Spin-orbit effects on magnetically induced current densities in the $M_4^2$ ($M = B, Al, Ga, In, Tl$) clusters

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ABSTRACT

We report about the spin-orbit effects on the aromaticity of the $B_4^2$, $Al_4^2$, $Ga_4^2$, $In_4^2$, and $Tl_4^2$ clusters via the magnetically-induced current density method. All-electron density functional theory (DFT) calculations were carried out using the four-component Dirac-Coulomb (DC) Hamiltonian, including scalar and spin-orbit relativistic effects. The relativistic values for ring current strengths were obtained by numerical integration over the current flow. These values were compared to the scalar relativistic and non-relativistic values, in order to assess the corresponding contributions to aromaticity. It was found that in the heavy cluster, $Tl_4^2$, there is a significant influence of both scalar and spin-orbit relativistic effects.

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1. Introduction

The most typical definition of aromaticity is related to benzene, where the presence of a π system above and below the plane of the hexagonal ring gives rise to a symmetric structure with bond length equalization, thermodynamic stability, reactivity, special magnetic properties, etc. The six π electrons in benzene is a special case of Hückel’s (4n + 2) π-electron rule that defines an aromatic hydrocarbon molecule. However, after the experimental preparation and theoretical characterization of the $Al_4^2$ cluster by Boldyrev and Wang et al. [1], the concept of aromaticity has been extended to all-metal and transition-metal systems and [2–4]. As a consequence, this concept has evolved and it has been given a variety of definitions [5]. Among the various indices of aromaticity, the magnetic criteria are the most accepted, because the delocalization of electrons around the molecular framework of a molecule, depend directly on the induced current upon the application of an external magnetic field. Schleyer and co-workers developed the concept of nucleus-independent chemical shifts (NICS) [6]. This index, implemented in most of the available quantum chemical software systems, has become a popular probe of aromaticity among chemists, due to its simplicity and low computational cost. Unfortunately NICS values cannot unambiguously determine aromaticity [7–12].

In this study, we employ the most reliable magnetic criterion, namely, the magnetically-induced current density (MICD) method which is based on the application of an external magnetic field, that induces a current density around the molecular frame [13–16]. This method provides both qualitative and quantitative descriptions of electron delocalization. In the qualitative description it is useful to draw current-density maps (CDMs) for the visualization of the streamlines that flow in a molecule or a ring [17–20]. In these CDMs, aromatic compounds support a diatropic current (clockwise direction) and antiaromatic compounds support a paratropic ring current (anticlockwise direction). In the quantitative description, an aromaticity index is obtained from integration of the current density over a plane that cuts a specific bond. This index is the net ring current strength (RCS) around the molecular ring [21–24]. For an up-to-date review of the subject see Ref. [25].

In this letter we study the influence of the spin-orbit (SO) effect on the aromaticity of the title clusters. Considering that, in the heavy indium and thallium clusters, strong relativistic effects are expected [26–29], we have carried out relativistic calculations using the four-component Dirac-Coulomb (DC) Hamiltonian. Previous theoretical studies have reported that all of these clusters are square planar and possess aromatic character. The $B_4$ cluster was first reported by Sundholm et al. [30]. Boldyrev et al. presented theoretical and experimental evidence of aromaticity in the all-metal $Al_4^2$ system [1]. The origin of the aromaticity in this cluster, was proposed to be both σ- and π-aromatic [1,31]. The $Ga_4^2$ and $In_4^2$ clusters were also experimentally reported, presenting double (σ- and π-) aromaticity [32]. The heaviest cluster

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