MINISTRY OF EDUCATION AND TRAINING QUY NHON UNIVERSITY

DUONG VAN LONG

A QUANTUM CHEMICAL RESEACH OF STRUCTURE AND AROMATICITY OF SOME BORON CLUSTERS

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DECLARATION

This dissertation was written on the basis of research work carried out at Quy Nhon University, Binh Dinh province, under the supervision of Professor Nguyen Minh Tho and Associate Professor Nguyen Phi Hung.

I hereby declare that the results presented are original from my own research work. Most of them were already published in peer-reviewed international journals. For the use of the results from joint papers, I received permissions from my coauthors.

> Quy Nhon Binh Dinh 06 November 2023 Author

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List of symbols and notations

2D	Two dimensional
3D	Three dimensional
ACID	Anisotropy of the induced current density
ADE	Adiabatic detachment energy
AdNDP	Adaptive Natural Density Partitioning
AO	Atomic orbital
ASBO	Average of the sum of the bond orders
CASSCF	Complete Active Space Self-Consistent Field
CBS	Complete basis set
CC	Coupled cluster
CCSD	Coupled cluster including singles and doubles
CCSD(T)	CCSD with a perturbative triples correction
CI	Configuration Interaction
СМО	Canonical Molecular Orbital
CTOCD-DZ2	Continuous transformation of the origin of the current density -
	diamagnetic zero, with shifting the origin toward the nearest nucleus
DFT	Density functional theory
DM	Disk model
DR	Double ring
ELF	Electron localization function
GA	Genetic algorithm
GGA	Generalized gradient approximation
GTO	Gaussian-type orbitals
HCM	Hollow cylinder model
HF	Hartree-Fock
HLG	Frontier orbital (HOMO – LUMO) energy gap
НОМО	Highest Occupied Molecular Orbital

IE _v	Vertical ionization energy
IR-UV2CI	Resonant infrared-ultraviolet two-color ionization spectroscopy
LCAO	Linear combination of atomic orbitals
LDA	Local density approximation
LUMO	Lowest Unoccupied Molecular Orbital
MBPT	Many-body perturbation theory
MEGA	Mexican Enhanced Genetic Algorithm
meta-GGA	Meta-generalized gradient approximation
МО	Molecular orbital
MPn	n-order Møller-Plesset perturbation method
MRCI	Multireference Configuration Interaction
NAC	Calculated net atomic charged
NICS	Nuclear independent chemical shift
PES	Photoelectron spectroscopy
PSM	Phenomenological shell model
QP	Quasi-planar
RMS	Root mean square
RSS	Residual sum of squares
SBO	Sum of bond orders
SOMO	Singly Occupied Molecular Orbital
SPION	Superparamagnetic iron oxide nanoparticles
STO	Slater-type orbitals
TD-DFT	Time dependent density functional theory method
TEA_{v}	Vertical two-electron affinity
UV	Ultraviolet
UV-Vis	Ultraviolet-Visible
VASP	Vienna ab initio simulation package (VASP)
VDE	Vertical detachment energy

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GENERAL INTRODUCTION

A. Research introduction

Nearly six decades have passed since the definition of the term *cluster* was formally conceived when F. A. Cotton, in 1964, first generalized a working definition of "*metal atom cluster*" as "a finite group of metal atoms which are held together mainly, or at least to a significant extent, by bonds directly between the metal atoms, even though some nonmetal atoms may also be intimately associated with the cluster" [1]. Ever since, experimental and theoretical studies of clusters has flourished and the atomic clusters has emerged as a multidisciplinary scientific field.

The cluster science is primarily concerned with finding the stable structures of a group of atoms and then explaining the stability of those structures, along with elucidating their characteristic physicochemical properties and the potential applications. Along the way of rationalizing the thermodynamic stability, the concept of aromaticity gradually emerged as a topic closely associated with cluster science. Although aromaticity was, and remains, a fundamental concept in modern chemistry, it is actually not a well-defined concept [2-5] that comes from the existence of several qualitative and even quantitative models that in the meantime support and oppose to each other. The most famous of these models is the Hückel model [6–8] which was originally conceived for the planar hydrocarbons. For an appropriate application of the Hückel model, we need to solve the secular equation for each specific structure to determine the exact number of electrons involved, but this requirement seems to have been forgotten, and only the qualitative (4n + 2)counting rule is remembered and used not only for planar molecules in circular form, but also for non-planar and other three-dimensional structures. The convenience of the (4n + 2) electron counting rule has caused it to be abused to the point that the essence and origin of the rule have often been forgotten and led to

erroneous interpretations. In this dissertation, we aim to establish appropriate models for aromaticity on the basis of the geometrical forms using rigorous mathematical treatments. Thus, the circular disk model, the ribbon model and the hollow cylinder model will be presented to emphasize the differences and similarities of the electron counting rules when the geometries of the species considered are significantly different from the planar circle of organic hydrocarbons.

B. Objectives and scope of the research

Research objectives: Determination of geometrical structures, electronic configurations and thermodynamic stability of some boron and doped boron clusters. Depending on the different geometries of the obtained clusters, corresponding aromaticity models are proposed to explain their stability.

Research scopes: The boron and doped boron clusters surveyed in the dissertation include $B_2Si_3^q$ and $B_3Si_2^p$ in different charged states, the neutral and dianionic $B_{70}^{0/2-}$, $B_{12}Li_n$ with n = 0 - 14 and the $B_{14}FeLi_2$. The ribbon model joins the Hückel model to explain properties related to $B_2Si_3^q$ and $B_3Si_2^p$ clusters. The stability of the quasiplanar isomer of $B_{70}^{0/2-}$ and the cone-like $B_{12}Li_4$ is well understood through the disk model. The hollow cylinder model contributes to the elucidation of the properties of $B_{14}FeLi_2$.

C. Novelty and scientific significance

- This dissertation aims to clarify the need to distinguish the classical Hückel model from the ribbon model and extend the basic concepts of the ribbon model.
- From a methodological viewpoint, the benchmark calculations have verified the suitability of using the density functional TPSSh for optimizing structures containing both B and Si atoms, while for simulating the results of photoelectron spectroscopy or resonant infrared-ultraviolet two-color

ionization spectroscopy, the B3LYP functional provides values closer to experimental data.

- This dissertation presents the discovery of a triplet ground state for a quasiplanar B₇₀ cluster, which is also identified using the topological leapfrog principle. This particular isomer is predicted to exhibit a high thermodynamic stability in the dianion state. To understand the structure and stability of both neutral and dianionic states of this quasi-planar structure, the disk model has been applied. Additionally, a new electron count for circular disk species is proposed.
- A comprehensive study of the lithium-doped boron clusters B₁₂Li_n with n = 1-14 is conducted, aiming to understand the growth mechanism of Li doping in boron clusters for potential applications in hydrogen storage materials or Li-ion batteries. The results suggest that B₁₂Li₈ is the most promising candidate among the studied mixed B₁₂Li_n series for experimental investigations as a hydrogen storage material in the future. Additionally, B₁₂Li₄ is a stable cone-shaped cluster similar to B₁₃Li, and a disk-cone model is proposed based on this study.
- This dissertation also clarifies the need to distinguish the hollow cylinder model (HCM) from the Hückel model. More specifically, an understanding of the HCM model helps us to rationalize the thermodynamic stability of tubular clusters as well as to make predictions for new stable clusters. The stability of B₁₄FeLi₂ is also elucidated using the HCM.

The coherent thread running throughout the dissertation lies in the original approach and novel findings achieved in this doctoral study, which involves the formulation of electron count rules to determine the aromatic character of atomic clusters. These rules are established on the basis of rigorous solutions of wave equations tailored to their respective geometric structures.

Chapter 1. DISSERTATION OVERVIEW

1.1. Overview of the research

In conjunction with the tremendous advancements in materials science which demand ever-decreasing scales, the field of cluster science, focused on the investigation of atomic clusters ranging from a few to several hundred atoms, has achieved remarkable progresses. Through theoretical investigations and provision of foundational insights, atomic clusters have transcended theoretical frameworks and found diverse practical applications. Cluster science plays a crucial role in understanding catalytic processes in which clusters can act as model systems to study the reactivity and selectivity of catalysts, providing insights into the mechanisms of complex catalytic cycles [9]. This basically led to the basis of single atom catalytic processes for chemical reaction. The tiny clusters, such as C_{60} , exhibit quantum confinement effects, allowing them to absorb and emit light at specific wavelengths, making them ideal for photovoltaic applications [10]. Coinage metal clusters are origin of specific luminescence giving rise to different types of sensors. Researchers have utilized gold clusters in surface-enhanced Raman spectroscopy which is a technique used for highly sensitive detection of chemicals having extremely low concentration in the atmosphere or in solution. Gold clusters deposited on a surface can greatly enhance the Raman scattering signal of nearby molecules, enabling the detection of trace amounts of substances like pollutants [11] or biomarkers [12]. Iron oxide clusters, known as "superparamagnetic iron oxide nanoparticles" (SPIONs), have been employed as contrast agents in magnetic resonance imaging. In fact, SPIONs can enhance the visibility of specific tissues or target areas of interest, aiding in the diagnosis and monitoring of diseases like cancer [13].

