point out that the spin-singlet N=4 planar cluster is more compact than the spin-triplet N=4 tetrahedral cluster. This leads to a larger electron density along the bond in the two-dimensional cluster as compared to the corresponding three-dimensional one. The increased electron density favors anti-symmetry in the spin, making the planar cluster less magnetic. Since the dimensionality of the cluster topology is linked to the magnetic order for $N < 7$ in mono-

valent metals, we can say that the jellium model would predict the wrong spin configuration for N = 4, 5, 6 clusters. We have found that the equilibrium geometry for N = 5 in Fig. 2(iv) has th^ spin orientation ↑↓ ↑↓↑ instead of ↑↓ ↑↑↑. As a further test, we have also calculated the ground state geometry of the four atom beryllium cluster. In this case, there are 8 valence electrons and the complete filling of the p-like states should result in three-dimensional clusters. As expected, we did obtain the equilibrium cluster as a tetrahedral arrangement of the four Be atoms instead of a planar one. The interplay between the electronic and the ionic arrangements may also reduce the total spin predicted by the jellium model in larger clusters than the ones considered here. This would explain why the half filled shells do not show up as magic numbers. Another explanation might be the reduction of the formation probability of odd numbered clusters as a result of larger reaction rates[14] of odd clusters as compared to the even ones: the odd clusters combine to form even clusters.

In conclusion, we have carried out self-consistent ab initio calculations of the equilibrium geometries, energies and ionization potentials of small Li clusters and compared the results with the predictions of the jellium model. We find that clusters with $N \leq 5$ are planar. The magnetism of these clusters is not governed by the exchange interaction alone. The N=4 and N=5 clusters in the planar structure are less magnetic than in the three-dimensional structure. The effect of correlation has been confirmed as crucial in determining the equilibrium geometries and ionization potentials of small metal clusters. These have important

connection with the interpretation of magic numbers observed in the experiments.

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Figure Caption

Fig. 1. Plot of second derivative of E(N) versus N i
of lithium atoms. E is given in atomic Hart

Fig. 2. Shapes of optimized geometries of lithium at
for N = 1-5.

Table 1

Total energy/atom and ionization potentials of lithium clusters calculated with and without correlation. The equilibrium bond lengths given here include the correlation effects.

N	Bond lengths (a_o)		Energy/atom (eV) for neutral clusters		Ionization potentia (eV)	
	Neutral cluster	Ionized Cluster	UHF	Correlation	UHF	Correlatio
1	-	-	-202.1296	-202.1296	5.32	5.32
2	a=5.32	a=6.02	-202.1819	-202.7264	4.21	5.30
3	a=5.41,b=6.65	a=5.83,b=5.84	-202.2859	-202.3948	3.83	3.77
4	a=5.96,b=5.19	a=6.14,b=5.41	-202.3135	-202.5589	3.62	4.19
5	a=5.93,b=6.63 c=5.85,d=5.87	a=10.95,b=6.14 c=5.54,d=6.14	-202.4459	-202.5608	3.95	3.66

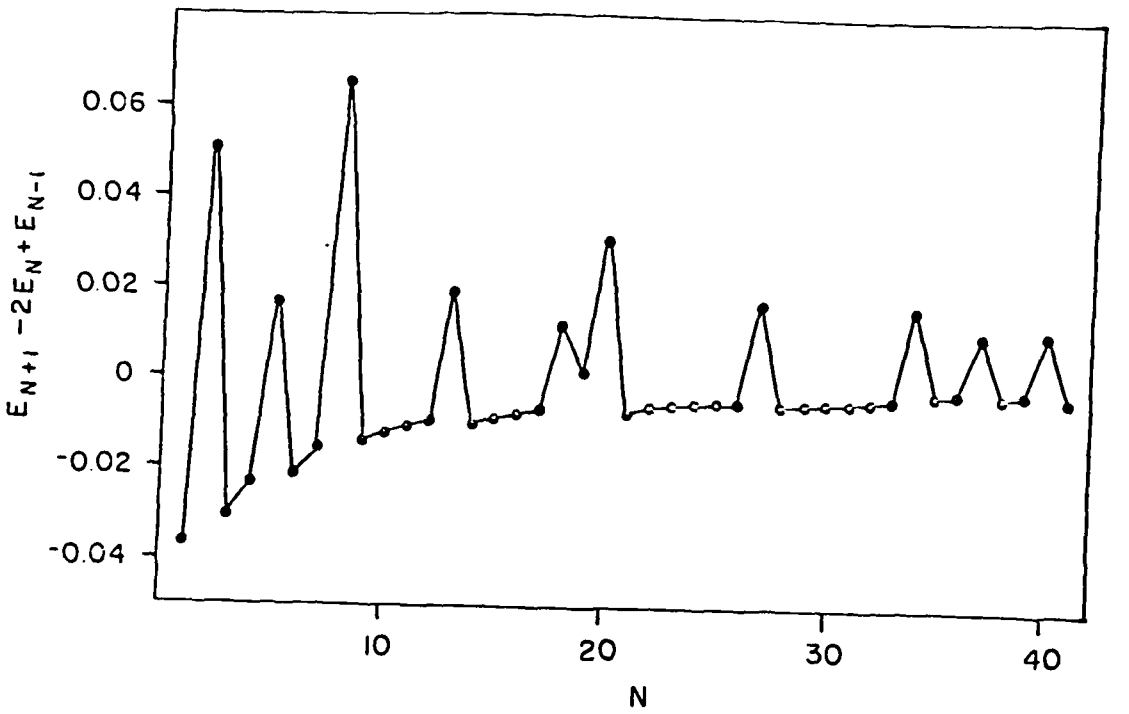

Fig. 1

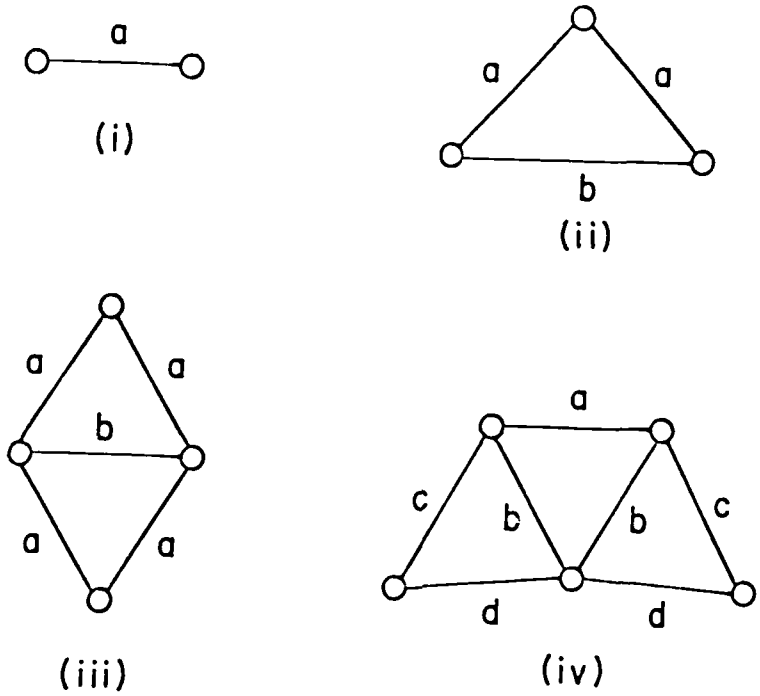

Fig. 2

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