Electronic structure calculations of small Al$_n$ ($n = 2$–8) clusters *

T. Bastug, W.D. Sepp, B. Fricke, D. Heinemann, and D. Kolb

Department of Physics, University of Kassel, W-3500 Kassel, Federal Repulic of Germany

Abstract. The electronic states of small Al$_n$ ($n = 2$–8) clusters have been calculated with a relativistic ab-initio MO-LCAO Dirac-Fock-Slater method using numerical atomic DFS wave-functions. The excitation energies were obtained from a ground state calculation of neutral clusters, and in addition from negative clusters charged by half an electron in order to account for part of the relaxation. These energies are compared with experimental photo-electron spectra.

PACS: 31.20.Ej; 36.40.+d

1. Introduction

In recent years clusters have become increasingly an interesting field of physics because they present a link between atoms and solids. Atoms are understood relatively well and can be described with high precision, whereas solids are still far beyond the scope of such ab initio descriptions. Clusters bridge this gap. Non-relativistic and relativistic (in perturbation theory) quantum chemical methods on HF or HF-CI level [1–8] or the Local Spin Density (LSD) approaches [9–12] using all electron (AE) or Effective Core (ECP) potentials can be applied for small n clusters (n = number of atoms in the cluster) while typical solid state methods, like jellium calculations [13], are suited for large n. ECP HF-CI calculations of Koutecký et al. [7–8] on structure information for low n clusters show, that clusters with a reasonably low number of atoms display astonishingly varying formation probabilities which reflects their stability in certain geometrical configurations. The structural, binding, and chemisorption properties of Al clusters have been investigated by L.G.M. Pettersson [14–15] and Upton [16].

In this work we have investigated the electronic structure of small Al$_n$ ($n = 2$–8) clusters with a fully relativistic all electron MO-LCAO-DFS method. This method is

* Dedicated to Prof. Dr. P. Kienle on the occassion of his 60th birthday

based on the solution of the Dirac equation. The spin-orbit splitting and the Darwin term, which usually have to be added to a non-relativistic calculation in order to include major relativistic effects, are taken care of automatically.

Using the electronic structure calculated here we attempt an interpretation of the photo-electron spectra observed for low n Aluminum clusters. The goal is to find an applicable method to actually calculate atomic clusters with many heavy constituents where relativistic effects may play an important role.

2. Method

The calculations are based on the Molecular Orbital Linear Combination of Atomic Orbitals (MO-LCAO) Dirac-Fock-Slater method. We will restrict ourselves to Al$_n$ clusters ($n = 2$–8) and use the Self Consistent Charge Dirac-Fock-Slater (SCF-DFS) method, originally developed by Rosén et al. [19–20] for molecular systems with many atoms.

We start with the relativistic one-electron equations:

$$[\mathbf{t}_i + \mathbf{V}_{\mathrm{eff}}(\mathbf{r})] \; \Psi_i(\mathbf{r}) = \varepsilon_i \, \Psi_i(\mathbf{r}) \tag{1}$$

where

$$\mathbf{V}_{\mathrm{eff}}(\mathbf{r}) = \mathbf{V}_n(\mathbf{r}) + \mathbf{V}_e(\mathbf{r}) + \mathbf{V}_{\mathrm{ex}}(\mathbf{r}) \tag{2}$$

and $\mathbf{t}$ is the relativistic kinetic energy operator. The three terms of the potential are: the external potential from the nuclei $\mathbf{V}_n$, the direct electronic Coulomb contribution $\mathbf{V}_e$, and the exchange potential of other electrons $\mathbf{V}_{\mathrm{ex}}$, being approximated by a local charge density function through Slater's X_α method with the exchange parameter α equal to 0.70.

$$\mathbf{V}_{\mathrm{ex}}(\mathbf{r}) = -3\alpha \, [(3/8\pi) \, \rho(\mathbf{r})]^{1/3} \tag{3}$$

A variational method is used to find the molecular wave-functions, given as a linear combination of symmetry orbitals constructed from relativistic numerical atomic basis functions. The Dirac-Fock-Slater and overlap matrix

elements were evaluated by the Discrete Variational Method (DVM) [17–18]. The molecular potential (2) is determined in successive iterations from Mulliken orbital population analysis [21]. Self-consistency is reached when the changes of the orbital occupation numbers between successive iterations are sufficiently small.