Of the atomic clusters, boron clusters have been, and still are, captivating and pose intriguing challenges for understanding due to their electron-deficient nature, diverse structures, and unique electronic properties. With fewer valence electrons than other elements, boron atom forms clusters that exhibit unconventional bonding patterns and a wide range of geometries including planar, quasi-planar, icosahedral, cage-like, tubular, fullerene, ... [14–18]. The size-dependent electronic structure of boron clusters offers an opportunity to explore novel electronic phenomena and study size-dependent effects. However, the actual synthesis and characterization of boron clusters can be demanding, requiring specialized techniques and precise control over their reactivity and stability. Despite these challenges, the fascinating properties of boron clusters make them a compelling area of research with promising applications in catalysis, drug delivery, electronics, and energy storage [19]. Understanding and harnessing the full potential of boron clusters pave the way for advancements in cluster science, and thereby in materials chemistry.

The stability of clusters is closely tied to the concept of aromaticity, and boron clusters are no exception to this relationship. Boron clusters are subjected to a variety of aromaticity models that contribute to their stability. One of such models is the Wade-Mingos rule [20, 21], which predicts the aromaticity of boranes based on the number of electron pairs participating in delocalized bonding. According to this rule, boranes with (2n+2) skeletal electron pairs (where n being an integer) are considered to be aromatic and exhibit enhanced stability. Additionally, other aromaticity models such as the Hückel rule [6–8] and Baird rule [22], have been applied to boron clusters, providing insights into their stability and electronic structure. The Möbius electron counting rule [23] which is a guideline used in organometallic chemistry to predict the number of electrons available for bonding in transition metal complexes [24], has also been applied.

In general, the stability of an atomic cluster is influenced not only by the number of atoms but also by its charge state. An illustrative example is the transformation of a stable configuration of the B_{12} in the quasi-planar form [15] (quasi-planar: having little deformation from a perfectly planar form), which undergoes a transition to the fullerene-like form upon doping with two Si atoms [25]. This results in the formation of the stable $B_{12}Si_2$ doped structure, as elucidated

by the modelling approach of the cylinder model [25]. Moreover, the addition of two extra electrons causes the $B_{12}Si_2$ skeleton to further transform into a ribbon-like configuration in the $B_{12}Si_2^{2-}$ dianion [26]. A ribbon model [26] has been developed to provide an explanation for the robustness exhibited by the $B_{12}Si_2^{2-}$ cluster. This demonstrates how the charge state, in conjunction with a specific atom arrangement, plays a pivotal role in determining the stability and structural characteristics of the cluster considered.

With such interest and challenges, this doctoral study focuses on investigating the stability of some pure and doped boron clusters, and based on the obtained geometries, offers a suitable explanation according to the aromaticity models. It is also interesting that the Hückel and Baird rules exhibit many associations with the results presented in this dissertation.

1.2. Objectives of the research

Geometrical and electronic structures of the pure boron and doped boron clusters: including the neutral and dianionic B_{70} , the mixed lithium boron $B_{12}Li_n$ with n = 0 - 14, the mixed $B_2Si_3^q$ and $B_3Si_2^p$, and the multiply doped $B_{14}FeLi_2$ boron cluster.

1.3. Research content

The aromaticity models including the conventional Hückel and Barid rules, along with the newly established disk model, ribbon model and hollow cylinder model are used to understand and/or rationalize the chemical properties, parameters related to the aromaticity and thereby the thermodynamic stability of the structures investigated.

1.4. Research methodology

1.4.1. Search for lower-lying isomers

The stochastic search algorithm [27, 28] combining a random kick [29] and a genetic algorithm (GA) [30, 31] (cf. Figure 1.1) is used to generate a massive

amount of initial geometries of the cluster being studied. All initial geometries are then optimized using the density functional theory with the TPSSh [32] density functional in conjunction with the dp-polarization 6-31G(d) basis set [33] without harmonic vibrational frequency calculations. Structures with relative energies lying in a range of ~2 eV as compared to the lowest-lying isomer energy are subsequently re-optimized using the same TPSSh functional with a larger basis set 6-311+G(d) [34, 35], and following by harmonic vibrational frequency calculations to ensure that the found structures are true minima. Structure optimization and vibrational computations are performed employing the Gaussian 16 program [36].



Figure 1.1. Illustration of a genetic algorithm (GA) procedure ([31]).

1.4.2. ELF – The electron localization function

The electron localization function (ELF) [37] which is an approach supplemented for analyses of topological bifurcation [38, 39] of the electron density, is used to analyse the chemical bonding phenomenon of clusters. The ELF is a local measure of the Pauli repulsion between electrons owing to the exclusion principle in 3D space. The definition of ELF, $\eta(\mathbf{r})$, is given by following equation:

$$\eta(\mathbf{r}) = \frac{1}{1 + (D_{\rm P}/D_{\rm h})^2}$$

$$D_{\rm P} = \frac{1}{2} \sum_{i=1}^{N} |\nabla \psi_i|^2 - \frac{1}{8} \frac{|\nabla \rho|^2}{\rho}$$

$$D_{\rm h} = \frac{3}{10} (3\pi^2)^{2/3} \rho^{5/3}$$

$$\rho = \sum_{i=1}^{N} |\psi_i(\mathbf{r})|^2$$
(1.1)

where $D_{\rm P}$ and $D_{\rm h}$ are the local kinetic energy density due to the Pauli exclusion principle and the Thomas–Fermi kinetic energy density, repsectively, and ρ is the electron density. These quantities can be evaluated using either Hartee–Fock or Koln–Sham orbitals. The total ELF can then be partitioned in terms of separated components for σ electrons ELF $_{\sigma}$ and π electrons ELF $_{\pi}$ [40] to give a more specific assessment of the aromatic character for the particular sets of σ and π electrons. A σ and/or π aromatic species possesses a high bifurcation value of either ELF $_{\sigma}$ or ELF $_{\pi}$, whereas the corresponding bifurcation value in an antiaromatic system is very low. In some structures, the σ localized electrons can easily be identified separately from the set of delocalized electrons, and in that case, the ELF $_{\sigma l}$ and ELF $_{\sigma d}$, separated from the ELF $_{\sigma}$ can give a more specific picture of the localization region of these types of electrons [41–43]. The total ELF and the partial ELF are constructed using the Dgrid-5.0 software [44] and their isosurfaces are plotted using the Gopenmol software [45] or ChimeraX software [46].

1.4.3. Ring current maps

The ring current methodology is a powerful tool for looking at and thereby understanding the aromatic character of molecules. In this study, the SYSMOIC program [47], which implements the CTOCD-DZ2 method [48, 49], is utilized for calculating and visualizing the magnetically induced current density. SYSMOIC computes the current density tensor for restricted Hartree-Fock (HF) [50] and density functional theory (DFT) [51–53] singlet wavefunctions.

In the orbital approximation for a closed-shell ground state, the *n*-electron wavefunction is a Slater determinant of n/2 doubly occupied spatial orbitals, chosen to be real:

$$\Psi(1,2,\cdots,n) = \frac{1}{\sqrt{n!}} \det[\psi_1 \alpha, \psi_1 \beta, \psi_2 \alpha, \psi_2 \beta, \cdots, \psi_{n/2} \alpha, \psi_{n/2} \beta]$$
(1.2)

and the current density tensor is a sum of orbital contributions:

$$\mathcal{T}_{\alpha}^{\mathbf{B}_{\beta}}(\mathbf{r}-\mathbf{r}'') = \sum_{j=1}^{n/2} \mathcal{T}_{\alpha j}^{\mathbf{B}_{\beta}}(\mathbf{r}-\mathbf{r}'')$$
(1.3)

The anisotropy of the induced current density (ACID) [54] is another approach, similar to the ring current of SYSMOIC, which map also demonstrates the aromaticity of a species when the clockwise ring current or the antiaromaticity when the electron flux is moving in opposite directions.



Figure 1.2. The current density maps of π electron contribution of **a**) C₄H₄ and **b**) C₆H₆ plotted by both SYSMOIC and ACID packages.

As for an illustration, the π electron contribution to the current density maps of cyclobutadiene and benzene are shown in Figure 1.2 that are plotted by the SYSMOIC and ACID packages. The counter-clockwise ring currents (paratropic) of C₄H₄ and the clockwise ring currents (diatropic) of C₆H₆ indicate that while C₄H₄ is a π -antiaromatic species, C₆H₆ is a π -aromatic species.

1.4.4. Bond order and net atomic charge

The net atomic charge (NAC) and bond order for each cluster are carried out using a density partitioning method, the DDEC6 atomic population analysis [55, 56]. The accurately computes NACs and bond orders by DDEC6 approach as a functional of the electron and spin density distributions. Numerous benchmarking computations have consistently demonstrated that the DDEC6 package exhibits a notable combination of heightened precision and efficient resource utilization in contrast to numerous alternative methodologies [55, 57, 58]. An additional salient attribute of DDEC6 pertains to its open-source nature, conferring the advantage of unrestricted accessibility.

Chapter 2. THEORETICAL BACKGROUNDS AND COMPUTATIONAL METHODS

2.1. Theoretical backgrounds of computational quantum chemistry

2.1.1. Schrödinger equation

The Schrödinger equation is a fundamental equation of quantum mechanics, describing the status of a quantum system, and it is represented as:

$$\widehat{H}\psi = E\psi \tag{2.1}$$

Here, \hat{H} is the Hamiltonian operator, ψ is the wave function, and E is the energy. Equation (2.1) provides two important quantities: the eigenvalue of energy E and the eigenvector ψ .

