

GEOMETRIC AND ELECTRONIC STRUCTURES FOR Mn AND Tc CLUSTERS BY DENSITY FUNCTIONAL METHOD

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Metal clusters are found to exhibit some properties different from those of bulk: bond length [1], ionization energy [2], magnetic moment [3], and chemical behavior [4]. The transition metal clusters are especially of interest since there is a large number of electronic states of different spin multiplicities and complexity of the metal bond due to the metal *s*, *p*, and *d* orbitals. We focus on the similarity and dissimilarity between Mn and Tc clusters. The electronic configurations of these atoms are different: that for Mn is [Ar]3d⁵4s², while that for Tc is [Kr]4d⁶5s¹, though Mn and Tc belong to the same group in the periodic table of the elements.

Manganese clusters show some interesting characteristics different from other 3d-transition metal clusters [5]. These mainly originate from the electronic configuration of the isolated Mn atoms 3d⁵4s². Ferromagnetic and antiferromagnetic or frustrated antiferromagnetic solutions have been reported by Pederson et al. [6]. Compared with the Mn clusters, there are few reports on Tc clusters. Klyagina et al. calculated the spin states of Tc dimers and concluded to be (4d)⁶(5s)¹ electronic structure [7]. However, they have not optimized the dimer bond length and it is easily expected that the spin states of Tc dimer should be strongly correlated with its bond length. In this study we obtain geometry of small Mn and Tc clusters by a density functional method. Furthermore, we focus on the spin states of these metal clusters and relating them with the geometry. We have performed geometry optimization for Mn_n (n = 2~8), Tc₂ and Tc₃ using a program package of Amsterdam Density-Functional (ADF) method [8].

The most stable structure for Mn_n (n = 2~8) obtained by ADF method is shown in Fig.1. Equilibrium bond length, total spin (S, which equals to half of the difference between number of α spins and that of β spins), magnetic moment per atom (μ_B) and symmetry are also described in the figure. For all clusters, variety of isomers and different magnetic moments were examined. As shown in Fig. 1, spin states for Mn clusters are almost the same for each atom, indicating to their ferromagnetic properties.