We obtained the geometrical structures of the Al_n from Na clusters [7], by re-scaling distances with the ratio of the radial maxima of Na and Al valence orbitals. Structures for Al_2 to Al_6 clusters were directly calculated in [14–15]; their atomic distances agree within 0.3 a.u. with those used for our calculations. Changes of this order of magnitude in the geometry do not affect the final results within our numerical accuracy.

Atomic wave functions ($1s_{1/2}, 2s_{1/2}, 2p_{1/2}, 2p_{3/2}, 3s_{1/2}, 3p_{1/2}, 3p_{3/2}, 3d_{3/2}, 3d_{5/2}$) (calculated numerically by an atomic DFS Code) form the basis. In order to construct the d-atomic basis functions they are calculated for an Al atom which is partly ionized. This leads to outer shell wavefunctions with maxima in the valence bond region of the molecule. Moreover, it accounts for the fact, that the electronic charge needed there leaves effectively charged atomic regions.

3. Results and discussion

We compared the results of our calculations with the experiment of G. Ganteför et al. [22] for Al_n^- clusters. In this experiment the anion clusters are excited by a 3.68 eV laser. This can be interpreted as an excitation of the anion into a virtual state which results directly in the emission of a photo-electron and a remaining neutral cluster in either the ground- or excited state (visualized in Fig. 1 as an example). The maximal possible energy of the photo-electrons corresponds to the ground state of the neutral clusters. Photo-electron energies smaller than the maximal value reflect the excited states of the neutral clusters. On the right hand side of Fig. 1 we demonstrate this interpretation for the experimental curve of Al_2.
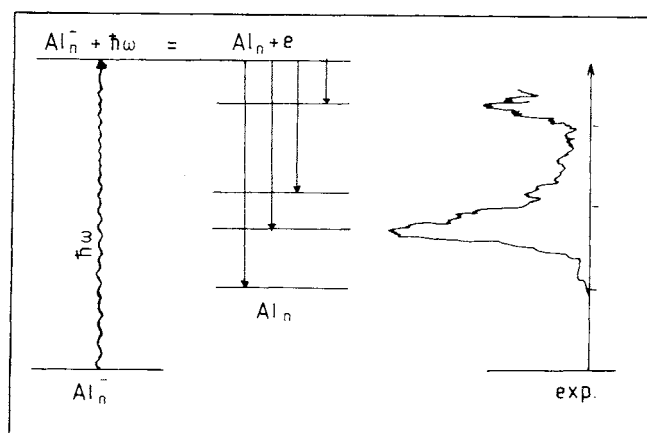
From a theoretical point of view the excitation energy of any quantum mechanical system is the difference between the total energy of the ground state and the excited state in question. This statement is not only true for differences between ground and excited state of the neutral clusters, but also for the differences between ground states of anions and neutral clusters. However, due to insufficient accuracy of the numerical method none of the interesting values can actually be calculated in this way. Total energies are large numbers with a certain error, thus the differences between these large numbers usually do not lead to good results. One possible way to circumvent this problem is to use an interpretation analog to Koopmans' theorem. The energy eigenvalues of the neutral systems Al_n are given in Fig. 2. If we use the so called transition state procedure with half-filled outer valence shells as suggested by Slater [23–24] we get energy eigenvalues in the outer shell which, in first order, can be used as ionisation energies from these shells. The energy eigenvalues of negative $Al_n^{-1/2}$ clusters (charged by half an electron) are given in Fig. 3. Occupied and unoccupied Molecular-Orbital (MO) levels are shown as full and dotted lines respectively. For simplicity of the figures non-relativistic group notations are used for the MO levels. A MO level is presented with na_m^i, where a_m describes the irreducible representation in the group, n is a counting label for the energetically ordered orbitals in this representation, and i is occupation of the orbital. We calculate the possible differences between the filled one-electron levels and all unfilled ones (Figs. 2, 3) within the few-eV energy range and get in first order the possible excitations. These values are given below the corresponding experimental spectra for ground state and negative clusters in Figs. 4, 5, respectively. As the absolute theoretical ionisation energies are not accurate enough (see above), we used the experimental threshold energy of the anion clusters as reference points. From this value we determined the relative position of the excited states.