The Schrödinger equation for a system with multiple electrons is written as:

$$\widehat{H}\psi(\vec{r},\vec{R}) = E\psi(\vec{r},\vec{R})$$
(2.2)

Assuming the many-electron system has M nuclei and N electrons, the Hamiltonian operator (H) consists of the kinetic energy of nuclei \hat{T}_n , the kinetic energy of electrons \hat{T}_e , the potential energy of interaction between nuclei \hat{V}_{nn} , the potential energy of interaction between nuclei and electrons \hat{V}_{ne} , and the potential energy of interaction between electrons \hat{V}_{ee} . It can be represented as follows:

$$\hat{H} = \hat{T}_n + \hat{T}_e + \hat{V}_{nn} + \hat{V}_{ne} + \hat{V}_{ee}$$
(2.3)

2.1.2. The Born–Oppenheimer Approximation

For a many-electron system, solving the Schrödinger equation is an extremely difficult and complex task. As for a solution, the process of solving the Schrödinger equation needs to be simplified. Born-Oppenheimer proposed a model to separate the motion of nuclei from the motion of electrons. Since electrons have smaller mass and move much fast as compared to the nuclei, the nuclei can be considered stationary with respect to the motion of the electrons. In this case, the kinetic energy of the nuclei \hat{T}_n has a value of zero, and the potential energy of interaction between nuclei \hat{V}_{nn} becomes a constant. The Hamiltonian operator is then represented as follows:

$$\hat{H} = \hat{T}_{e} + \hat{V}_{nn} + \hat{V}_{ne} + \hat{V}_{ee} = \hat{H}_{e} + V_{nn}$$
(2.4)

in which

$$\widehat{H}_e = \widehat{T}_e + \widehat{V}_{ne} + \widehat{V}_{ee} \tag{2.5}$$

In the Born-Oppenheimer approximation, the wave function of the entire system can be written in the form of a product of two components. The first component describes the motion of the electrons around the stationary nuclei $\psi_e(\vec{r}, \vec{R})$, and the second component describes the motion of the nuclei $\psi_n(\vec{R})$:

$$\psi_{ne}(\vec{r},\vec{R}) = \psi_n(\vec{R})\psi_e(\vec{r},\vec{R})$$
(2.6)

After applying the Born-Oppenheimer approximation and separating the motion of the nuclei and electrons, the Schrödinger equation for electrons becomes an equation specifically describing the motion of the electrons in the system. This equation takes the form:

$$\hat{H}_e \psi_e = E_e \psi_e \tag{2.7}$$

The total energy of the system is the sum of the electronic energy and the potential energy of the nuclei:

$$E = E_e + E_n \tag{2.8}$$

The electronic energy plays the role of potential energy for the motion of nuclei in the Schrödinger equation describing the nuclei motion. Following the movement of nuclei during a chemical transformation, the electrons generate a surface of corresponding electronic energies, called *potential energy surface*, which constitutes a cornerstone of the quantum chemical approaches to the molecular

geometries and spectroscopic properties, as well as reactivities and kinetics of the system considered.

The Born-Oppenheimer approximation assumes that the nuclei are stationary; however, in reality, within a molecule, the nuclei still experience vibrations and motion around their equilibrium positions. In addition to the electronic and nuclear repulsion (potential) energies of the nuclei, a molecule also possesses energy from its vibrational and rotational motions. The total energy of the molecule is then given by:

$$E = E_e + E_n + E_{vib} + E_{rot} \tag{2.9}$$

The energies of vibrational and rotational motions are often calculated using approximate models in statistical mechanics, such as the harmonic oscillators for vibrations and rigid rotors for rotations, as their values are much smaller as compared to the energy of electrons and repulsion energy of nuclei.

2.1.3. *Ab initio* computational method

All integrations in the process of solving the Schrödinger equation are carried out analytically. The Hamiltonian operator and molecular wave function are directly built up from the fundamental equations of quantum. The *ab initio* computational method is thus considered as the most advanced current approach. However, for systems with multiple electrons, the number of integrals to be computed is very large, requiring significant memory and high computational speed. Ab initio computational methods that are based on the wave function include the wellestablished methods such as the Hartree-Fock, and Roothaan (practical approaches of the HF) methods that do not include the correlation energy. Methods having a partial treatment of the correlation energy include the perturbation method (in which the Møller-Plesset perturbation (MPn) is the most popular one), Configuration Interaction (CI), Multi-configuration (MCSCF), Multi-reference Configuration Interaction (MRCI), Coupled-cluster (CC) ... methods.

2.1.4. The Hartree-Fock Method

The Hartree-Fock (HF) method is a fundamental approach in quantum chemistry used to describe the electronic structure of atoms and molecules. Developed independently by Douglas Hartree [59] and Vladimir Fock [60] in the 1920s and 1930s, respectively, the HF method provides a starting point for more advanced computational methods that include electron correlation effects.

The Hartree–Fock method makes five major simplifications in order to deal with this task:

• The Born–Oppenheimer approximation: the Hartree–Fock method inherently assumes the Born–Oppenheimer approximation. This approximation separates the electronic and nuclear motions in molecules, considering the electronic motion quantum mechanically and the nuclear motion either classically or quantum mechanically. Consequently, the full molecular wave function is treated as a function of the electrons' coordinates determined at a fixed nuclear coordinates.

• Neglect of relativistic effects: typically, relativistic effects are completely neglected in the Hartree–Fock method. The momentum operator is assumed to be entirely non-relativistic, disregarding relativistic corrections to the kinetic energy of electrons and other relativistic effects. While relativistic Hartree–Fock methods exist, the standard approach is non-relativistic.

• Finite basis set: the Hartree–Fock method uses a variational solution to determine the electronic energy which assumes that the wave function can be approximated as a linear combination of a finite number of basis functions. These basis functions are usually chosen to be orthogonal, simplifying the calculations. However, the finite basis set is an approximation to a complete basis set, which can, as expected, affect the accuracy of the results.

• Single Slater determinant: Each energy eigenfunction in the Hartree– Fock method is assumed to be represented by a single Slater determinant. A Slater determinant is an antisymmetrized product of one-electron wave functions

or orbitals, accounting for the exchange symmetry of identical particles. This assumption simplifies the calculations but neglects the effects of electron correlation beyond mean-field approximation.

• Mean-field approximation: The HF method implies the mean-field approximation, neglecting effects arising from deviations from this assumption. These effects are collectively known as electron correlation, encompassing both Coulomb correlation and Fermi correlation. The method captures electron exchange (Fermi correlation) but neglects Coulomb correlation, including London dispersion forces. Consequently, the HF method is not able to fully account for dispersion interactions.

Improvement of the last two approximations leads to many post-Hartree–Fock methods, which consider electron correlation effects omitted at the Hartree–Fock treatment. These methods aim to improve the accuracy of electronic structure calculations by incorporating more sophisticated treatments of electron correlation and dispersion forces. As mentioned above, examples of post-Hartree–Fock methods include the configuration interaction, coupled cluster, and many-body perturbation theory ... methods.

2.1.5. Density Functional Theory

Density functional theory (DFT) is a powerful computational method widely used in quantum chemistry and solid-state physics to study electronic structures and properties of molecules, materials, and condensed systems. Unlike the wave function-based method which treats electrons as independent particles moving in the average field of other electrons, DFT takes into account the electron density directly.

In DFT, the key quantity of interest is the electron density, $\rho(\vec{r})$, which describes the probability of finding an electron at position \vec{r} in space. The main idea of DFT is to express the total energy of a system as a functional of its electron density. This means that the energy of the system is a unique and explicit function

of the electron density, and there is no need to solve for individual wave functions as in the HF method.

In practice, the central formalism of DFT boils down to the Kohn-Sham equation, named after Walter Kohn and Lu Sham who developed this approach in 1965 [61]. The Kohn-Sham equation is analogous to the Schrödinger equation in its structure but introduces an effective potential, $\vartheta_{eff}(\vec{r})$, that depends on the electron density and leads to a set of single-electron equations. The Kohn-Sham equation can be written as:

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + \vartheta_{eff}(\vec{r})\right)\psi_i(\vec{r}) = \varepsilon_i\psi_i(\vec{r})$$
(2.10)

where \hbar is the reduced Planck's constant, *m* is the electron mass, $\psi_i(\vec{r})$ is the Kohn-Sham orbital of the ith electron with corresponding eigenvalue ε_i . The effective potential, $\vartheta_{eff}(\vec{r})$, is made up of several components, including the external potential from the nuclei, the electron-electron repulsion, and an exchangecorrelation potential.

The exchange-correlation potential embodies the effects of electron correlation, which remains the main challenge in treatment of many-body quantum systems. This term includes both the exchange interaction, arising from the anti-symmetrization of the wave function, and the correlation effects, accounting for the electron-electron interactions beyond the mean-field approximation. The exchange-correlation potential is typically approximated using various exchange-correlation functionals, which can be derived from theoretical considerations or empirical data.

o Functionals in DFT

In practice, applications of DFT are dependent on the use of the density functionals. Different types of exchange-correlation functionals have been developed to balance accuracy and computational cost. Some commonly used functionals include:

• Local density approximation (LDA): LDA approximates the exchange-correlation functional based on the electron density at a given point in

space. It assumes a uniform electron gas with a constant exchange-correlation energy density throughout the system.

• Generalized gradient approximation (GGA): GGA extends LDA by considering not only the electron density but also its spatial derivatives. GGA functionals include information about the gradient of the electron density, providing a more accurate description of the electron distribution.

