

# A valence bond study of the $\sigma$ and $\pi$ aromatic species $\text{Al}_4^{2-}$

Remco W.A. Havenith<sup>a,\*</sup>, Joop H. van Lenthe<sup>b</sup>

<sup>a</sup> Department of Chemistry, University of Warwick, Coventry CV4 7AL, UK

<sup>b</sup> Debye Institute, Theoretical Chemistry Group, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands

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## Abstract

Ab initio valence bond calculations were performed to assess the  $\sigma$  and  $\pi$  aromatic character of the all-metallic species  $\text{Al}_4^{2-}$ . The results show that the  $\sigma$  system is composed from two independent systems (built from the radial and tangential p-orbitals), each containing two delocalised electrons, providing the conduction. The resonance energy of the  $\sigma$  system is significantly higher than that of the  $\pi$  system (123 vs. 40 kcal/mol), and the  $\pi$  resonance energy is substantially lower than that of the  $\pi$  isoelectronic hydrocarbon  $\text{C}_4\text{H}_4^{2+}$  (167 kcal/mol).

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## 1. Introduction

$\sigma$  aromaticity is a concept that has been invoked to explain the extraordinary behaviour of (small) ring systems [1–4], in analogy with the concept of  $\pi$  aromaticity. A definition of aromaticity is the ability of a molecule to sustain (diatropic) ring currents, induced by an external magnetic field [5–9]. Something else that all  $\pi$  aromatic molecules have in common is that their electronic structure cannot be described by one Lewis structure only, but only an adequate picture is obtained when resonance between two or more structures is considered. Up until now,  $\sigma$  aromatic systems, like cyclopropane, obey for example the magnetic criterion for aromaticity [10], but spin-coupled VB calculations did not show any evidence of resonance [11].

However, recently, the concept of aromaticity has been extended to include all-metallic species, as  $\text{Al}_4^{2-}$  [12],  $\text{XAl}_3^-$  (X = Si, Ge, Sn, Pb) [13] and  $\text{Hg}_4^{6-}$  [14]. These clusters possess two delocalised  $\pi$  electrons, satisfying the  $(4n + 2)$  electron-counting rule for aromatic

compounds. Furthermore, the  $\text{Al}_4^{2-}$  anion obeys the geometric criterion for aromaticity: it has a  $D_{4h}$  symmetric structure, thus all Al–Al bond lengths are equal. Magnetic property studies showed that indeed this molecule is able to sustain a diatropic ring current [15–18], but direct visualisation of the induced current density showed that these ring currents were mainly associated with the  $\sigma$  electrons [16,18]. An estimate of the resonance energy has been made [19] based on reaction energies, and it was found to be between –2 and 97 kcal/mol with a best estimate of 48 kcal/mol (CCSD(T)/6-311+G(2df)). This unusually high resonance energy (compare ca. 20 kcal/mol [20] for benzene, based on the reaction scheme  $\text{C}_6\text{H}_6 + 3\text{CH}_2\text{CH}_2 \rightarrow 3\text{CH}_2\text{CHCHCH}_2$ ) has been attributed to the double ( $\sigma + \pi$ ) aromatic character of the metallic cluster. The fundamental difference between this system, and other  $\sigma$  aromatic systems is that  $\text{Al}_4^{2-}$  cannot be described by one Lewis structure, and resonance between several structures is mandatory to give a picture of its electronic structure. Different resonance pictures have been proposed in the literature [21,22].

The approach to assess the aromatic nature of  $\text{Al}_4^{2-}$  in terms of resonating structures is the use of ab initio valence bond (VB) theory. Using the VB approach, the resonance energy as defined by Pauling and Wheland [23] as the energy difference between the total VB energy and the energy of the most stable structure, can be

\* Corresponding author. Fax: +44-24765-23258.

E-mail addresses: [r.w.a.havenith@warwick.ac.uk](mailto:r.w.a.havenith@warwick.ac.uk), [r.w.a.havenith@chem.uu.nl](mailto:r.w.a.havenith@chem.uu.nl) (R.W.A. Havenith), [joop@chem.uu.nl](mailto:joop@chem.uu.nl) (J.H. van Lenthe).

