JAHN-TELLER DISTORTION, HUND'S COUPLING AND METASTABILITY IN ALKALI TETRAMERS

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ABSTRACT

The equilibrium geometries of small metal clusters are strongly influenced by the number of valence electrons available. These electrons occupy the molecular energy levels in different ways depending upon the degeneracies of the one-electron states. The symmetry of the atomic arrangements guide the degeneracies and the consequent spin configuration of the clusters. The interplay of the geometry and the spin configuration is demonstrated using model clusters of Na_4 and Li_4.

INTRODUCTION

Recently, there has been considerble interest in the electronic structure and geometries of small metal clusters. Ab-initio theoretical studies on small simple metal clusters show that their ground state structures are very different from their bulk counterparts. In addition to the true ground state, the clusters can also exist in metastable states corresponding to various geometric or spin structures. There are two effects which seem to govern the equilibrium geometries of small clusters. First, the Jahn-Teller effect tries to lower the total energy of the system by breaking any electronic state degeneracies arising due to spatial symmetry, thus giving rise to a less symmetric structure. The ground state of alkali trimers as obtuse angled triangular structures instead of equilateral triangle, and the rhombus instead of square or tetrahedral structure for a tetramer are the classic examples.[1] Secondly, high symmetric arrangement of atoms in a cluster can lead to degeneracies in electronic levels. In such situations, the cluster can lower its energy by maximizing its spin multiplicity through the exchange or Hund's rule coupling. Thus, the Jahn Teller effect and Hund's rule appear to play competing roles in determining the ground state geometries of microclusters. We illustrate these rules by considering Na_4 and Li_4 clusters as model systems and where the atoms are confined to lie on a plane. We further show that in three dimensional structures of alkali tetramers, the Jahn-Teller effect and Hund's rule work together to lower the energy where the ground state is a distorted tetrahedron with spin triplet configuration.

CALCULATIONS AND RESULTS

Our studies on Na_4 were based on the density-functional approach. The effect of core electrons was treated through a non-local, norm-conserving pseudopotential proposed by Bachelet et al.[2] The exchange-correlation corrections were incorporated in the local-spin-density approximation. The Kohn-Sham equations were solved by expanding the molecular orbitals as a sum of Gaussian atomic orbitals. For other details of the method, the readers are referred to articles[3] available in the literature. For Li_4, we have used unrestricted Hartree-Fock method with configuration interaction. One can refer to a recent article[1] for details of the calculational procedure.

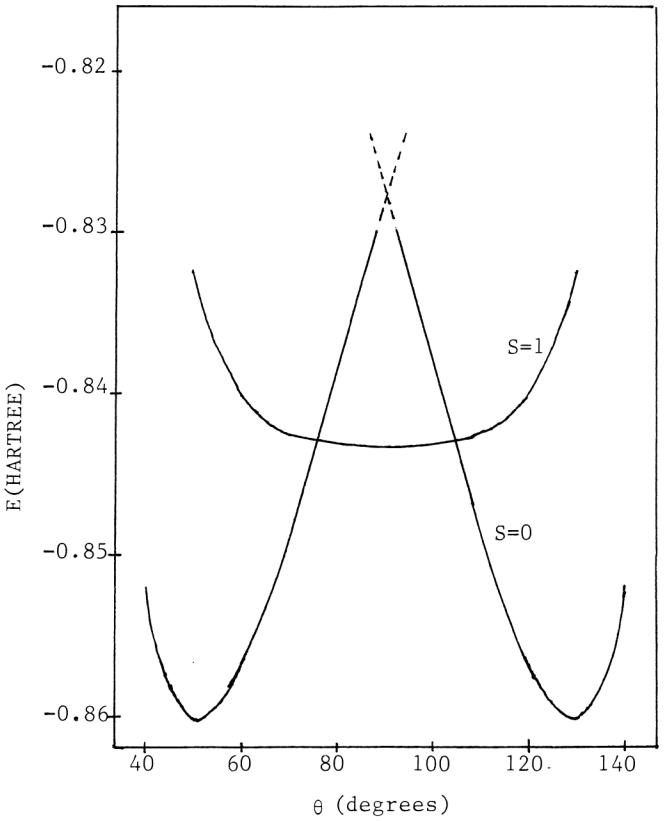

Fig.1 Variation of the total energy of a sodium tetramer, in singlet and triplet state, as a function of the angle θ for plane rhombus configurations. (For each θ, the length ,a, of each side of rhombus has been optimized)

In Fig. 1 we show the total energy of Na_4 as a function of the apex angle θ for the planar rhombus configurations corresponding to singlet and triplet states. For a fixed value of θ , the bond lengths have been optimized. It is seen that as the apex angle is increased from $\theta = 52°$, the total energy of the singlet state rises and at an angle of $\theta = 76°$, the triplet becomes lower than the singlet. As θ is further increased towards