• Hybrid functionals: Hybrid functionals combine a fraction of exact (Hartree-Fock) exchange with a local or semi-local exchange-correlation functional. These functionals improve the description of electronic properties, especially for systems with localized electrons, such as transition metals.

• Meta-generalized gradient approximation (meta-GGA): Meta-GGA functionals go beyond GGAs by incorporating not only the electron density but also its gradient and Laplacian. These functionals offer improved accuracy for describing non-local electron density properties.

The choice of the exchange-correlation functional depends on the system of interest, the desired accuracy, and the available computational resources. Researchers often select functionals based on their performance in benchmark calculations and their applicability to specific types of systems.

It is important to note that development of accurate exchange-correlation functionals is an ongoing intensive research area in DFT, as there is no exact functionals known for general use. Therefore, researchers in the field continue to explore and develop new functionals to address specific challenges and improve the accuracy of DFT calculations for various chemical systems, as benchmarked by data from experiment and/or high level wave function methods.

• Basis sets

A *basis set* is used to build up the approximate wavefunction of electrons in a chemical system. It consists of a set of mathematical functions that are combined to describe the one-electron state. These functions represent the spatial distribution of electrons and allow for the building-up of the molecular wave function or electron

density, and thereby calculation of various electronic properties. Basis sets can be broadly categorized into two types, namely atomic orbital basis sets and plane wave basis sets.

• Atomic orbital basis sets: These are commonly used in molecular wave function and DFT calculations, where the electronic structure is described in terms of canonic molecular orbitals (CMO). These basis sets are usually constructed by a linear combination of atomic orbitals centered on each atom in the system corresponding to different types such as s, p, d, f... orbitals. Examples of atomic orbital basis sets include Slater-type orbitals (STOs) and Gaussian-type orbitals (GTOs).

- Slater-type orbitals (STOs): STOs are product of radial functions multiplied by spherical harmonics to incorporate angular dependence. They have desirable mathematical properties to approach the molecular wave functions or to accurately describe electron density in molecules, but the difficulties in computing molecular integrals of STO prevent its practical use.

- Gaussian-type orbitals (GTOs): GTOs are widely used due to their flexibility and computational efficiency. They are expressed as a product of a Gaussian function and an angular part. A large GTOs set is expected to approximate a STO set. GTOs sets can be optimized to describe specific electronic and/or molecular properties accurately.

The choice of atomic orbital basis sets is crucial in computations; it depends on the system or property under study, the level of accuracy required, and available computational resources. In practice, basis sets are typically specified by a set of contracted Gaussian functions with numerical exponents and coefficients that determine the shape and size of the atomic orbitals.

• Plane wave basis sets: these are mainly used in solid-state DFT calculations where the electronic structure is described in terms of extended periodic wavefunctions. In this approach, the electron density and the potential are expanded in terms of plane waves using the Fourier series. Plane wave basis

sets are suited for periodic systems such as crystals, surfaces, and nanoparticles. They can be used for molecular systems but mainly for rapid exploration of the potential energy surface.

2.1.6. Benchmarking the functional and basis set in DFT

DFT is a computational quantum mechanical method used to study the electronic structure and properties of atoms, molecules and materials. In DFT, the choice of density functional and basis set are crucial aspects that significantly impact the accuracy and efficiency of calculations. The preliminary benchmark of functional and basis set is important in DFT study:

• Accuracy of results: different exchange-correlation functionals in DFT have varying levels of accuracy in describing the electron density and energy of a chemical system. Some functionals perform well for certain types of systems or properties, while others may be more accurate for different situations. Benchmarking functionals against experimental data or high-level wave function methods is essential to assess their reliability and limitations.

• System-dependent performance: no single functional is universally accurate for all types of systems or properties. The performance of functionals depends on the nature of the chemical system being studied. By benchmarking various functionals against experimental data or reference results, researchers can identify the functional which is best suited for a specific type of problem.

• Basis set quality: basis sets are sets of mathematical functions used to approximate the electronic wavefunctions or electron densities. Larger basis sets allow for more accurate representations of electronic states, but they also increase the computational cost. Benchmarking different basis sets helps determine the trade-off between accuracy and efficiency. Using a minimal basis set may result in faster calculations but could sacrifice accuracy, while using a very large basis set may lead to highly accurate results but at a higher computational cost. In general, it has been established that while the quality of

wave functions is inherently dependent on the size of basis sets employed, such a dependency is much less severe for DFT results.

• Comparison of methods: a benchmarking different functionals and basis sets allows a fair comparison between different DFT methods and even with other computational techniques, such as wave function-based methods. The strengths and weaknesses of different methods could be evaluated through comprehensive benchmarks and thereby the most appropriate one could be selected for a specific research question.

• Validation and trustworthiness: benchmarking provides us with a way of validating the accuracy and reliability of DFT results. If a functional or basis set is shown to perform well across a wide range of systems and properties, it gains more trust from the scientific community and can be confidently used in forthcoming diverse applications.

• Method development and improvement: the process of benchmarking helps in developing and refining new functionals and basis sets. By understanding the shortcomings of an existing approach, researchers can work towards designing improved methods that could increase the accuracy and efficiency.

In summary, benchmarking the functional and basis set in DFT is essential to ensure the reliability and accuracy of the computed results, select the most suitable method for a particular research question, and drive the development of improved computational approaches in the field of quantum chemistry and materials science.

The computations reported of this dissertation are carried out in the context where the TPSSh [32], PBE0 [62], and HSE06 [63] functionals have widely been employed to investigate the geometric structures of boron clusters or boron-based compounds [64–66]. However, whenever possible, the study of this dissertation also conducts benchmarking studies of these functionals to further demonstrate their suitability for the objectives of this research. As for a representative functional, a brief overview of the TPSSh functional is hereafter presented.
The TPSSh [32] functional, short for Tao, Perdew, Staroverov and Scuseria hybrid functional, represents a significant advancement in DFT computations. It is a hybrid functional that combines the traditional pure functional (TPSS [67]) of the same group of authors with a fraction of exact Hartree-Fock exchange. TPSSh turns out to overcome some of the limitations of pure DFT methods by incorporating a portion of non-local exchange, making it particularly well-suited for systems with challenging electronic properties, such as those of transition metals, open-shell systems, and systems with strong correlation effects. The inclusion of Hartree-Fock exchange enhances the description of van der Waals interactions and improves the accuracy of bond dissociation energies and reaction barrier heights. As a result, TPSSh has gained popularity among researchers studying a wide range of chemical phenomena, offering an concrete approach for tackling complex molecular systems and providing valuable insights into their electronic structure and reactivity.

Nowadays, while DFT is a powerful and widely used computational method, it contains inherent approximations and shortcomings that can lead to errors in the prediction of certain properties. To assess the accuracy and reliability of DFT calculations, it is common practice to compare, where possible, the results with higher-level post-Hartree-Fock methods. Due to the fact that the density functionals are more and more optimized by different groups in incorporating a large number of numerical parameters that are not well defined, it is not clear over where a certain improvement of results comes from. In this sense, DFT tends to become a kind of *semi-empirical* methods rather than fully *ab initio* ones. In addition, there is no uniform set of error margins on DFT data. Differently put, DFT results on different chemical systems can better be compared within the same functional.

2.1.7. Post-Hartree-Fock methods

Post-Hartree-Fock methods are advanced wave function approaches used in quantum chemistry to improve upon the inherent limitations of the HF method. While HF provides a good starting point for describing electronic structure, it neglects important electron correlation effects which are crucial for accurately predicting molecular properties. Post-Hartree-Fock methods thus aim to incorporate electron correlation more rigorously in the wave functions leading to more accurate results.

There are several widely used post-Hartree-Fock methods, including configuration interaction (CI), many-body perturbation theory (MBPT), multiconfiguration (MC), coupled cluster (CC) and multi-reference CI (MRCI)... These methods include electron correlation contributions taking the HF wavefunctions as reference for generating electronic configurations via electron excitations. Accordingly, electronic configurations include the singly excited (called the singles), doubly excited (doubles), triply excited (triples)... wavefunctions. The most commonly used CC methods are the CCSD (coupled cluster including singles and doubles), CCSD(T) (CCSD with a perturbative triples correction), and CCSDT (CC with all possible singles, doubles and triple excitations). CCSD(T) is often referred to as a "gold standard" method in computational quantum chemistry in view of its high accuracy results and computational demands, as compared to higher levels such as the CCSDT, CCSDTQ... methods. Such a designation stems from its high level of accuracy and reliability in treating electron correlation effects. With the test of time, CCSD(T) has become a benchmark against other methods that are evaluated and compared.

The CCSD(T) method is known for its remarkable accuracy in predicting molecular energetics and properties, including total atomization energies, bond dissociation energies, reaction energies, and other parameters related to a potential energy surface. However, it is important to note that CCSD(T) is typically limited to moderate-sized molecules due to its high computational cost, and its applicability to larger systems (over 20 atoms) is expected to be challenging, even with access to high-performance computers (HPC).

The choice of basis set in CCSD(T) calculations also requires a careful consideration. In the case of large molecules, performing CCSD(T) calculations can be computationally expensive, leading to a temptation of selecting excessively small

basis sets that may compromise the accuracy of the results. It does not make sense running a high level post-HF computation using a small basis set.