The theoretical results are in reasonable agreement with experimental results. For Al_2^-, Al_5^-, Al_6^- and Al_8^- clusters the agreement is quite good. Of course, the line widths need to be folded in. Some of the theoretical structures are not reproduced in the experiment. The reason may very well be that the selection rules were neglected in our interpretation and transition probabilities were not calculated here. We will attempt however, to incorporate this in future calculations.

4. Conclusion and outlook

Summarizing we can say that the Dirac-Fock-Slater approximation in our relativistic ab initio SCC cluster calculations leads to reasonably good results for the excited states of small neutral clusters. However the calculations still have a number of deficiencies, the most serious being the inability to calculate the total energy accurate enough to extract ionisation or excitation energies directly. Some results from very precise Finite Difference [25] and Finite Element [26] fully numerical calculations make us believe that these deficiencies are caused by numerical inaccura-
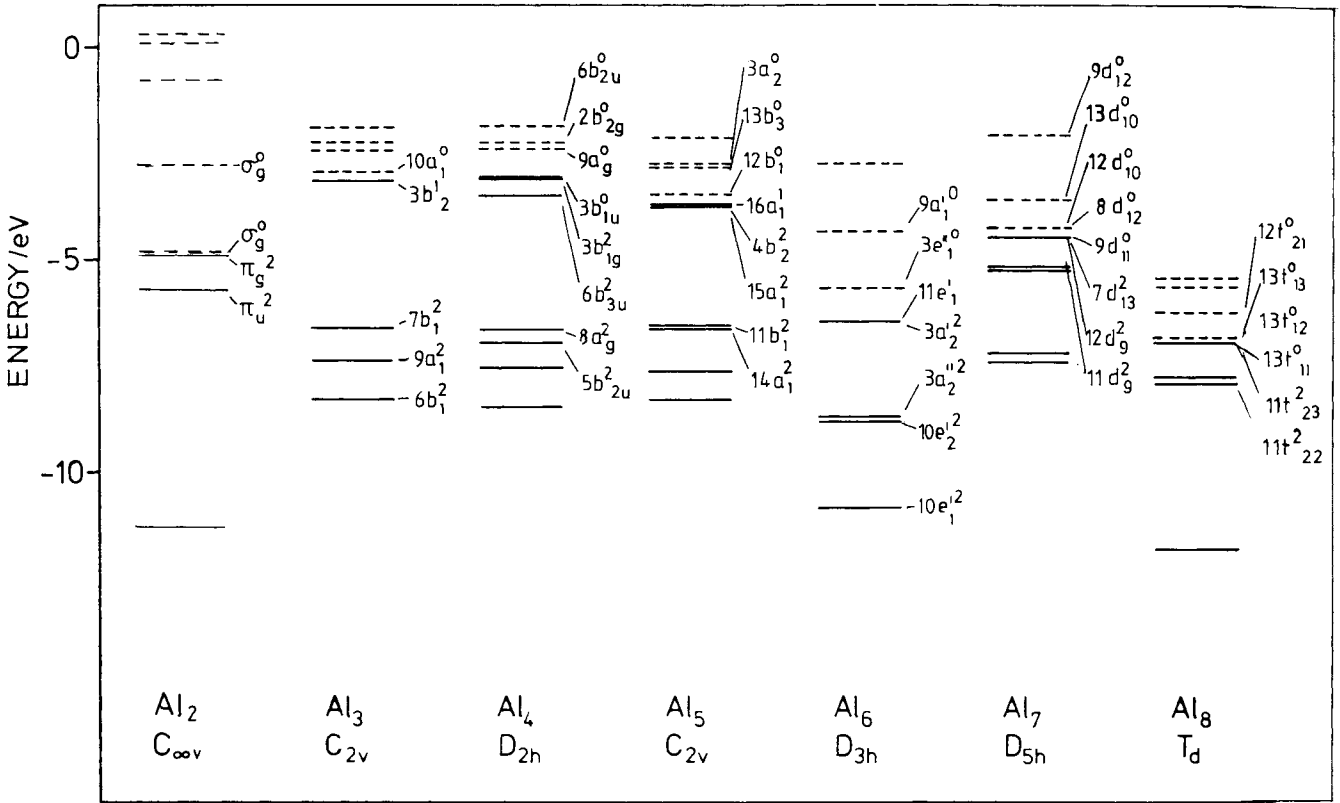

