Density Functional Calculations of Structures and Ionization Energies for Heavy Group V Cluster Anions

R. KASCHNER, U. SAALMANN, AND G. SEIFERT

Institut für Theoretische Physik, Technische Universität Dresden, Mommsenstr. 13, D-01062 Dresden, Germany

M. GAUSA

Universität Bielefeld, Fakultät für Physik, D-33615 Bielefeld, Germany

ABSTRACT

The structure and electronic structure of heavy-group V cluster anions (Sb_n^-, Bi_n^-) are calculated with density functional methods within the local spin density approximation (LSDA). The influence of gradient corrections of the exchange and correlation energy is investigated. The calculated vertical and adiabatic ionization energies are in very good agreement with data from photoelectron spectroscopy (PES) for Sb_n^-, whereas the relatively large deviations for Bi_n^- can be reduced by the consideration of relativistic effects in a scalar-relativistic manner. Concerning the structures, a strong similarity to the corresponding P_n^- clusters was found. In particular, the negatively charged pentamers are planar rings (with similarities to the aromatic $[C_5H_5]^-$ anion) with especially high ionization energies. © 1995 John Wiley & Sons, Inc.

Introduction

The structural and electronic properties of small clusters have generated considerable interest in the last years. In particular, the clusters of the elements of the V-th main group are of special interest because in this group the variation of the properties, if going from the lightest to the heaviest members, is large: The group starts with (diatomic molecule forming) nitrogen, goes over phosphorus and arsen with their (structural manifold) insulating solids, and ends with antimony and bismuth, which form metallic modifications. The clusters of the group V elements show plenty of structures, and a key question is the interplay between the geometrical and the electronic structure of these clusters. Especially, phosphorus clusters have been investigated extensively in recent

years [1, 2]; for neutral arsenic and antimony clusters, see e.g., [1, 3].

To gain experimental information about the electronic structure of clusters, e.g., the ionization energies and electron affinities, photoelectron spectroscopy (PES) was shown to be a powerful tool. Measurements of these quantities could have been performed recently, especially for the clusters of the heavier group V elements, i.e., antimony and bismuth [4–6]. For lighter group V clusters, such measurements are more complicated because their ionization energies and affinities are larger (deeper-lying occupied electronic levels). The most detailed measurements exist for the ionization energies of the *anionic* clusters because they have relatively low ionization energies and can be separated easily by electrical and magnetic fields [4–6].

Hence, in this article, we concentrate on the ionization energies of the antimony and bismuth cluster anions, corresponding to the photoelectron process:

$$A_n^- + h\nu \to A_n^0 + e^-.$$
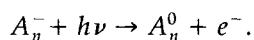
Here, one has to distinguish between the *adiabatic ionization energy* (AIE) and the *vertical detachment energy* (VDE): The VDE is the energy difference between the anionic cluster (in its equilibrium geometry) and the corresponding neutral cluster with the *same* geometry, i.e., for the vertical transition; the AIE is the corresponding energy difference if also the neutral cluster has its relaxed geometry. The AIE is also the (adiabatic) electron affinity of the neutral cluster. In the photoelectron spectrum, the VDE corresponds to the first peak and the AIE is the threshold energy [6].

We calculated these energies (AIE and VDE) by means of a density functional method and compared them with the experiments for Sb and Bi clusters with up to five atoms. For this, we determined and discussed the equilibrium structures of these clusters, which were expected to be similar to the known (from [1]) structures of the corresponding phosphorus clusters. The experimental method and the photoelectron spectra are presented elsewhere [6]. The photoelectron spectra and ionization energies of the pentamer cluster anions have been considered in detail already in [7]. In this article, we focus on the density functional calculations. The density functional method has become now a successful method to calculate also such quantities as ionization energies and affinities [8]. Accurate Hartree–Fock and "post-Hartree–Fock" calculations on anionic antimony and bismuth clusters have been realized only for the dimers [9, 10].

Our density functional calculations, namely, the solution of the Kohn–Sham equations, are done with a localized basis set method (LCAO treatment). This method is described roughly in the section Description of the Method, and the choice of the LCAO basis set and its influence on the accuracy of the results is discussed (for Sb_2) in the section Discussion of the Basis Set.

