

From: PHYSICS AND CHEMISTRY OF SMALL CLUSTERS
Edited by P. Jana, B.K. Rao, and S.N. Khanna
(Plenum Publishing Corporation, 1987)

ANALYSIS OF THE ELECTRONIC PROPERTIES OF SMALL NIOBIUM CLUSTERS

Tomas Wahnström, Arne Rosén, and Tapio T. Rantala*

Department of Physics, Chalmers University of Technology
and University of Göteborg, S-412 96 Göteborg, Sweden

*Department of Physics, University of Oulu
SF-90570 Oulu 57, Finland

ABSTRACT

The electronic structures of small niobium clusters have been calculated within the local spin density approximation using the LCAO method. The calculations were done for optimized number of interaction bonds at the bond length in the bulk and a bond length assuming to be valid for the dimer. The changes in the Fermi energy is found to be more smooth as a function of cluster size compared with similar calculations for cobalt clusters. This may indicate that the change in reactivity for hydrogen chemisorption on niobium clusters as a function of cluster size is not a pure electronic structure effect but geometrical.

INTRODUCTION

After the access to modern computers molecular cluster calculations within different approximations have been performed to evaluate the electronic structures of bulk materials and different well characterized surfaces ¹⁻³. In these works much efforts have been directed to extend the calculations to bigger clusters in order to better model the electronic properties of the bulk material or an extended surface. The new technique of producing small clusters of virtually any element ⁴ has however resulted in a growing interest also for theoretical studies of molecular clusters of small and medium size ⁵⁻⁷. The new experimental data open a possibility for detailed studies of the gap between atoms or small molecules and the bulk by the successive addition of atoms to the clusters ⁸⁻¹¹. Further, the experimentally observed irregular behaviour of abundances in photoionization mass spectra ¹², ionization potentials ¹³, stability etc. as a function of cluster size have made the research on clusters a real challenge for the theoreticians.

Studies on transition metal clusters open another dimension of research due to the technological use of these elements in commercial catalysts and as model systems for applied and basic surface research ¹⁴⁻¹⁷. Of particular interest and very challenging for the theoreticians are the recent observations ^{4,18-22} of the strong variation in reactivity as a function of cluster size for adsorption of D₂, O₂, H₂S and N₂ on some transition element clusters. Copper clusters, for example, were found to be quite inert to D₂, while the activity for hydrogen chemisorption changed quite dramatically as a function of the number of atoms for clusters of cobalt and niobium. It is for example

known from surface studies²³ that adsorption of tungsten on different tungsten surfaces give a change of the workfunction which could be compared with the change of ionization thresholds observed between neighbouring metal clusters¹³. Selective behaviour of reactivity of species on different surfaces of the same type of element have also been found in surface studies²⁴. If however, this dramatic change in reactivity for clusters of Nb is due to electronic or geometric structure is still an open question²⁵. However, the trends in reactivity for the transition elements are quite similar to the trends in hydrogen chemisorption on transition metal surfaces as recently summarized by Scillard and Hoffmann²⁶ and Nordlander et al.²⁷. One would therefore expect that the different models for chemisorption, which with great success have been used in surface physics would be applicable for reaction studies of metal clusters^{17,28-31}. Recently, we evaluated the electronic structures of small cobalt clusters³² and found a striking correlation between the cluster size dependence of the Fermi energy, and the magnetic moments to the experimentally observed reactivity of hydrogen chemisorption. We have now extended these type of calculations to clusters of niobium for which also ionization thresholds have been measured quite recently³³.

COMPUTATIONAL APPROACH

The electronic structures of the small niobium clusters presented in this work were calculated within the local-density approximation^{34,35} with the spin-polarized exchange correlation potential by von Barth and Hedin³⁶. A variational method is used to find the molecular wave functions which are determined within the LCAO method with numerical basis functions. The one electron equations are solved within the self-consistent multipolar (SCM) method³⁷ with a multipole expansion in $l \leq 2$ in addition to the occupation charges calculated in the self consistent charge method³⁸. The basis functions have been generated from a free atom Nb $4d^45s^15p^0$ configuration with the addition of $4d$, $5s$ and $5p$ wave functions generated from a free ion Nb^{4+} with the $4d^15s^05p^0$ configuration. This type of basis has in calculations for Nb_2 ³⁹ been found to be variationally better compared with the use of a neutral atom basis consisting of occupied and virtual orbitals.