Fig. 1. Schematic energy level diagram of the transition of the anion cluster to the ground or excited states of the neutral cluster via absorption of a 3.46 eV photon and emission of a photo-electron. To the right we demonstrate the photo-electron spectra observed as well as the scaling used by the experimental group

Fig. 2. Eigenvalues of neutral clusters in the ground state. Occupied and unoccupied levels are shown by full and dotted lines, respectively. The non-relativistic group notations are used
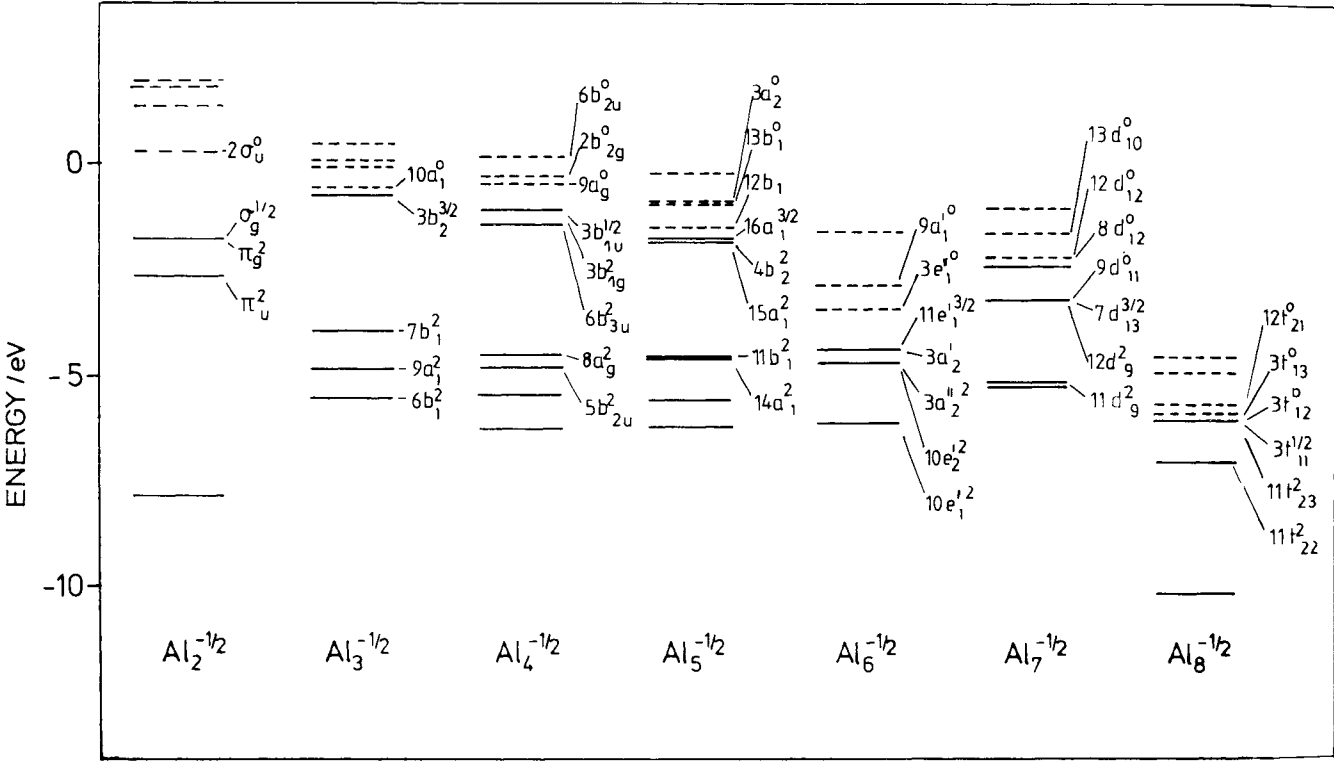