Density functional calculations can be performed only with an approximate expression for the exchange and correlation energy. The most common approximation is the local density approximation (LDA), or—considering the spin explicitly—the local spin density approximation (LSDA). Great success has been achieved in the calculation of binding energies of molecules and clusters [1] by considering the (so-called) gradient corrections (GC) [11]. Furthermore, for bismuth clusters, relativistic effects should be taken into account. All these corrections and effects are studied in detail for Sb_2^- and Bi_2^- in the section Influence of Gradient Corrections....

In the section Equilibrium Structures..., the calculated equilibrium structures and the adiabatic and vertical ionization energies of the Sb_n^- and Bi_n^- clusters for $n = 2...5$ are summarized. The structures and energies obtained from the density functional calculations are compared with the structures of the corresponding phosphorus clusters and with the values from the PES, respectively. Finally, in the section Size Dependence..., the size dependence of the ionization energies is discussed.

Method of the Calculations

DESCRIPTION OF THE METHOD

We applied the Amsterdam density functional ("adf") program of Baerends et al. [11, 12]: The Kohn–Sham equation is solved with an LCAO ansatz for the one-particle wave function; all integrals are evaluated numerically with Gauss–Legendre-based integration algorithms [13], where the space is separated in a special manner. The densities are fitted to a sum of Slater-type functions to simplify the numerical calculation of the multicenter Coulomb integrals.

For the wave functions, Slater-type orbitals as basis functions were used; we found a basis set

with triple-zeta quality including rather diffuse functions as sufficient for the calculations. The $4d$ function (for Sb) or the $5d$ function (for Bi), respectively, were considered also in the valence basis. The core orbitals up to $4p$ for Sb and $5p$ for Bi were treated as frozen. The basis-set effects are discussed in more detail in the section Discussion of the Basis Set. We used the gradient corrections (GC) of Becke [14] for the exchange part and of Perdew [15] for the correlation part; for a more detailed discussion of these effects, see the sections Discussion of the Basis Set and Influence of Gradient Corrections....

Relativistic effects were studied approximately with a semirelativistic method, which means inclusion of the scalar-relativistic terms (Darwin and mass-velocity term) into the Hamiltonian and neglecting of the spin–orbit coupling. The first-order scalar-relativistic (Pauli) Hamiltonian is diagonalized within the nonrelativistic basis set, using the relativistic core densities of the atoms. Such treatment can reproduce all relativistic "shift" effects (see, e.g., [16]). However, for the calculation of the total energy, this method is still not sufficient; therefore, the relativistic code was not used to determine equilibrium geometries. The equilibrium structures are determined by a geometry optimization using a steepest-descent method. The ionization energies are obtained from the total energy differences of the neutral and anionic clusters. For the VDE, we also used the transition-state method [17]. The differences of the results for VDE from these two treatments are small in comparison with the differences from the gradient corrections or from the LSDA (instead of the common LDA).

DISCUSSION OF THE BASIS SET

Description of the Basis Set

Each basis function consists of a set of Slater-type functions (STFS) describing the (frozen) core states of the atoms and the actual basis for the LCAO ansatz. The exponents for these STFS are for the double-zeta basis:

Sb: $5s$ 1.70 2.85 $5p$ 1.20 2.25 ($4d$ 3.05 5.45)
Bi: $6s$ 1.85 3.15 $6p$ 1.30 2.45 ($5d$ 3.25 5.75).

In the triple-zeta basis, one more exponent is added:

Sb: $5s$ 1.50 2.30 3.40 $5p$ 1.00 1.60 2.65 ($4d$ 2.45 3.70 5.70)

Bi: $6s$ 1.55 2.35 3.55 $6p$ 1.10 1.80 2.95 ($5d$ 2.45 3.90 6.15).

Such a triple-zeta basis contains rather diffuse functions. Furthermore, an auxiliary basis from STFS for the density expansion is used. For more details, see [12].

We used the following basis sets: I. Double-zeta quality with frozen core orbitals up to $4d$; II. double-zeta quality with frozen core orbitals up to $4p$; III. triple-zeta quality with frozen core orbitals up to $4d$; and IV. triple-zeta quality with frozen core orbitals up to $4p$.