<sup>1</sup> Current address: Theoretical Chemistry Group, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands.

directly calculated. Furthermore, insight in the electronic structure in terms of spinbonds is obtained. Here, we provide estimates of the Pauling resonance energy, associated with the  $\sigma$  and  $\pi$  systems. The resonance energy of the  $\pi$  system is compared to the value obtained for the planarised  $C_4H_4^{2+}$  [24], the carbon analogue with the same number of  $\pi$  electrons.

## 2. Methods

The calculations were performed with the 6-31G\*\* basis set, using GAMESS-UK [25] and TURTLE [26]. The geometries used for the VB calculations were optimised at the CASSCF(2,4)/6-31G\*\* level of theory. The optimised Al–Al distance at this level of theory is 2.606 Å, in excellent agreement with the previous reported values of 2.58 Å at the CCSD(T)/6-311+G\* level [12] and 2.601 Å at the RHF/6-311++G(3df) level of theory [16]. For  $C_4H_4^{2+}$ , C–C bond lengths of 1.436 Å are found, in line with the previously reported value of 1.434 Å for planarised  $C_4H_4^{2+}$  [24].

Two different orbital optimisation models were used, viz. (1) where all orbitals are kept strictly atomic, and (2) where the orbitals are predominantly atomic in nature, but are allowed to delocalise [27–29]. The  $\pi$  and  $\sigma$  systems are treated separately: in the  $\pi$  VB calculations, the  $\sigma$  skeleton is described by a Hartree–Fock core, i.e. doubly occupied orthogonal molecular orbitals. In the VB calculations for the  $\sigma$  system, the situation is reversed.

## 3. Discussion

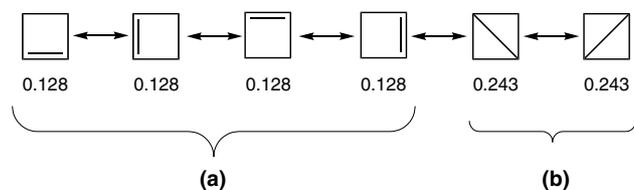
The  $\pi$  system of  $Al_4^{2-}$  and  $C_4H_4^{2+}$  is described using the six possible valence bond structures, shown in Scheme 1 together with their weights in the (local) VB wave function for  $Al_4^{2-}$ . Similar VB vectors are obtained for  $Al_4^{2-}$  and planarised  $C_4H_4^{2+}$ : the most stable structures, those with the highest weight, are the Dewar-like structures **b** in Scheme 1. The Pauling resonance energy obtained using the local approach is 44.78 kcal/mol (delocal 38.66 kcal/mol). These are substantially higher than the Pauling resonance energy obtained for benzene

using the same approaches (19.82 kcal/mol [28,29]), but substantially lower than the resonance energies obtained for  $C_4H_4^{2+}$  (166.60 kcal/mol (local), 104.63 kcal/mol (delocal)). The much higher  $\pi$  resonance energy of  $Al_4^{2-}$  and  $C_4H_4^{2+}$  compared to benzene can be attributed to the fact that both species have to stabilise a double negative/positive charge. The relatively low resonance energy of  $Al_4^{2-}$  indicates that this species is less  $\pi$  aromatic than  $C_4H_4^{2+}$ .

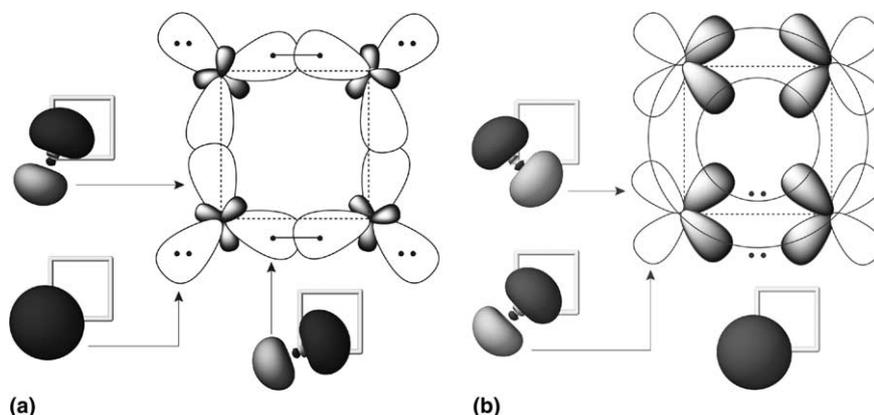
The  $\sigma$  aluminium valence bonds are made up of singly occupied orbitals. Different spin coupling schemes were used to address the plausibility of the different bonding modes, which were put forward in the literature [21,22] (Scheme 2). The first coupling mode consists of Al–Al bonds made up of  $sp^2$ -like hybrids, with four Al lone pairs, as depicted in Scheme 2a [21]. In total, six different structures can be formed in this way. In Scheme 2a, a contour diagram is shown of the optimised (strictly local) symmetry distinct  $\sigma$  orbitals. The total energy obtained using this wave function is  $-967.2406555E_h$ , with a resonance energy of 2.63 kcal/mol (local approach).