The conformation or the geometry of small Nb clusters is not known and the calculations of all the clusters were performed with the bond-distance of the bulk⁴⁰, $d(Nb-Nb) = 5.4$ a.u. However, in order to test the sensitivity of the electronic structure and particularly the properties of levels close to the Fermi level calculations were also done for a bond-distance of $d(Nb-Nb) = 3.97$ a.u. which is close to the equilibrium value found by Walch and Bauschlicher⁶ in extensive CASCF calculations. Calculations for bond distances of the two extremes are therefore expected to show the general trends of the electronic structure for these niobium clusters.

Optimization of the geometry by minimization of the total energy would be highly desirable but would lead to too extensive calculations for the series of clusters treated in this work. Nb form in the bulk a bcc structure which in a molecular cluster calculation can be treated with Nb_9 and Nb_{15} clusters including the nearest and second nearest neighbor atoms. To investigate the electronic structure for the small clusters calculations were done for clusters with the optimum number of bonds of equal length which can be done within the same symmetry group C_{3v} . Nb_3 is in our calculations treated as a triangle with extension to a pyramid and double pyramid for Nb_4 and Nb_5 , respectively. Nb_6 has been calculated as a double pyramid with four atoms in a plane, one below and one above the plane which geometry can also be oriented to C_{3v} symmetry. This geometry has then been extended to the bigger clusters up to Nb_7 and Nb_8 and Nb_{10} . The calculation for the Nb_9 was done in C_{4v} symmetry in bcc structure since we found it difficult to

construct, such a cluster in C_{3v} symmetry. The levels close to the Fermi level have been occupied with a Fermi-Dirac distribution corresponding to a temperature of about 160 K or a thermal energy of about 14 meV.

RESULTS AND DISCUSSION

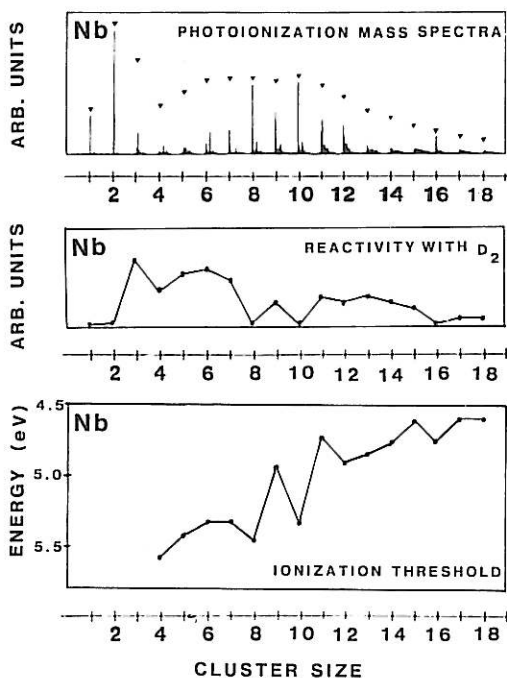


Fig. 1. A schematic overview of reactivity²¹ and ionization threshold³³ for small Nb_N clusters.

minimization of the total energy for the different clusters. It is however from the experimental values difficult to derive some absolute number of the relative reactivity for the different clusters.

Recently³⁹ we investigated changes in the electronic structure of Nb_2 for different bond lengths and found that the energy of the last occupied level changed of the order of 0.4 eV, when the bond length was changed by ± 0.2 a.u. Calculations for reasonable geometries and a fixed bond length is therefore expected to show some indication of abrupt changes of the electronic structure by the addition of an atom to a smaller cluster. Molecular one electron eigenvalues for the Nb_N clusters for $N=1-10$ calculated for a bond length of the dimer⁶ is shown in Fig. 2. We notice how the position of the last occupied levels i.e. the Fermi level generally shifts up for the bigger clusters except for the Nb_4 , Nb_8 and Nb_{10} clusters for which the trend is broken. The general trends of the experimental values seem therefore to be reproduced by these theoretical values. In order to get some indication of the sensitivity of the electronic structure as a function of bond length calculations were done for the bond distance in the bulk. In this case a more smooth change take place as a function of cluster size although there is some indication of small changes for the Nb_4 , Nb_8 and Nb_{10} clusters.