When the size of the molecule or the level of electron correlation requires a sophisticated treatment, the complete basis set (CBS) extrapolation is a method used to determine the total energy of a chemical species as if it is computed with an infinitely large basis set. It involves performing calculations using a series of basis sets of increasing size and then extrapolating the results to the limit of an infinite basis set. The CBS extrapolation helps to reduce the basis set dependence of the computed results and provides a more accurate value of the system's electronic energy, which is important in obtaining reliable and accurate theoretical results. Performing CCSD(T) calculations using a series of two or three basis sets, namely aug-cc-pVDZ, aug-cc-pVTZ, and aug-cc-pVQZ (in which cc stands for correlation consistent) is a common practice in quantum chemistry. The CBS energy can be estimated from the equation:

$$E(x) = E_{CBS} + Be^{-(x-1)} + Ce^{-(x-1)^2}$$
(2.11)

where x = 2, 3, and 4 for the aug-cc-pVDZ, aug-cc-pVTZ, and aug-cc-pVQZ basis sets, respectively [68]. Alternatively, for a simpler approach (although it requires more RAM resources during calculations), the CBS values can be readily extrapolated using a pre-established keyword in the ORCA program [69].

In addition to its computational cost, the CC method has limitations in accurately describing spin-contaminated structures, which are typically characterized by T1 values greater than 0.02 for closed electron systems and 0.04 for open electron systems [70]. In other words, because the CC method is based on HF reference, it is mainly good for systems that can be characterized by a single reference. To address this challenge and obtain a more precise electronic structure description of such molecules, alternative methods that consider multi-reference methods become necessary. Two common multireference approaches that can handle spin-contaminated systems are the multi-configurational (MC) method and

the Multi-reference Configuration Interaction (MRCI). In particular, the Complete Active Space Self-Consistent Field (CASSCF) which is a specific version of the MC method, can be carried out by several non-commercial software such as the GAMES, ORCA, MOLCAS... The CASSCF wave function is in turn used as reference for a following treatment by 2d-order perturbation theory leading to the CASPT2 method. For its part, the MRCI method used the MC wave functions as references for a subsequent expansion of the configuration interaction whose convergence is variationally determined. By definition, these methods allow us to treat with confidence systems having a multi-reference character and imperatively the excited states. Nevertheless, the main limitation of these methods is that they usually require a huge amount of computing time. For their routine use, an access to superior supercomputing resources is necessary!

2.2. Aromaticity models in boron clusters

Aromaticity models are an integral part of cluster science, providing insights into the stability, magnetic responses, and various other properties of molecules. As of 2017, 45 aromaticity models had been proposed [71]. Within the confines of this dissertation, only the models that have been used will be presented here.

2.2.1. The Hückel and Baird rules

The aromaticity concept began as a descriptor of the special stability of the ring of six carbons, benzene (C₆H₆), the simplest organic and parent hydrocarbon of numerous important aromatic compounds. Since being discovered by Faraday in 1825 [23], many chemical models [72–79] have been developed to account for interesting and unique properties of benzene and at the end the Hückel [6–8] model for aromaticity has proved to be the most suitable, and thereby the most widely used by chemists.

The Hückel theory [7] relies on a separation of cyclic C_nH_n annulenes formed by n carbon atoms into two independent ensembles. The first one consists of n *sp*²-hybridized carbon atoms that determine a σ -framework of C–C and C–H bonds. The second ensemble describes the π system as an ensemble of electrons moving within the effective field determined by the rigid σ -structure, in which all carbon atoms are equivalent. These electrons behave as independent particles. The molecular orbitals (MOs) of this π -system are described as a linear combination of unhybridized *p*-atomic orbitals (AOs). If the molecular plane *xy* determines the σ framework of the annulene under study, the π -system is then defined by n unhybridized *p_z* AOs whose linear combinations generate an ensemble of π -MOs:

$$|\psi\rangle = \sum_{i=1}^{n} c_i |\phi_i\rangle \tag{2.12}$$

where ϕ_i is p_z AO of atom *i*, c_i the contributing coefficient. The wave function (2.12) is now substituted in the Schrödinger equation:

$$\widehat{H}|\psi\rangle = E|\psi\rangle \tag{2.13}$$

$$\widehat{H}\sum_{i=1}^{n}c_{i}|\phi_{i}\rangle = E|\psi\rangle \qquad (2.14)$$

The expectation value of the Hamiltonian operator gives the energy of the system:

$$E = \frac{\langle \psi | \hat{H} | \psi \rangle}{\langle \psi | \psi \rangle} \tag{2.15}$$

We now substitute wave function (2.12) into equation (2.15) and get the energy:

$$E = \frac{\int \left(\sum_{j} c_{j} \phi_{j}\right)^{*} \widehat{H}(\sum_{i} c_{i} \phi_{i}) d\tau}{\int \left(\sum_{j} c_{j} \phi_{j}\right)^{*} \left(\sum_{i} c_{i} \phi_{i}\right) d\tau}$$
(2.16)

Let us suppose that we use real AOs with the real coefficients, the equation (2.16) becomes:

$$E = \frac{\sum_{ij} c_j c_i \int \phi_j \hat{H} \phi_i d\tau}{\sum_{ij} c_j c_i \int \phi_j \phi_i d\tau}$$
(2.17)

We define the Hamiltonian matrix elements (H_{ij}) and the overlap integrals (S_{ij}) as:

$$H_{ij} = H_{ji} = \int \phi_j \widehat{H} \phi_i d\tau \qquad (2.18)$$

$$S_{ij} = S_{ji} = \int \phi_j \phi_i d\tau \tag{2.19}$$

The energy expression in terms of these matrix elements now becomes:

$$E = \frac{\sum_{ij} c_j c_i H_{ij}}{\sum_{ij} c_j c_i S_{ij}}$$
(2.20)

According to the variational principle, the best approximate to the wavefunction is obtained when the energy of the system is minimized. Therefore, we now need to minimize *E* with respect to the coefficients c_i . We can first write equation (2.20) as:

$$E\sum_{ij}c_jc_iS_{ij} = \sum_{ij}c_jc_iH_{ij}$$
(2.21)

Taking the partial derivative of the above with respect to the coefficients c_i and using product rule on the left-hand side, we have:

$$\frac{\partial}{\partial c_i} \left[E \sum_{ij} c_j c_i S_{ij} \right] = \frac{\partial}{\partial c_i} \left[\sum_{ij} c_j c_i H_{ij} \right]$$
$$\frac{\partial E}{\partial c_i} \sum_{ij} c_j c_i S_{ij} + E \sum_j c_j S_{ij} = \sum_j c_j H_{ij}$$
(2.22)

Note that the derivative of a double summation returns to a single summation. One can imagine this by thinking about the term-wise differentiation in the double summation.

Now, setting $\frac{\partial E}{\partial c_i} = 0$ in the above equation to obtain the coefficients with which the energy of the system is minimized. Thus, equation (2.22) becomes:

$$E\sum_{j}c_{j}S_{ij} = \sum_{j}c_{j}H_{ij}$$
(2.23)

which can be equivalently written as:

$$\sum_{j} (H_{ij} - ES_{ij}) c_j = 0$$
(2.24)

or, in the matrix form

$$(\boldsymbol{H} - \boldsymbol{E}\boldsymbol{S})\boldsymbol{c} = \boldsymbol{0} \tag{2.25}$$

For a simplification, the matrix elements in the secular equations can be written in terms of parameters α and β where:

$$\alpha_i = H_{ii} \tag{2.26}$$

$$\beta_{ij} = H_{ij} \tag{2.27}$$

Equation (2.25), when written out in full, now has the form:

$$\begin{pmatrix} \alpha_{1} - E & \beta_{12} & \beta_{13} & \cdots & \beta_{1N} \\ \beta_{21} & \alpha_{2} - E & \beta_{23} & \cdots & \beta_{2N} \\ \beta_{31} & \beta_{32} & \alpha_{3} - E & \cdots & \beta_{3N} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ \beta_{N1} & \beta_{N2} & \beta_{N3} & \cdots & \alpha_{N} - E \end{pmatrix} \begin{pmatrix} c_{1} \\ c_{2} \\ c_{3} \\ \vdots \\ c_{N} \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \\ \vdots \\ 0 \end{pmatrix}$$
(2.28)

To obtain non-trivial solutions of linear combinations of atomic orbitals of a system, we set the *secular determinants* to zero, viz.,

$$\begin{vmatrix} \alpha_{1} - E & \beta_{12} & \beta_{13} & \cdots & \beta_{1N} \\ \beta_{21} & \alpha_{2} - E & \beta_{23} & \cdots & \beta_{2N} \\ \beta_{31} & \beta_{32} & \alpha_{3} - E & \cdots & \beta_{3N} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ \beta_{N1} & \beta_{N2} & \beta_{N3} & \cdots & \alpha_{N} - E \end{vmatrix} = 0$$
(2.29)

This allows obtaining N solutions of the *eigenvalues* E, each of which can be substituted back to equation (2.15) to obtain the coefficients (*eigenvectors*) that obtain the linear combination of atomic orbitals (LCAO) corresponding to the energy. These are negative parameters that are approximately the energy of orbital i and the energy of the interaction of the adjacent orbitals i and j, respectively.

To simplify further the solutions, the Hückel approximations assumes that:

- (1) the overlap between orbitals is neglected, $S_{ij} = 0$,
- (2) the atomic orbitals are normalized, $S_{ij} = 1$, and
- (3) only adjacent orbitals have interactions, $H_{ij} \neq 0$ only if *i* and *j* are adjacent to each other.