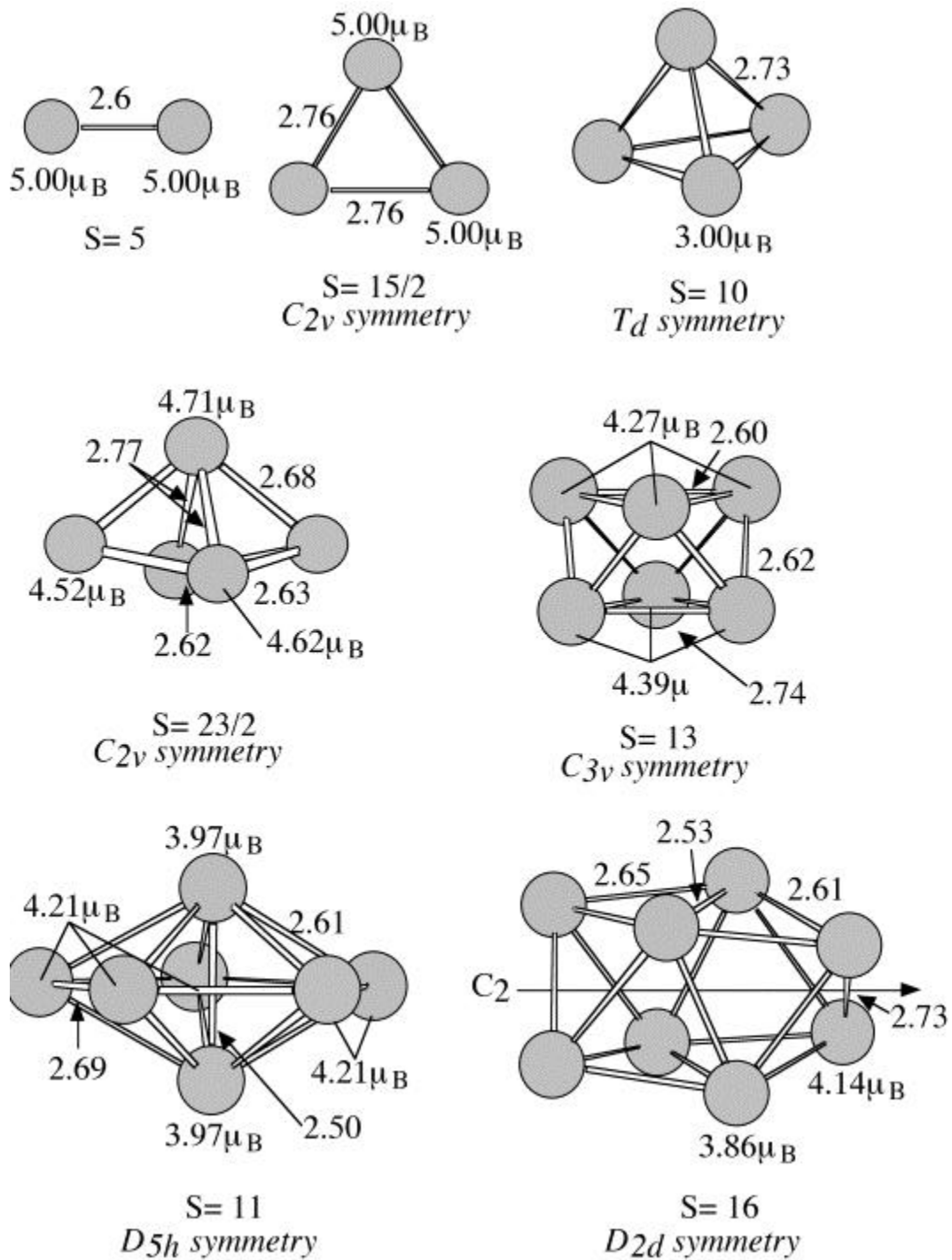


Fig.1 The most stable structures for Mn clusters (n=2-8).

The bond length in Å is indicated.

The result for Tc dimer and trimers are shown in Fig. 2. The dimer (a) shows the spin states with $1.00\mu_B$, suggesting that each $(d)^6$ spin makes antiferromagnetic pair while the both $(s)^1$ spin makes the ferromagnetic pair. The spin states for the trimers are very complicated