Fig. 3. Eigenvalues of negative charged clusters $Al_n^{-1/2}$ calculations. Occupied and unoccupied levels are shown by full and dotted lines respectively. The non-relativistic group notations are used
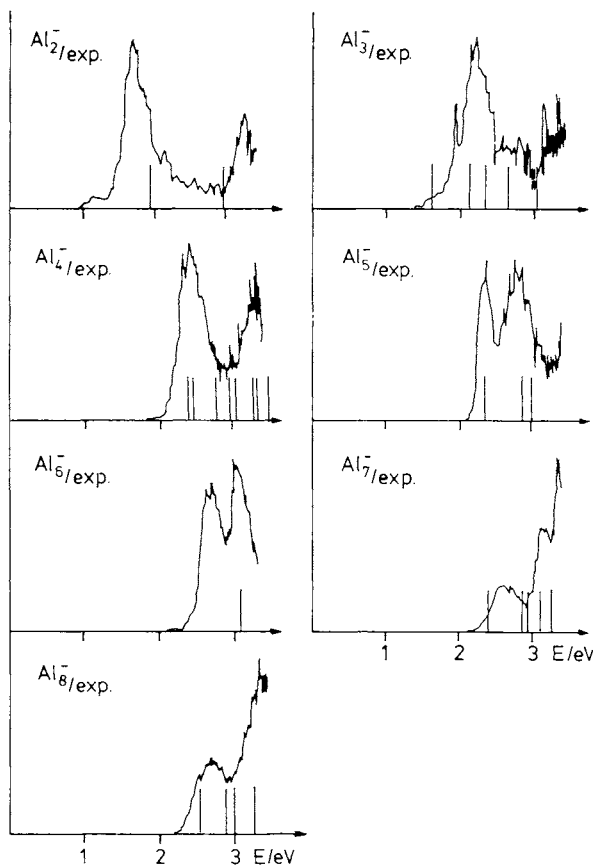
Fig 4. Comparison of excitation energies of ground state calculations with experimental spectra
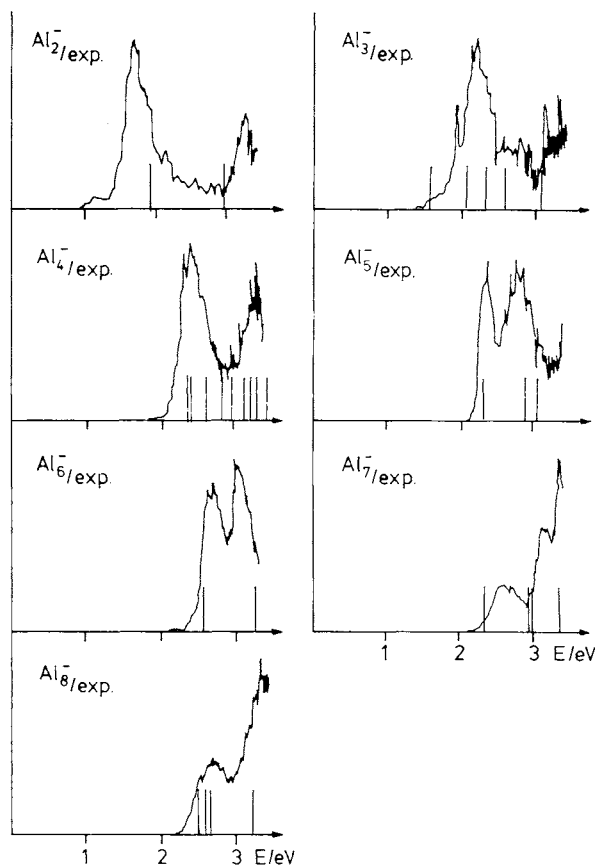

Fig. 5. Comparison of excitation energies of negative charged cluster calculations with experimental spectra

cies and basis set errors rather than the DFS many-body approximation.