Equation (2.29) when written out in full, now has the form:

$$\begin{vmatrix} \alpha - E & \beta & 0 & \cdots & \beta \\ \beta & \alpha - E & \beta & \cdots & 0 \\ 0 & \beta & \alpha - E & \cdots & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ \beta & 0 & 0 & \cdots & \alpha - E \end{vmatrix} = 0$$
(2.30)

The secular determinant for benzene is now available:

$$\begin{vmatrix} \alpha - E & \beta & 0 & 0 & 0 & \beta \\ \beta & \alpha - E & \beta & 0 & 0 & 0 \\ 0 & \beta & \alpha - E & \beta & 0 & 0 \\ 0 & 0 & \beta & \alpha - E & \beta & 0 \\ 0 & 0 & 0 & \beta & \alpha - E & \beta \\ \beta & 0 & 0 & 0 & \beta & \alpha - E \end{vmatrix} = 0$$
(2.31)

If both sides of (2.31) are divided by β^6 and a new variable x is defined as:

$$x = \frac{\alpha - E}{\beta} \tag{2.32}$$

the secular determinant for benzene becomes:

$$\begin{vmatrix} x & 1 & 0 & 0 & 0 & 1 \\ 1 & x & 1 & 0 & 0 & 0 \\ 0 & 1 & x & 1 & 0 & 0 \\ 0 & 0 & 1 & x & 1 & 0 \\ 0 & 0 & 0 & 1 & x & 1 \\ 1 & 0 & 0 & 0 & 1 & x \end{vmatrix} = 0$$
(2.33)

with the six roots $x = \pm 2, \pm 1, \pm 1$. This corresponds to the following energies (ordered from the most stable to the least since $\beta < 0$):

 $\begin{array}{l} \circ \quad E_1 = \alpha + 2\beta \\ \circ \quad E_2 = \alpha + \beta \\ \circ \quad E_3 = \alpha + \beta \\ \circ \quad E_4 = \alpha - \beta \\ \circ \quad E_5 = \alpha - \beta \\ \circ \quad E_6 = \alpha - 2\beta \end{array}$

The two pairs of $E = \alpha \pm \beta$ energy levels are two-fold degenerate (Figure 2.1):



Figure 2.1. The π molecular orbitals of benzene according to the Hückel theory. The dashed line represent the energy of an isolated *p* orbital, and all orbitals below this line are bonding. All orbitals above it are antibonding.

Each of the carbons in benzene contributes one electron to the π -bonding framework (Figure 2.1). This means that all bonding MOs are fully occupied, and benzene then has an electron configuration of $\pi_1^2 \pi_2^4$.



Figure 2.2. MO energy diagrams of C_4H_4 (in both singlet and triplet states), C_6H_6 , C_8H_8 (in both singlet and triplet states), and $C_{10}H_8$. The blue/red labels indicate the aromatic/antiaromatic species.

Figure 2.2 represent the MO energy diagrams for hydrocarbon compounds containing 4, 6, 8 and 10-membered rings. The benzene and naphthalene possess 6 and 10 π -electrons, respectively, and thus they satisfy the electron counting rule (4*n* + 2) with n = 1 for benzene and n = 2 for naphthalene. Both benzene and naphthalene were confirmed as aromatic species [80–83].

The singlet states of both C_4H_4 and C_8H_8 have two π -electrons filling one MO in a two-fold degenerates level and these structures are distorted following the Jahn-Teller effect [84] which leads to a breaking in degeneracy which stabilizes the structures and as a consequence, reduces its symmetry. The 4 and 8 π -electrons of the singlet of C₄H₄ and C₈H₈, respectively, follows the electronic counting rule 4*n* and these isomers are considered as antiaromatic species [82, 83, 85].

The triplet ground state of the planar $C_5H_5^+$ cation which owns 4 π electrons [86, 87] supports the Baird rule of a 4*n* triplet aromatic [22]. The Baird rule turns the triplet states of C₄H₄ and C₈H₈ into aromatic species.

In general, the Hückel rule, which is originally applied to a cyclic, planar, and fully conjugated molecule, is that a compound contains $(4n + 2) \pi$ electrons in a closed-shell system is an aromatic species. In contrast, a structure with $4n \pi$ -electrons in a closed-shell system is antiaromatic and then very unstable.

The Baird rule is used for counting backwards for the cyclic, planar, and fully conjugated systems in the triplet state. The Baird rule claims that in the open-shell state, while $4n \pi$ electrons lead to an aromatic character, $(4n + 2) \pi$ electrons correspond to an antiaromaticity species.

Both Hückel rule and Barid rule are used to predict the chemical and physical properties of organic and inorganic compounds. They are used to predict the electrical conductivity of conducting polymers, the magnetic properties of magnetic organic compounds, research new organic compounds with superior electrical or magnetic properties, ... [88–91]. As mentioned above, these electron counts were first account for π electrons in planar cyclic hydrocarbons, they are along the years widely applied to all kinds of 2D and 3D structures [92–94], not

only for π electron systems but also for σ and δ electron systems mostly in atomic clusters [95–97].

2.2.2. Ribbon aromaticity

The ribbon structure of boron derivatives has attracted much interest in the last decade because of its exceptional stability. A double chain of boron atoms in the $B_{22}H_2^{2-}$ dianion can be elongated to 17.0 Å while the distance between two chains is only about 1.5 Å [98]. Systematic studies on ribbon structures [98, 99] pointed out that a common point in ribbon structures with outstanding stability is that their electrons satisfy the electron configuration of $\pi^{2(n+1)}\sigma^{2n}$ (cf. Figure 2.3). An example of π and σ electrons assignment is given in Figure 2.4.



Figure 2.3. Calculated curves as a function of size n for (**a**) adiabatic detachment energies of $Li_2B_nH_2^-$ (n = 6–22) ribbon clusters, and (**b**) Ionization energies of $Li_2B_nH_2$ (n = 6–22) ([98]).

Different approaches such as the electron localization function (ELF), AdNDP, and nuclear independent chemical shift (NICS) analyses were used to reveal the aromaticity of ribbon structures. To have a closer look at the origin of the aromatic character in ribbon structures, the researcher group, including doctoral student, proposed a ribbon aromatic model in 2017 based on an analysis for the silicon-doped boron structures $B_{10}Si_2^{2-}$ and $B_{12}Si_2^{2-}$ [26].



Figure 2.4. The electron configuration $\pi^6 \sigma^4$ of the ribbons $B_{10}H_2^{2-}$ and $B_{11}H_2^{-}$.

Based on the long and narrow structure of a ribbon, electrons are assumed to move freely along a one-dimensional box. The corresponding Schrödinger equation for a particle of mass m moving in the x-direction is:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x)$$
(2.34)

where V(x) is the potential energy of the particle at position x, E is the (constant) total energy, and ψ is the wave function. For the present system the potential-energy function is (cf. Figure 2.5):

$$V(x) = \begin{cases} 0, & \text{for } 0 < x < l\\ \infty, & \text{for } x \le 0 \text{ and } x \ge l \end{cases}$$
(2.35)

For the particle within the box, we have the boundary value problem:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} = E\psi(x)$$
(2.36)

with boundary conditions:

$$\psi(0) = \psi(l) = 0$$

$$V = \infty \qquad (2.37)$$

$$V = \infty \qquad V = 0 \qquad V = \infty \qquad x$$



The equation (2.36) has a general solution in trigonometric form:

$$\psi(x) = A\cos(\omega x) + B\sin(\omega x)$$
(2.38)

with

$$\omega = \frac{2mE}{\hbar^2} \tag{2.39}$$

We now apply the boundary conditions (2.37). At x = 0:

$$\psi(0) = A\cos(0) + B\sin(0) = A = 0 \tag{2.40}$$

and at x = l:

$$\psi(0) = B\sin(\omega l) \tag{2.41}$$

It follows that, because the sinus function is equal to zero only when its argument is a multiple of π ($\omega l = n\pi$) where *n* is an integer:

$$\omega = \frac{n\pi}{l}, \quad n = 0, \pm 1, \pm 2, \dots$$
 (2.42)

The normalized solutions of the boundary value problem are therefore:

$$\psi_n(x) = \sqrt{\frac{2}{l}} \sin\left(\frac{n\pi x}{l}\right), \quad n = 1, 2, 3, \dots$$
(2.43)

The value n = 0 has been discounted because the trivial solution $\psi_0(x) = 0$ is not a physical solution, and negative values of n have been discounted because $\psi_{-n}(x) = -\psi_n(x)$ is merely $\psi_n(x)$ with a change of sign.

The energy of each wave function:

$$E_n = \frac{n^2 h^2}{8ml^2}$$
(2.44)

As illustrated in Figure 2.4, the sets of π and σ electrons can be viewed as sinus wavefunctions of equation (2.43) where the electrons move in onedimensional boxes of length l_{π} and l_{σ} , respectively, and have energies levels defined by:

$$E_{n_{\pi}} = \frac{n_{\pi}^2 h^2}{8m l_{\pi}^2} \tag{2.45}$$

$$E_{n_{\sigma}} = \frac{n_{\sigma}^2 h^2}{8m l_{\sigma}^2} \tag{2.46}$$

The energy levels obtained from quantum chemical calculations such as density functional theory and the energy levels from the equations (2.45) and (2.46) are related to the energies from DFT approach by the expressions:

$$E_{DFTn_{\pi}} = E_{n_{\pi}} + C_{1\pi} = C_{2\pi}n_{\pi}^2 + C_{1\pi}$$
(2.47)

$$E_{DFTn_{\sigma}} = E_{n_{\sigma}} + C_{1\sigma} = C_{2\sigma}n_{\sigma}^{2} + C_{1\sigma}$$
(2.48)

with $C_{2\pi} = \frac{h^2}{8ml_{\pi}^2}$ and $C_{2\sigma} = \frac{h^2}{8ml_{\sigma}^2}$.