Test of the Basis Set

To test the quality of the basis set, the dimer Sb_2 was investigated. For the neutral dimer, the experimental bond length is known as 2.48 Å [18]. We calculated (without relativistic corrections) the equilibrium bond length with the basis sets I ... IV and using the LDA with or without the GC of Becke and Perdew. The LSDA does not change the results because $S = 0$ for the ground state of Sb_2 (closed-shell system). The results for the four basis sets I ... IV are given in Table I. As can be seen, the best result that we got was for basis set IV.

As a further check, the reliability of the basis sets I ... IV for the Sb_2^- anion was investigated (in LSDA) (see also Table I). Its equilibrium bond length that we obtained changed similarly as for the neutral dimer, going from basis set I to IV. A stronger basis-set effect can be seen in the dependence of the vertical detachment energy (VDE) on the basis set: Using basis set IV, we got a value (1.39 eV) in very good agreement with the experiment (1.34 eV) (see Tables II and III). With a smaller basis set, the calculated VDE deviates clearly from the experi-

TABLE I

Equilibrium bond length of Sb_2 and Sb_2^-, in Å.

Basis set	Sb_2 LDA	Sb_2 GC	Sb_2^- LDA	Sb_2^- GC
I	2.60	2.61	2.70	2.74
II	2.58	2.61	2.64	2.68
III	2.55	2.55	2.68	2.72
IV	2.51	2.52	2.60	2.64
Exp.	2.48			

TABLE II

Vertical detachment energy (VDE) for Sb_2^-, in eV.

		LDA	GC
Nonrelativistic	No LSDA	1.38	1.32
	LSDA	1.46	1.39
Relativistic	No LSDA	1.25	1.20
	LSDA	1.33	1.31

mental value. In particular, with basis set II, which contains less diffuse functions than does IV, we calculated 1.58 eV. (The influence of diffuse functions, especially polarization functions, on the electronic affinity of alkali—metal clusters is discussed, e.g., in [19].) Hence, we used basis set IV for the Sb calculations. The inclusion of the GC changes the results only very little. Furthermore, it can be seen from Table I that for Sb it is not necessary to include relativistic corrections; see also the next section for this discussion. For Bi, we used the corresponding basis set: with triple-zeta quality and "5p frozen," which also contains the 5d function in the valence basis. For Bi_2, we got with this basis set a bonding length of 2.74 Å, which agrees well with the calculated value (2.76 Å) of Balasubramanian [10]. The effects of GC and LSDA for the anionic dimers are considered in detail in the next section.

Results

INFLUENCE OF GRADIENT CORRECTIONS AND LOCAL SPIN DENSITY APPROXIMATION; INVESTIGATION OF RELATIVISTIC EFFECTS

In this subsection, we present the results for the vertical ionization (or detachment) energies (VDE) of the Sb and Bi dimer anions calculated with or without (i) LSDA, (ii) GC, and (iii) semirelativistic corrections (see Tables II and IV). It can be seen that the GC diminishes the VDE generally by ap-

proximately 0.05 eV. The LSDA enhances the VDE generally by approximately 0.08 eV. These changes lie within the error bars of the available experimental data.

It can be seen that the relativistic effects are small for the antimony dimer: The nonrelativistic results for Sb agree again (as in Table I) very well with the experiment (see Table III). For larger Sb clusters, the relativistic effects are also found to be small. For example, for the Sb_5^- cluster, where the largest relativistic effects are expected (cf. Table V), the semirelativistic calculation for the VDE yields 3.60 eV in comparison with the nonrelativistic value 3.73 eV (see Table III), which lies within the error bars of the experiment. The relativistic corrections for the Bi dimer are about twice as large as for Sb_2^-; and for the larger Bi clusters, these corrections increase up to an amount of 0.3—0.4 eV (see Table V). Therefore, for antimony, the nonrelativistic method and, for bismuth, the semirelativistic treatment were applied.

EQUILIBRIUM STRUCTURES AND COMPARISON OF THE IONIZATION ENERGIES WITH THE EXPERIMENT

The geometry parameters of the equilibrium geometries of the anionic and neutral clusters are given in Table VI; these geometries are presented qualitatively in Figure 1 (see also Table VII). The geometries of the (neutral and anionic) Sb and Bi clusters differ approximately only by a bond length scaling (with a factor of ≈ 1.1 from Sb to Bi). This holds—with a scaling factor of ≈ 1.3 from P to Sb —also for the comparison to phosphorus clusters, at least for the clusters considered here.