The second coupling mode consists of two separate  $\sigma$  systems with each two electrons, made up from the radial and tangential p-orbitals on each aluminium atom, with four Al lone pairs, as depicted in Scheme 2b [22], resulting in a total of 36 structures. Again, contour plots of the strictly local symmetry distinct orbitals are shown in the scheme. The total VB energy in this case is  $-967.4064762E_h$  (delocal  $-967.4829661E_h$ , cf. the Hartree–Fock energy of  $-967.4400467E_h$ ) (104.06 kcal/mol lower than mode 1), with a resonance energy of 123.24 kcal/mol. The delocal orbital model yields a larger resonance energy of 194.75 kcal/mol. This increase in resonance energy is not expected, as delocalisation of the orbitals usually reduces the resonance energy. This is observed in the  $\pi$ -only calculation and in valence bond calculations on benzene [28,29]. However, the different structures in most  $\pi$ -only valence bond calculations are of similar nature, whereas, as exemplified in Scheme 3, the  $\sigma$  Lewis structures here are rather dissimilar. The electrons in structure (a) (the most stable structure) are spatially further separated than in for example structure (b). Orbital optimisation leads to an overall lower total energy, and in this case it proves to be favourable to lower the energy of the less stable structures (reduction of the electron repulsion) at the expense of a slight increase of the energy of the most stable structure, thus leading to an increase of the Pauling resonance energy.

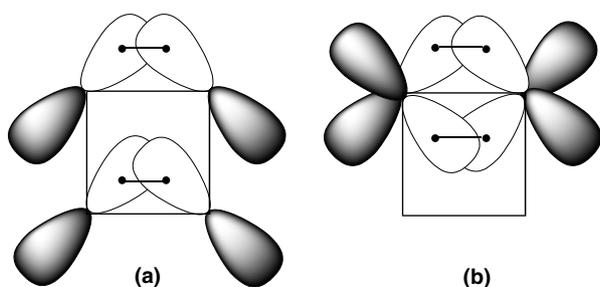
The much lower total energy suggests that the  $\sigma$  skeleton of the  $Al_4^{2-}$  anion is best described as two different delocalised systems, a radial and tangential one, with each system holding two electrons. The large resonance energy associated with this bonding mode indicates that the  $\sigma$  system is indeed more aromatic than the  $\pi$  system, as was concluded from the induced current density studies [16,18].



Scheme 1. The weights of the six different  $\pi$  Lewis-structures, calculated using the local orbital approach.



Scheme 2. Schematic representations of the spin-couplings schemes and contour plots of the optimised orbitals using the local approach (a) for the spin-coupling mode which represents localised Al–Al bonds; (b) for the spin-coupling mode which represents the two independent delocalised  $\sigma$  systems.



Scheme 3. Schematic representation of 2 of the 36 possible Lewis-structures included in the valence bond calculation of the spin-coupling mode representing the two delocalised  $\sigma$  systems. Structure **a** is the most stable structure.

#### 4. Conclusions

The all-metallic aromatic systems do have a  $\sigma$  electron structure, just as a  $\pi$  system of aromatic hydrocarbons: several Lewis structures are mandatory to get a qualitative correct description, and an extra stabilisation is associated with their resonance. An intriguing picture of the  $\sigma$  system arises from the valence bond calculations: two independent ring systems provide the conduction.

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