In the recent calculations for Co clusters the majority up-spin was found to become stabilized and the minority down-spin to be destabilized for clusters up to the size of five atoms. For Co_6 , which was the first big

The main intention with these calculations is to find some model which can explain the dramatic change of observed cluster size dependence of hydrogen chemisorption on small Nb microclusters which for convenience is displayed in the upper part of Fig. 1. The activity for hydrogen chemisorption is given by the difference in intensity of the photoionization mass spectra between the beam of pure Nb and the beam seeded with D_2 as visualized in the middle of Fig. 1. The recently measured photoionization thresholds³³ for these small clusters are displayed in the lower part of Fig. 1. We notice how the clusters Nb_8 and Nb_{10} which are inert for hydrogen chemisorption have higher ionization thresholds compared with the neighbouring reactive ones. This does not hold for Nb_4 which is reactive but has also a high ionization threshold. Whether, the changes in ionization thresholds and reactivity as a function of cluster size is due to changes of the electronic or in geometrical structure requires extensive

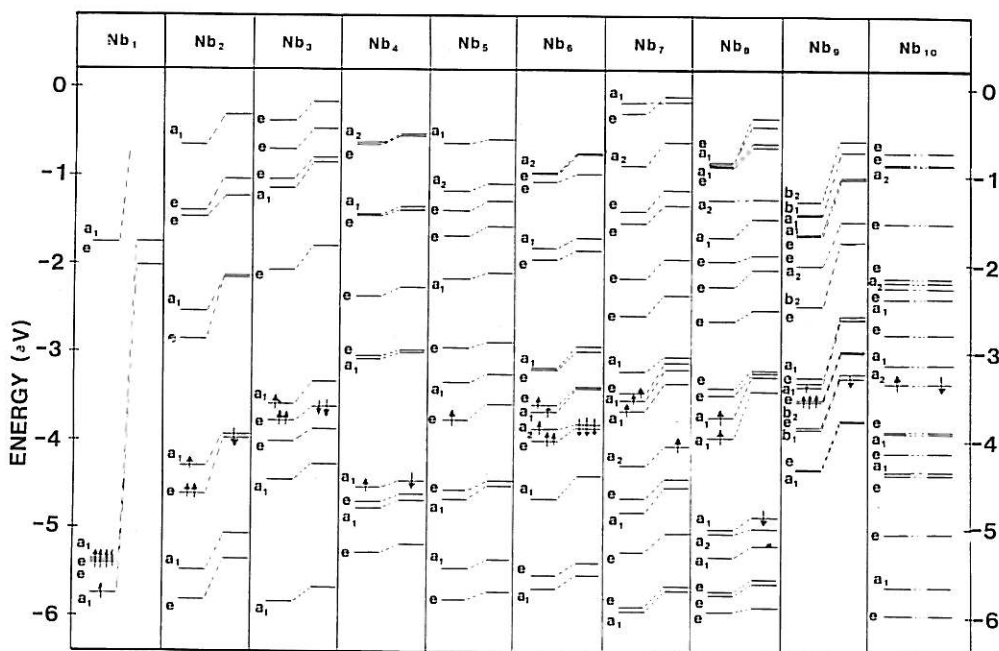


Fig. 2. Energy level diagram of the molecular one electron levels in the Nb_N clusters for N = 1-10 calculated for a bond length of 3.97 a.u. The labeling of the levels refer to C_{3v} symmetry except for Nb₉ which is treated in C_{4v} symmetry. The levels to the left are those with majority up-spin while those to the right are those with minority down-spin. Occupancies of the last occupied levels are marked with arrows.

cluster inert for hydrogen chemisorption, the position of the last occupied levels of up and down spin were located at the same energy. The exchange splitting for the Nb clusters seem to be considerably smaller and very close to zero for some of the clusters which are inert to hydrogen chemisorption as Nb₄, Nb₁₀.