The interesting result of a—remarkably stable —planar ring [see Fig. 1(e)] for the pentamer anion was already discussed in [7]. The nonlinear geometries of the neutral and anionic trimers [see Fig. 1(a)] are Jahn–Teller distorted triangles. Furthermore, the tetrahedron is stable for the neutral

TABLE III

Adiabatic ionization energies (AIE) and vertical detachment energies (VDE) for Sb_n^- clusters, in eV.

	n							
	2		3		4		5	
	AIE	VDE	AIE	VDE	AIE	VDE	AIE	VDE
Experiment	1.25	1.34	1.76	1.98	1.20	1.53	2.80	≥ 3.8
Calculation	1.32	1.39	1.78	1.97	1.23	1.81	2.86	3.73

		LDA	GC
Nonrelativistic	No LSDA	1.43	1.38
	LSDA	1.51	1.46
Relativistic	No LSDA	1.26	1.20
	LSDA	1.33	1.30

TABLE VI _____
Geometry parameters of the relaxed clusters (lengths in Å); for the numbering of the atoms, see Figure 1.

|	Sb_2^-	Bi_2^-		Sb_2	Bi_2
d_{12}	2.64	2.77	d_{12}	2.52	2.74

	Sb_3^-	Bi_3^-		Sb^3	Bi^3
d_{12}	2.71	3.04	d_{12}	2.72	2.97
α_{123}	69.8°	67.0°	α_{123}	64.6°	63.4°

	Sb_4^-	Bi_4^-		Sb_4	Bi_4
d_{12}	2.92	3.04	d_{12}	2.90	3.11
d_{23}	2.97	3.18			
α_{132}	58.9°	57.0°			
α_{314}	75.6°	76.8°			

	Sb_5^-	Bi_5^-		Sb_5
d_{12}	2.72	3.03	d_{12}	2.91
			d_{13}	3.02
			d_{35}	2.95
			α_{132}	57.7°
			α_{314}	81.3°
			α_{354}	83.8°

tetramer but is unstable for the corresponding anion: The lowest unoccupied level $(1t_1)$ of the neutral cluster is threefold degenerated, which yields for the anion a Jahn–Teller distortion. The corresponding equilibrium geometry is a "roof" structure [see Fig. 1(c)]. Such a "roof" geometry exists also as stable isomer for the neutral P_4 molecule [1].

In Tables III and IV, the calculated VDEs and AIEs for the small Sb and Bi cluster anions are given (using LSDA and GC). For the Bi clusters, only the VDE is presented because the total energy differences calculated with the semirelativistic method are not satisfactory (see section Description of the Method). For this reason, the geometry optimization for the Bi clusters was performed with the nonrelativistic code. For the calculation of the semirelativistic VDE, the transition-state method was used.

The agreement of the (nonrelativistic) results for Sb with the experiments is very good. For Bi, the semirelativistic results agree much better with the experiments than do the nonrelativistic ones. The remaining small differences between theoretical and experimental values for Bi may be ascribed to spin–orbit coupling effects. These effects are for Bi_2 and Bi_3 clusters discussed in detail in [10]. The nonrelativistic results for the Sb and Bi clusters differ only slightly.

	n
	2	3	4	5
Experiment	1.33	1.61	1.42	2.89
Nonrelativistic calc.	1.46	2.02	1.87	3.59
Semirelativistic calc.	1.30	1.71	1.72	3.15

SIZE DEPENDENCE OF THE IONIZATION ENERGIES

In Figure 2, the calculated values for the VDE from Tables III and V are plotted as a function of the cluster size (number of atoms n) for antimony and bismuth. The values for the atoms were added (calculations from [20]). It can be seen that the pentamer clusters have an especially high VDE; this indicates that this cluster has a high relative stability and deep-lying occupied electronic levels [7].

As can be seen in Figure 2, there is an indication for an even–odd alternation of the VDE of the clusters as a function of the cluster size. Such even–odd alternations are well established, e.g., for the ionization energies of the neutral phosphorus clusters [1]. This alternation is also typical for many metal clusters, especially for alkali–metal clusters (see, e.g., [18] and references therein).