As a next step we will try to improve the absolute accuracy of the calculations and to compute the transition strengths in the dipole approximation within the single-particle picture.

The present approach has the advantage that clusters including very heavy atoms can be treated. The DFS-SCC method used here is presently the only method permitting ab initio calculations up to very heavy systems see e.g. Rosén et al. [27]. In a forthcoming paper we would like to demonstrate this fact now that the method used has proven to give reasonable results.

References

1. Strömberg, D., Wahlgreen, U.: Chem. Phys. Lett. **169**, 109 (1990)
2. Strömberg, A., Gropen, O., Wahlgreen, U.: J. Chem. Phys. **80**, 1593 (1984)
3. Wahlgreen, U., Pettersson, L.G.M., Siegbahn, P.: J. Chem. Phys. **90**, 4613 (1989)
4. Balasubramanian, K.: Chem. Rev. **89**, 1801 (1989)
5. Balasubramanian, K.: J. Chem. Phys. **89**, 6310 (1988)
6. Boustani, I., Koutecký, J.: J. Chem. Phys. **88**, 5657 (1988)
7. Koutecký, V.B., Fantucci, P., Koutecký, J.: Phys. Rev. B**37**, 4369 (1986)
8. Fantucci, P., Koutecký, J.: Chem. Rev. **86**, 939 (1986)
9. Baykara, V.A., McMaster, B.N., Salahub, D.R.: Mole. Phys. **52**, 891 (1984)
10. Fournier, R., Andzelm, J., Salahub, D.R.: J. Chem. Phys. **90**, 6371 (1989)
11. Snijders, J.G., Bearends, E.J., Ros, P.: Mole. Phys. **38**, 1909 (1979)
12. Versluis, L., Ziegler, T.: J. Chem. Phys. **88**, 322 (1988)
13. Ekard, W.: Phys. Rev. B**29**, 1558 (1984); Martin, T.P., Bergmann, T., Göhlich, H., Lange, T.: Phys. Rev. Lett. **65**, 748 (1990): Penzar, Z., Ekardt, W.: Z. Phys. D – Atoms, Molecules and Clusters **17**, 69 (1990)
14. Bauschlicher, Jr., C.H., Pettersson, L.G.M.: J. Chem. Phys. **84**, 2226 (1986)
15. Pettersson, L.G.M., Bauschlicher, Jr., C.H., Halicioglu, T.: J. Chem. Phys. **87**, 2205 (1987)
16. Upton, T.H.: Phys. Rev. Lett. **56**, 2168 (1986)
17. Ellis, D.E., Painter, G.S.: Phys. Rev. B**2**, 2887 (1970)
18. Awerill, F.W., Ellis, D.E.: J. Chem. Phys. **59**, 6412 (1973)
19. Rosén, A., Ellis, D.E.: J. Chem. Phys. **62**, 3039 (1975)
20. Rosén, A., Ellis, D.E., Adachi, H., Awerill, F.W.: J. Chem. Phys. **65**, 3629 (1976)
21. Mulliken, R.S.: J. Chem. Phys. **23**, 1833 (1955)
22. Ganteför, G., Gausa, M., Meiwes-Broer, K.H., Lutz, H.O.: Z. Phys. D – Atoms, Molecules and Clusters **9**, 253 (1988)
23. Slater, J.C.: Quantum theory of moleculs and solids V. I and II. New York: McGraw-Hill 1963
24. Slater, J.C.: The calculation of molecular orbitals. New York: Wiley 1979
25. Laaksonen, L., Sundholm, D., Pyykkö, P.: Comp. Phys. Rep. **4**, 313 (1986)
26. Heinemann, D., Fricke, B., Kolb, D.: Phys. Rev. A**38**, 4994 (1988)
27. Rosén, A., Grundevik, P., Morovic, T.: Surf. Sci. **95**, 477 (1975); Rosén, A., Westin, E., Matthias, E., Nielsen, H.B., Reif, J.: Phys. Scr. T**23**, 184 (1988)