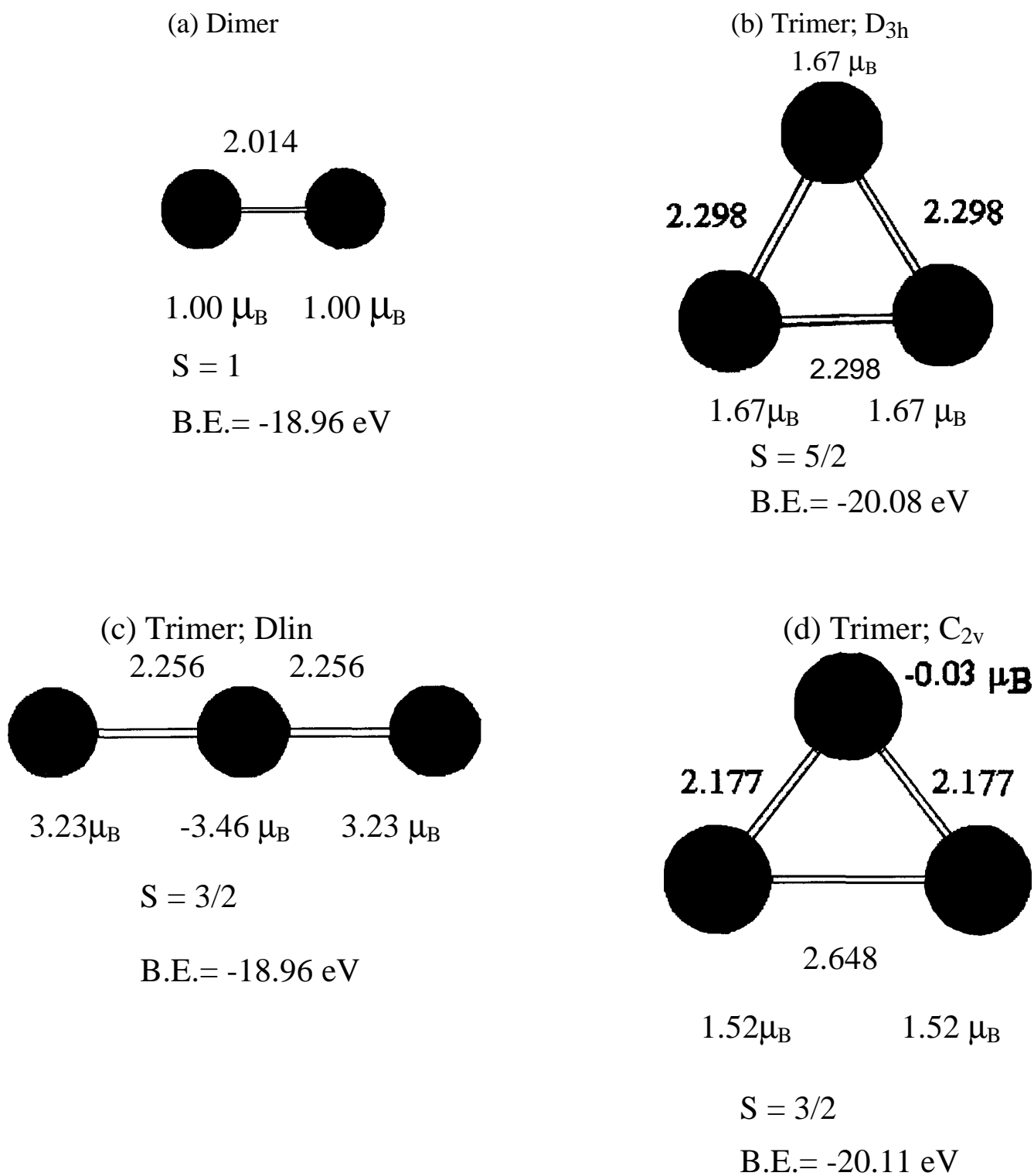


Fig.2 Optimized geometry for Tc dimer and trimers. B.E. is the binding energy. The bond length in \AA is indicated.

The most stable structure for the Tc trimer has the C_{2v} structure (d). However, the second most stable structure in D_{3h} symmetry (b) has the almost the same B.E. energy with that in the C_{2v} structure. The less stable cluster in linear structure (c) showed strong antiferromagnetic character. Since the spin states are different for these isomers, it is expected that the magnetic property of Tc is very sensitive to the geometry of clusters.

References.

1. K. Kimura, *Phase Transitions*, **24-26**, 493 (1990).
2. W. A. de Heer, *Rev. Mod. Phys.*, **65**, 611 (1993)
3. I. M. L. Billas, A. Châtelain, W. A. de Heer, *Science*, **265**, 1682 (1994); J. A. Alonso, *Chem. Rev.*, **100**, 637 (2000)
4. M. Brack, *Rev. Mod. Phys.*, **65**, 677 (1993); H. Haberland (Ed.), "*Clusters of Atoms and Molecules*", Springer-Verlag, Berlin Heidelberg (1994).
5. A. Kant, S. Lin, and B. Strauss, *J. Chem. Phys.*, **49**, 1983 (1968); C. A. Baumann, R. J. Van Zee, S.V. Bhat, and W. Weltner, Jr., *J. Chem. Phys.*, **78**, 190 (1983); N. Fujima and T. Yamaguchi, *J. Phys.Soc. Jpn.*, **64**, 1251 (1995); S. K. Nayak and P. Jena, *Chem. Phys. Lett.*, **289**, 473 (1998).
6. M. R. Pederson, F. Reuse and S. N. Khanna, *Phys. Rev. B*, **58**, 5632 (1998).
7. A.Klyagina,; V.Fursova, A.Levin; G.Gutsev, *Dokl. Akad. Nauk SSSR.*, **292**, 122 (1987).
8. Release 2.3, *Scientific Computing & Modelling, Vrije Universiteit; Chemistry Department, De Boelelaan 1083; 1081 HV Amsterdam; The Netherlands*, e-mail adf@chem.vu.nl.