The even–odd alternation in Figure 2 becomes stronger if one considers for the trimer anions the _linear_ geometry. This linear trimer anion is a local minimum of the total energy and even the most stable geometry for the azide ion N_3^- (see, e.g., [21]). For this metastable structure, we got a higher
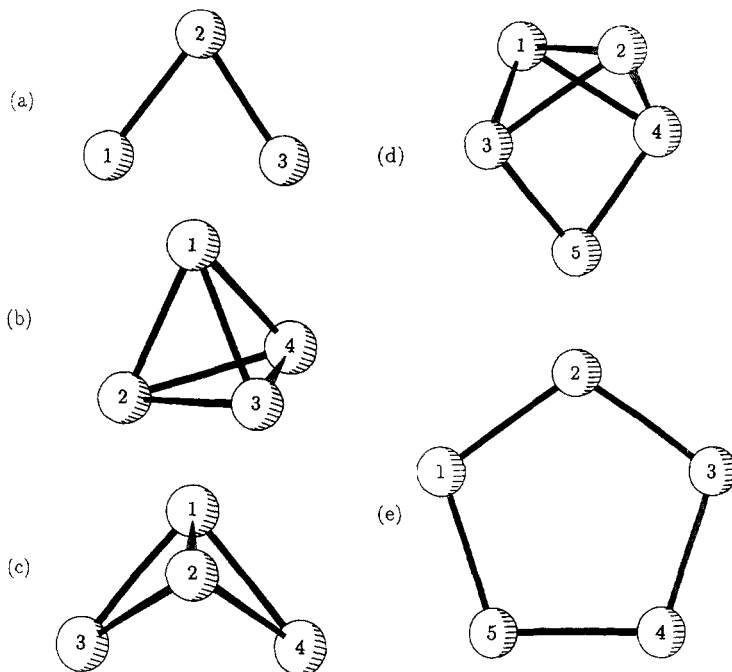
FIGURE 1. Equilibrium structures of the clusters: (a) A_3 and A_3^- (nonlinear); (b) A_4 (tetrahedron); (c) A_4^- ("roof"); (d) A_5 ("bridged roof"); (e) A_5^- (planar pentagon).

TABLE VII
Equilibrium geometries.

n	A_n	A_n^-
3	Nonlinear	Nonlinear
4	Tetrahedron	Roof
5	Bridged roof	Planar "ring"

VDE, e.g., for antimony 2.95 eV, which leads to a stronger even–odd alternation in Figure 2. However, this value of 2.95 eV for the VDE of Sb_3^- is much larger than the experimental one (1.90 eV). This confirms the existence of the nonlinear trimer cluster Sb anion (with the calculated VDE of 1.97 eV) as the most stable one, as we found in our geometry optimization. The discussion for Bi_3^- is analogous.

Summary

We performed density functional (LCAO) calculations of structures and ionization energies for small antimony and bismuth cluster anions. The influence of basis sets, gradient corrections (GC), local spin density approximation (LSDA), and rela-
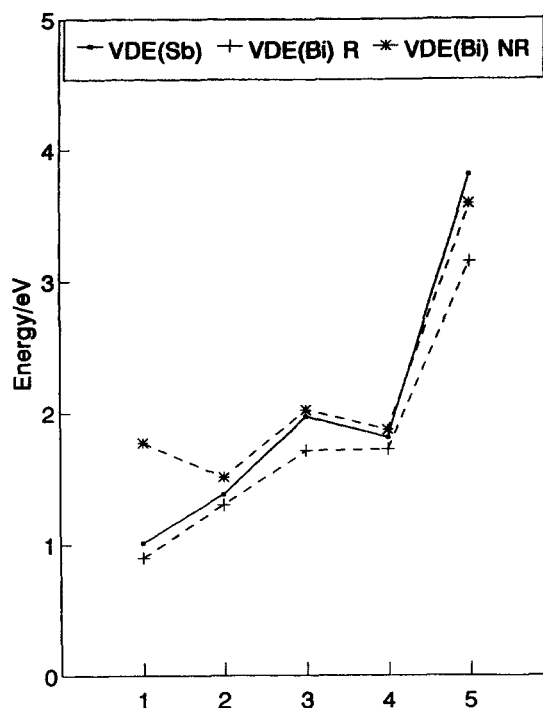
FIGURE 2. Calculated vertical detachment energies (VDE), in eV, for negatively charged Sb and Bi clusters as a function of the cluster size (number of atoms). Full line: Sb (nonrelativistic); dashed lines: Bi, nonrelativistic (NR) and semirelativistic (R).