A commonly discussed feature in these type of calculations has been the relative importance of d and s electrons. In order to investigate this further for the Nb clusters the molecular orbitals were analyzed through a Mulliken orbital and spin analysis in terms of our basis functions. In this analysis the contribution of the same orbital symmetry for the neutral and ionized basis have been added together. The net spindensity from the 4d wavefunctions are reduced to less than one electron for clusters bigger than three while the contribution from the 5s wavefunctions vary between 0.4-0.0 electrons for these clusters. The net spin density contribution from all basis functions add up to zero for the Nb₄ and Nb₁₀ clusters.

The models for chemisorption^{17,28-31} of H₂ on transition metal clusters require participation of an unfilled d-shell and a reduction of the 5s contribution. Our spin-polarized calculations seem to indicate that chemisorption of molecules on small transition metal clusters require a net but not too big spin contribution which holds for Nb₃, Nb₅₋₇, and Nb₉. Breaking of the log² bond in H₂ requires a transfer of

electrons to the metal cluster followed by a backdonation to the anti-bonding σ_u levels of H_2 . The possibility of this charge transfer to take place needs the opening of channels for both spin directions in the HOMO as well as LUMO levels of the substrate. In the case that the HOMO levels of the substrate were filled as in the case of Nb_4 and Nb_{10} would mean that the electrons have to be transferred to the LUMO levels. The efficiency of the different charge transfers will depend on the energy spacing of the HOMO and LUMO levels of the substrate as well as on the symmetries of the HOMO and LUMO levels of the substrate and adsorbate which with great success has been used in the interpretation of CO chemisorption on transition metal complexes and surfaces.⁴¹⁻⁴³ These require more detailed calculations on the combined systems which are now in progress.

ACKNOWLEDGEMENTS

The authors wish to thank P. Siegbahn and various colleagues in the molecular and surface physics groups at Chalmers for enlightful discussions. This work has been supported by the Swedish National Research Council (NFR), Joint Committee of the Nordic National Science Research Council (NOS-N) and Nordic Research Courses (Nordic Council of Ministers).

REFERENCES

- 1.
2. R.P. Messmer in "The Physical Basis for Heterogeneous Catalysis", Eds. E. Drauglis and R.I. Jaffee, Plenum, New York (1975).
3. T.N. Rhodin, G. Ertl, "The Nature of the Surface Chemical Bond", North Hollan, Amsterdam (1979).
4. R.E. Smalley, in "Comparison of Ab Initio Quantum Chemistry with Experiment for Small Molecules, the State of the Art", Ed. R.J. Bartlett, D. Reidel Publ. Comp. Dordrecht, Holland (1985). In this review references are given to experimental works on clusters from a number of groups.
5. W. Weltner, Jr. and R.J. Van Zee, Ann. Rev. Phys. Chem. 35, 291 (1984). References are given to a number of calculations.
6. S.P. Walch and C.W. Bauschlicher, Jr., in "Comparison of Ab Initio Quantum Chemistry with Experiment for Small Molecules, the State of the Art", D. Reidel Publ. Comp. Dordrecht, Holland (1985).
7. B. Delley, D. Ellis, A. Freeman, E. Baerends and D. Post, Phys. Rev. B27, 2132 (1983).
8. D.E. Ellis, B. Delley, in "Local Density Approximations in Quantum Chemistry and Solid State Physics", Eds. J.P. Dahl and J. Avery, Plenum Publ. Corp. (1984).
9. B.K. Rao and P. Jena, J. Phys. F: Met. Phys. 16, 461 (1986).
10. J. Koutecky, G. Pacchioni, G.H. Jeung, E.C. Hass, Surf. Sci. 156, 650 (1984).
11. J.L. Martins, J. Buttet, R. Car, Phys. Rev. B31, 1804 (1985).
12. W.D. Knight, K. Clemenger, W.A. de Heer, W.A. Saunders, M.Y. Chou, and M.L. Cohen, Phys. Rev. Lett. 52, 2141 (1984).
13. R.L. Whetten, D.M. Cos, D.J. Trevor, A. Kaldor, Phys. Rev. Lett. 54, 1494 (1985); J. Phys. Chem. 89, 566 (1985).
14. D.A. King, D.P. Woodruff, "The Chemical Physics of Solid Surfaces and Heterogeneous Catalysis, Vol. 1. Clean Solid Surfaces, Vol. 2. Adsorption at Solid Surfaces, Vol. 3. Chemisorption Systems, Vol. 4. Fundamental Studies of Heterogeneous Catalysis". Elsevier, Amsterdam (1983).
15. G.A. Somorjai, Science 227, 902 (1985).
16. E. Shustorovich, R.C. Baetzold, Science 227, 876 (1985).