Use of nonlinear minimization algorithm leads to the residual sum of squares (RSS):

$$RSS_{\pi} = \sqrt{\sum_{i=1}^{N_{\pi}} (E_{DFTn_{\pi}} - E_{n_{\pi}})^2}$$
(2.49)

$$RSS_{\sigma} = \sqrt{\sum_{i=1}^{N_{\sigma}} (E_{DFTn_{\sigma}} - E_{n_{\sigma}})^2}$$
(2.50)

In such a way that the minima can be achieved and derive the constants $C_{1\pi}$, $C_{2\pi}$, $C_{1\sigma}$, and $C_{2\sigma}$, and consequently determine the lengths of the 1D box l_{π} and l_{σ} , respectively. The numbers N_{π} and N_{σ} are of the considered CMOs. A minimum of two π -CMOs is required to be able to determine l_{π} and a minimum of 2 σ -CMOs is also required to determine l_{σ} .

The validity of the ribbon model has clearly been demonstrated in the previous study [26] through an analysis of structures of $B_{12}Si_2^{2-}$ and the singlet and triplet states of $B_{10}Si_2^{2-}$. To show the universality of the model, we restate hereafter the model through the analysis of the boron hydride dianion $B_{14}H_2^{2-}$, and the singlet and triplet states of $B_{12}H_2^{2-}$.



Figure 2.6. A comparison between the l_{π} , l_{σ} and the distance of between the two most distant B atoms of $B_{14}H_2^{2-}$.

This simple solution for the wavefunction of the particle in one-dimensional box model provides a result for the ribbon $B_{14}H_2^{2-}$ with a length of 12.4 Å for l_{π} and 11.1 Å for l_{σ} . Both l_{π} and l_{σ} are slightly greater than the distance 10.6 Å of between the two most distant B atoms of $B_{14}H_2^{2-}$ (cf. Figure 2.6). This means that the one-dimensional box model is suitable for describing the electrons in the ribbon structure. The extension from π and σ electrons can be rationalized in terms of the hybridization of the 2*p*-AO in the ribbon structure, where l_{π} is larger because the 2*p_z*-AO is more favourable for hybridization.



Figure 2.7. **a**) The ribbon structure of $B_{14}H_2^{2-}$. **b**) ELF_{σ l} plot for $B_{14}H_2^{2-}$, and **c**) ELF_{π} (yellow basins) and ELF_{σ d} (green basins) are plotted simultaneously for $B_{14}H_2^{2-}$.

The first success of the model of a particle moving in a one-dimensional box showed that both sets of π and σ electrons fit this model well. However, this also does not provide an explanation for the $\pi^{2(n+1)}\sigma^{2n}$ electronic configuration observed in the "*magic*" ribbon clusters. To provide with an answer for this, an analysis of the relationship between the ELF maps and bond lengths in ribbon $B_{14}H_2^{2-}$ is performed as shown in Figure 2.7.

The ELF_{σ 1} map in Figure 2.7.b collects 16 localized σ CMOs of B₁₄H₂²⁻ that shows the existence of 16 (2-center – 2-electrons) basins in 14 peripheral B-B bonds and 2 B-H bonds. The 16 localized σ CMOs create a steady framework for the ribbon, and it also constitutes a reason for why the peripheral B-B bonds in boron ribbon are always shorter than the inner B-B bonds that do not include any localized electron.

Figure 2.7.c represents simultaneously the plots of ELF_{π} in the yellow basins and $\text{ELF}_{\sigma d}$ in the green basins of $B_{14}H_2^{2-}$. The bond length (Å) of $B_{14}H_2^{2-}$ also shown in Figure 2.7.a in which the yellow areas represent the regions which experience most interaction from π electrons. The red and green bond length labels in this Figure indicate the bonds shortened by π and σ electrons, respectively.

We now split the $B_{14}H_2^{2-}$ ribbon into two different rows: the top row includes B1 to B7 and the bottom row includes B8 to B14. At the first glance, we can recognize that the π basins tend to shorten the bond distances that connect two atoms from different rows (type-1 bonding) whereas the σ basins reduce the lengths of the bonds that connect two atoms of the same row (type-2 bonding). The delocalized σ electrons also affect the type-1 bonding but with a rather weak intensity, due to the fact that the basins located inside the structure of ELF_{σ} analysis thus points out that delocalized σ electrons prefer to move from outside to inside of the structure. This phenomenon is well known with π electrons.

Although such an observation is qualitative, the bond length differences are significantly clear for a distinction over the regions where π basins or delocalized σ basins are, and where they are not. For B₁₄H₂²⁻, the B2–B3 and the B9–B10 by the C_{2h} symmetry distances are the longest of the peripheral B–B bonds, because there is no basin from delocalized electrons in this place, and the B2–B12 and B9–B5 are the longest bond among the whole B–B bonds, because they are received the least

enhancement from σ localized and delocalized electrons and π electrons (Figure 2.7)



Figure 2.8 **a**) The ribbon structure of the singlet $B_{12}H_2^{2-}$; **b**) ELF_{σ 1} plot for the singlet $B_{12}H_2^{2-}$, and **c**) ELF_{π} (yellow basins) and ELF_{σ d} (green basins) are plotted simultaneously for the singlet $B_{12}H_2^{2-}$.

Closest to the centre of the huge ELF_{π} basins, the B1–B14 and B7–B8 bond length amount just to about 1.55 Å. The B1–B14 and B7–B8 distances in B₁₄H₂²⁻ are terminal bonds. A shortening of these bonds leads to an increase of interatomic Coulombic repulsion which results in a high potential border, in such a way that delocalized π and σ electrons can now move into a one-electron box. We would name this shortened terminal bond phenomenon in ribbon structures as a *self-locked* phenomenon.

To highlight the alternant interaction of the ELF_{π} and $\text{ELF}_{\sigma d}$ basins which stabilizes the ribbon structures through an electron configuration of $\pi^{2(n+1)}\sigma^{2n}$, we

perform a similar analysis for the dianion $B_{12}H_2^{2-}$ in both singlet and triplet states (Figures 2.8 and 2.9).



Figure 2.9. **a**) The ribbon structure of the triplet $B_{12}H_2^{2^-}$. **b**) ELF_{σ l} plot for the triplet $B_{12}H_2^{2^-}$. **c**) ELF_{π} (yellow basins) and ELF_{σ d} (green basins) are plotted simultaneously for the triplet $B_{12}H_2^{2^-}$. **d**) and **e**) are the ELF_{π} and ELF_{σ d} plotted simultaneously for the triplet $B_{12}H_2^{2^-}$ from α and β electrons, respectively.

At the theoretical level of TPSSh/6-311++G(d,p), the singlet and triplet states of $B_{12}H_2^{2-}$ have an energy difference of no more than 1 kcal/mol. However, while its triplet state is a stable structure with the smallest frequency about 68 cm⁻¹, the singlet state of $B_{12}H_2^{2-}$ is unstable with a negative frequency about -178 cm⁻¹.

The B₁₂H₂²⁻ singlet includes 8 delocalized π and 4 delocalized σ electrons that satisfy the electron configuration of $\pi^{2n}\sigma^{2n}$ instead of the $\pi^{2(n+1)}\sigma^{2n}$. As a result, there is a disconnection between both ELF_{π} and ELF_{σd} basins (cf. Figure 2.8). These basins leave the rhombus B2–B3–B10–B11 (and B4–B5–B8–B9 by symmetry)

with the least enhancement. These rhombus units are the weakened bridges between the three remaining parts of the structure. Therefore, a ribbon structure with the electron configuration of $\pi^{2n}\sigma^{2n}$ turns out to be a ribbon antiaromatic species.

The ribbon $B_{12}H_2^{2-}$ has the electron configuration of $\pi^{2n+1}\sigma^{2n-1}$ with 4 α and 3 β electrons π and 3 α and 2 β electrons σ . The ELF_{π} and ELF_{σd} maps made only for α and only for β spin electrons are ploted in Figure 2.9 (d and e). These basins are interconnected with each other. Some bonds can be supported by α electrons, and some others by β electrons or both. Therefore, Figure 2.9.c shows a spread of both ELF_{π} and ELF_{σd} basins of all α and β electrons. The weakened bridge is eliminated in this form.

Although the triplet state is not the preferred state of doped boron structures, the $\pi^{2n+1}\sigma^{2n-1}$ electronic configuration provides a guaranty for a certain stability to the ribbon structure and is therefore named as the ribbon triplet aromaticity.