tivistic corrections on the results for the dimers is investigated in detail. The influence of GC and LSDA are found to lie within the accuracy of the experiments. The agreement of the ionization energies with the experiments (PES) is very good for Sb; for Bi, the remaining differences are due to the spin–orbit coupling which is not included in the semirelativistic treatment used here. The equilibrium structures of the neutral and anionic clusters are the same as for the corresponding phosphorus clusters. The ionization energies show only a weak even–odd alternation as a function of the cluster size.

References

1. R. O. Jones and D. Hohl, J. Chem. Phys. **92**, 6710 (1990); R. O. Jones and G. Seifert, J. Chem. Phys. **96**, 7564 (1992); P. Ballone and R. O. Jones, J. Chem. Phys. **100**, 4941 (1994).

2. M. Häser, U. Schneider, and R. Ahlrichs, J. Am. Chem. Soc. **114**, 9551 (1992).

3. G. Igel-Mann and H. Stoll, Comp. Mater. Sci. **2**, 413 (1994), and references therein.

4. M. L. Polak, J. Ho, G. Gerber, and W. C. Lineberger, J. Chem. Phys. **95**, 3053 (1991); M. L. Polak, G. Gerber, J. Ho, and W. C. Lineberger, J. Chem. Phys. **97**, 8990 (1992).

5. M. Gausa, H. O. Lutz, and K.-H. Meiwes-Broer, Z. Phys. D **26**, S146 (1993).

6. R. Kaschner, U. Saalmann, G. Seifert, M. Gausa, H. O. Lutz, and K.-H. Meiwes-Broer, J. Chem. Phys., submitted.

7. M. Gausa, R. Kaschener, H. O. Lutz, G. Seifert, and K.-H. Meiwes-Broer, Chem. Phys. Lett. **230**, 99 (1994).

8. T. Ziegler, Chem. Rev. **91**, 651 (1991).

9. K. Balasubramanian and J. Li, J. Mol. Spectrosc. **135**, 169 (1989); K. Balasubramanian, Chem. Rev. **90**, 93 (1990).

10. K. Balasubramanian and D. W. Liao, J. Chem. Phys. **95**, 3064 (1991); K. Balasubramanian, K. Sumathi, and D. Dai, J. Chem. Phys. **95**, 3494 (1991); H. Zhang and K. Balasubramanian, J. Chem. Phys. **97**, 3437 (1992).

11. R. Kaschner and G. Seifert, Int. J. Quantum Chem. **52**, 957 (1994), and references therein.

12. E. J. Baerends and P. Ros, Int. J. Quantum Chem. Symp. **12**, 169 (1978); for technical details of the program, see J. Krijn and E. J. Baerends, Internal Report (Free University of Amsterdam, 1984).

13. P. M. Boerrigter, G. te Velde, and E. J. Baerends, Int. J. Quantum Chem. **33**, 87 (1988); G. te Velde and E. J. Baerends, J. Comp. Phys. **99**, 84 (1992).

14. A. D. Becke, Phys. Rev. A **38**, 3098 (1988).

15. J. P. Perdew, Phys. Rev. B **33**, 8822 (1986).

16. V. Heera, G. Seifert, and P. Ziesche, J. Phys. B **17**, 519 (1984).

17. J. C. Slater and J. H. Wood, Int. J. Quantum Chem. **4S**, 3 (1970).

18. H. Sontag and R. Weber, J. Mol. Spectrosc. **91**, 72 (1982).

19. I. Boustani, W. Pewerstoff, P. Fantucci, V. Bonacic-Koutecky, and J. Koutecky, Phys. Rev. B **35**, 9437 (1987); V. Bonacic-Koutecky, P. Fantucci, and J. Koutecky, Chem. Rev. **91**, 1035 (1991).

20. M. Richter, private communication.

21. L. Pauling, *The Nature of the Chemical Bond* (Verlag Chemie, Weinheim, 1976).