17. E. Shustorovich, R.C. Baetzold, E.L. Muetterties, *J. of Phys. Chem.* 87, 1100 (1983).
18. S.J. Riley, E.K. Parks, G.C. Nieman, L.G. Pobo, S. Wexler, *J. Chem. Phys.* 80, 1360 (1984).
19. S.C. Richtsmeier, E.K. Parks, K. Lin, L.G. Pobo, S.J. Riley, *J. Chem. Phys.* 82, 3659 (1985).
20. E.K. Parks, K. Lin, S.C. Richtsmeier, L.G. Pobo, S.J. Riley, *J. Chem. Phys.* 82, 5470 (1985).
21. M.E. Geusic, M.D. Morse, R.E. Smalley, *J. Chem. Phys.* 82, 590 (1985).
22. R.L. Whetten, D.M. Cox, D.J. Trevor, A. Kaldor, *Phys. Rev. Lett.* 54, 1494 (1985); *J. Phys. Chem.* 89, 566 (1985).
23. K. Besocke and H. Wagner, *Phys. Rev.* B8, 4597 (1973); *Surf. Sci.* 53, 351 (1975).
24. G.A. Samorjai, N.D. Spencer, and R.C. Schoonmaker, *J. Catal.* 74, 129 (1982).
25. J.C. Philips, *J. Chem. Phys.* 84, 1951 (1986).
26. J.E. Scillard, R. Hoffmann, *J. Am. Chem. Soc.* 106, 2006 (1984). This work gives references to experimental and theoretical works on metallorganic compounds and surfaces.
27. P. Nordlander, S. Holloway, J.K. Norskov, *Surf. Sci.* 136, 59 (1984). This work gives references to earlier studies of hydrogen chemisorption on surfaces.
28. J.K. Norskov, A. Houmøller, P.K. Johanssen, and B.I. Lundqvist, *Phys. Rev. Lett.* 46, 257 (1981).
29. P. Madhavan and J.L. Whitten, *J. Chem. Phys.* 77, 2673 (1982).
30. P.E.M. Siegbahn, M.R.A. Blomberg, and C.W. Bauschlicher, *J. Chem. Phys.* 81, 1373 (1984).
31. J. Harris, S. Andersson, *Phys. Rev. Lett.* 55, 1583 (1985).
32. A. Rosén and T.T. Rantala, *Z. Phys.* (1986).
33. R.L. Whetten, M.R. Zakin, D.M. Cox, D.J. Trevor and A. Kaldor, *J. Chem. Phys.* 85, 1697 (1986).
34. P. Hohenberg, W. Kohn, *Phys. Rev.* 136, B864 (1964).
35. W. Kohn, L.J. Sham, *Phys. Rev.* A140, 1133 (1970).
36. U. von Barth, L. Hedin, *J. Phys.* C5, 1629 (1972).
37. B. Delley, D.E. Ellis, *J. Chem. Phys.* 76, 1949 (1982).
38. A. Rosén, D.E. Ellis, H. Adachi and F.W. Averill, *J. Chem. Phys.* 65, 3629 (1976).
39. A. Rosén and T. Wahnström, this volume.
40. J.C. Slater, "Quantum Theory of Molecules and Solids", Vol. 2, McGraw-Hill Book Comp., New York (1965).
41. G. Blyholder, *J. Phys. Chem.* 68, 2772 (1964).
42. E.W. Plummer, W. Eberhardt, *Adv. Chem. Phys.* 49, 533 (1982).
43. Sung Shen-Shu and R. Hoffmann, *J. Am. Chem. Soc.* 107, 578 (1985).