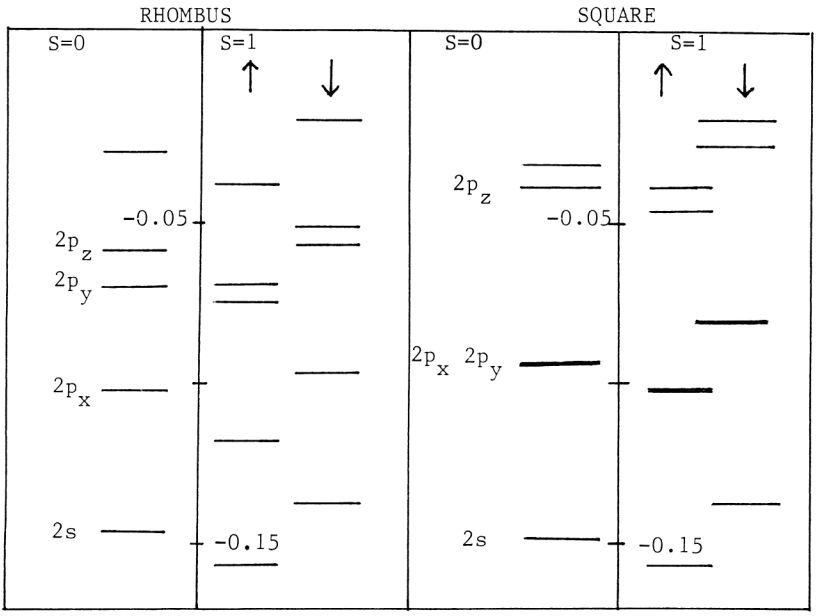

Fig.2 One electron energy levels (in Hartree) corresponding to singlet and triplet state for rhombus(θ=52°) and square geometries.

$\theta = \pi/2$, the triplet energy decreases towards its minimum value at $\theta = \pi/2$. In order to understand this transition, we show in Fig. 2 the valence electron levels for θ = 52° and θ = 90° for the singlet and triplet configurations of the Na_4 cluster. Using the terminology of the jellium model, we have labeled the valence states as 2s, $2p_x$, $2p_y$, and $2p_z$. As θ tends toward $\pi/2$, the difference between p_x and p_y levels decreases until they become degenerate at $\theta = \pi/2$. There is a range of θ values around $\theta = \pi/2$ for which the difference in the one electron levels is smaller than the exchange energy and the cluster prefers a triplet configuration with an electron in both p_x and p_y levels instead of a singlet with both electrons in lowest p_x levels. The triplet state at $\theta = \pi/2$ has a non-degenerate electronic configuration. As θ decreases towards 52°, the degeneracy in the p_x, p_y-like orbital is lifted. The gap in the energy of these orbitals becomes larger than the exchange energy gained by putting two electrons of parallel spin in p_x and p_y orbital. Consequently, as seen in Fig. 1, the cluster assumes a spin singlet configuration. The Li_4 clusters exhibit exactly the same trend.

To understand if the preferred spin structure of the tetramer is symmetry related (ie. dependent only on θ) or also dependent on spatial parameters (ie. bond lengths), we plot in Fig. 3 a phase diagram showing regions of spin singlet and triplet state for a given value of the bond length a and bond angle θ . The fact that the plot of a vs θ has a weak θ-dependence clearly suggests that the magnetism of clusters is a symmetry driven problem.

One can also study the spin-problem by inducing degeneracy in p_x, p_y, and p_z orbitals by going to a tetrahedral configuration. Elsewhere in this book[4] we show the total energy of the Li_4 as a function of the dihedral angle (shown in the insert). One notices a transition as a function of the

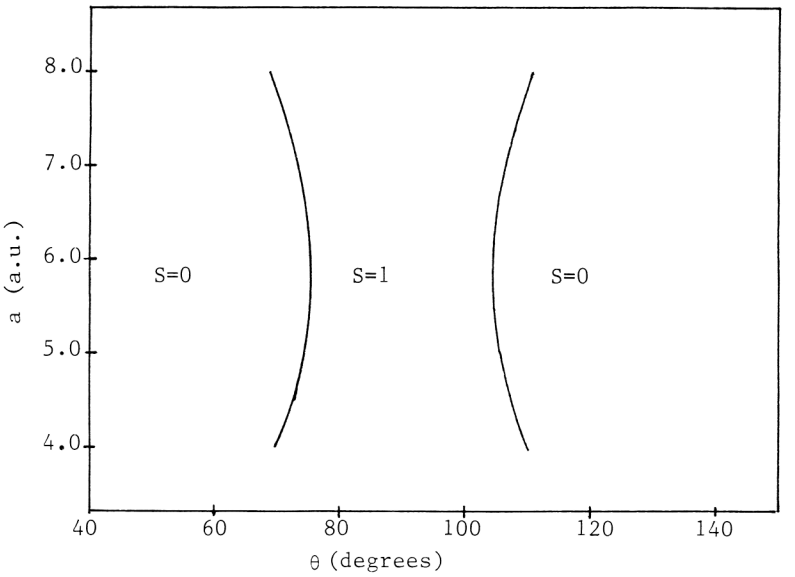

Fig.3 Multiplicity of the minimum energy state for rhombus configurations of a sodium tetramer.

dihedral angle and the existence of a metastable triplet minimum. It is interesting to note that the triplet minimum does not correspond to a perfect tetrahedron which would occur at $\theta \cong 70°$. A perfect tetrahedron leads to a degeneracy of p_x, p_y and p_z. Since the electronic levels are degenerate, the tetrahedral structure has triplet lower than the singlet. However, contrary to the case of square (2 dimensions), parallel arrangement of spins does not remove the electronic state degeneracy. The tetrahedral triplet has a degenerate electronic ground state and consequently undergoes a Jahn-Teller distortion lowering its energy through a deformation of the perfect tetrahedron. Thus, the Hund's rule coupling and the Jahn-Teller distortion now act together to lower energy, resulting in a distorted tetrahedron in the spin triplet configuration.

In conclusion, we have demonstrated through model calculations the relative roles played by Jahn-Teller effect and Hund's rule in determining the ground state geometry and spin structure of clusters. We have also demonstrated that the nature of these interactions are qualitatively different in two and three dimensions. Thus, it is essential to study the possible spin multiplicity of clusters before deciding on their true equilibrium geometry, for these two are intimately related.

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4. B. K. Rao, S. N. Khanna, and P. Jena, page 369 in this book. See Fig.5.