2.2.3. Disk aromaticity

Although the solution of the wave function for a disk has been known and popularized in a general textbook on chemistry [100], the application of this model to the explanation for the stability of a molecule was proposed by Tai *et. al.* for the first time in 2012 [101]. In the disk aromaticity model, a type of electron (e.g., σ or π) is considered as a free particle moving on a plane encircled by infinite walls. The radius of the disk is denoted by R. In polar coordinates, the Schrödinger equation for this geometric shape is written as follows:

$$-\frac{\hbar^2}{2\mu} \left(\frac{\partial^2 \psi}{\partial r^2} + \frac{1}{r} \frac{\partial \psi}{\partial r} + \frac{1}{r^2} \frac{\partial^2 \psi}{\partial \theta^2} \right) = (E - V)\psi$$
(2.51)

with

$$V(r,\theta) = \begin{cases} 0, & \text{for } r < R, \text{ (inside the box)} \\ \infty, & \text{elsewhere} \end{cases}$$
(2.52)

and r is the distance from the origin at the centre of the box.

Multiply the equation (2.51) by $-2\mu r^2/\hbar^2$ and setting:

$$\alpha^2 = \frac{2\mu E}{\hbar^2} \tag{2.53}$$

for the particle within the box, with V = 0, we have:

$$r^{2}\frac{\partial^{2}\psi}{\partial r^{2}} + r\frac{\partial\psi}{\partial r} + \alpha^{2}r^{2}\psi + \frac{\partial^{2}\psi}{\partial\theta^{2}} = 0$$
(2.54)

This equation can now be reduced to two ordinary equations by writing the wave function as a product:

$$\psi(r,\theta) = \mathcal{R}(r) \times \Theta(\theta) \tag{2.55}$$

Substitution of this wavefunction in equation (2.54) and division by $\psi = \mathcal{R}\Theta$ then give:

$$\left[\frac{r^2}{\mathcal{R}}\frac{d^2\mathcal{R}}{dr^2} + \frac{r}{\mathcal{R}}\frac{dR}{dr} + \alpha^2 r^2\right] + \left[\frac{1}{\Theta}\frac{d^2\Theta}{d\theta^2}\right] = 0$$
(2.56)

Each set of terms in square brackets must be constant so that, with separation constant C,

$$r^{2}\frac{d^{2}\mathcal{R}}{dr^{2}} + r\frac{dR}{dr} + \alpha^{2}r^{2}\mathcal{R} = C\mathcal{R}$$
(2.57)

for the radial motion of the particle in the box, and

$$\frac{d^2\Theta}{d\theta^2} = -C\Theta \tag{2.58}$$

for the angular motion of the particle.

The equation (2.58) has a general solution which is in exponential form:

$$\Theta(\theta) = c_1 e^{i\omega\theta} + c_2 e^{-i\omega\theta}$$
(2.59)

The function $\Theta(\theta)$ is defined in the interval and must satisfy the periodic boundary condition:

$$\Theta(\theta) = \Theta(\theta + 2\pi) \tag{2.60}$$

for continuity round the circle. It means that:

$$c_1 e^{i\omega\theta} + c_2 e^{-i\omega\theta} = c_1 e^{i\omega\theta} e^{i\omega 2\pi} + c_2 e^{-i\omega\theta} e^{-i\omega 2\pi}$$
(2.61)

The condition (2.60) is then satisfied if both $e^{i\omega 2\pi} = 1$ and $e^{-i\omega 2\pi} = 1$, or $\omega 2\pi$ is a multiple of 2π :

$$\omega 2\pi = m2\pi, \qquad m = 0, \pm 1, \pm 2, \dots$$
 (2.62)

The possible values of ω are then (using *m* to table the values) $\omega_m = m$, and the corresponding solutions are:

$$\Theta(\theta) = c_1 e^{im\theta} + c_2 e^{-im\theta}, \quad m = 0, \pm 1, \pm 2, \dots$$
(2.63)

We note that the states of the system with quantum number $m \neq 0$ occur in degenerate pairs, Θ_m and Θ_{-m} :

$$\mathcal{H}\Theta_m = E_m \Theta_m \quad \text{and} \quad \mathcal{H}\Theta_{-m} = E_m \Theta_{-m}$$
 (2.64)

By the principle of superposition, every linear combination of a pair of degenerate eigenfunctions is itself an eigenfunction with the same eigenvalue:

$$\mathcal{H}(a\Theta_m + b\Theta_{-m}) = E_m(a\Theta_m + b\Theta_{-m}) \tag{2.65}$$

where *a* and *b* are arbitrary constants. It is physically possible to distinguish degenerate states of a quantum system only by the application of an external force to break the degeneracy. In the absence of such a force, therefore, every choice of coefficients c_1 and c_2 is equally good. It is conventional to choose $c_2 = 0$ in equation (2.63), to give the set of eigenfunctions:

$$\Theta_m(\theta) = c_1 e^{im\theta}, \quad m = 0, \pm 1, \pm 2, \dots$$
 (2.66)

Choice of c_1 to normalize these functions leads to the normalized eigenfunctions:

$$\Theta_m(\theta) = \frac{1}{\sqrt{2\pi}} e^{im\theta}, \quad m = 0, \pm 1, \pm 2, \dots$$
 (2.67)

Substitution of equation (2.67) into equation (2.58) to get the separation constant $C = m^2$. With $C = m^2$, the radial equation (2.57) is:

$$r^2 \frac{d^2 \mathcal{R}}{dr^2} + r \frac{d\mathcal{R}}{dr} + (\alpha^2 r^2 - m^2)\mathcal{R} = 0$$
(2.68)

The equation is transformed into the Bessel equation by means of the change of variable $x = \alpha r$. Then:

$$\frac{d\mathcal{R}}{dr} = \frac{d\mathcal{R}}{dx}\frac{dx}{dr} = \alpha, \qquad \frac{d^2\mathcal{R}}{dr^2} = \alpha^2 \frac{d^2\mathcal{R}}{dx^2}$$
(2.69)

and equation (2.69) becomes the Bessel equation:

$$x^{2}\frac{d^{2}\mathcal{R}}{dx^{2}} + x\frac{d\mathcal{R}}{dr} + (x^{2} - m^{2})\mathcal{R} = 0$$
(2.70)

When n is a positive integer or zero, the solution of this equation is wellknown as the Bessel function expressed as:

$$J_m(x) = \left(\frac{x}{2}\right)^m \sum_{p=0}^{\infty} \frac{(-1)^p}{p! (m+p)!} \left(\frac{x}{2}\right)^p$$
(2.71)

This is the **Bessel function of the first kind of order** *m*.

Therefore, the solutions of the radial equation are:

$$\mathcal{R}_m(r) = J_m(\alpha r), \quad m = 0, 1, 2, 3, \dots$$
 (2.72)

These solutions are subjected to the condition that the wavefunction vanishes at the boundary of the box, when r = R. We thus have:

$$\mathcal{R}_m(R) = J_m(\alpha R) = 0 \tag{2.73}$$

and the possible values of α are determined by the zeros of the Bessel function.

The graphs of the Bessel functions (cf. Figure 2.10) have properties similar to those of the trigonometric functions. However, the values of x for which $J_m(x) = 0$, the zeros of the functions, are not equally spaced in such a way that the functions do not have a fixed wavelength. If the zeros of $J_m(x)$ are labelled $x_{m,1}, x_{m,2}, x_{m,3}, \dots$, the allowed values of α are:

$$\alpha_{m,n} = \frac{x_{m,n}}{R}, \qquad n = 1,2,3,...$$
 (2.74)

Here *n* is a radial quantum number that counts the zeros. Notice that we remove the solution $x = \alpha R = 0$ in this case because $\alpha \neq 0$ and $R \neq 0$. Some of the roots $\alpha_{m,n}R$ are shown in Table 2.1.

Table 2.1. First three roots $(\alpha_{m,n}R)$ of the Bessel functions of the first kind, with the integer constant *m* ranging from 0 to 4.

n	$\alpha_{0,n}R$	$\alpha_{1,n}R$	$\alpha_{2,n}R$	$\alpha_{3,n}R$	$\alpha_{4,n}R$
1	2.405	3.832	5.136	6.380	7.588
2	5.520	8.417	9.761	11.065	12.339
3	8.654	10.173	11.620	13.015	14.373



Figure 2.10. The Bessel functions $J_m(x)$ with m = 0, 1, and 2.



Figure 2.11. Symmetries of some wavefunctions in the disk model. The two colours red and blue indicate the opposite signs of the wave functions.

By equation (2.53), the energy of the system is given by $E = \alpha^2 \hbar^2 / 2\mu$, leading to the energy quantized with values:

$$E_{m,n} = \frac{\alpha_{m,n}^2 \hbar^2}{2\mu} = \frac{x_{m,n}^2 \hbar^2}{2\mu R^2}, \qquad n = 1, 2, 3, \dots, \qquad m = 0, \pm 1, \pm 2, \dots$$
(2.75)

and the corresponding total wave functions are:

$$\psi_{m,n}(r,\theta) = \mathcal{R}_{|m|,n}(r)\Theta_m(\theta) \tag{2.76}$$

An example of the representation of some low energy wavefunctions is shown in Figure 2.11. In summary, equations (2.76) and (2.75) show that the wavefunctions and their respective energies in the circular disk model are distinguished by two quantum numbers, namely, the radial n = 1,2,3,... and the rotational $m = 0, \pm 1, \pm 2, \pm 3,...$ The rotational quantum numbers are usually denoted by Greek letters: $m = \sigma, \pi, \delta, \phi, \gamma, ...$ (sometimes these could be confused with the bond type notations as $\sigma, \pi, ...$). States with nonzero values for m will be 2fold degenerate. The lowest eigenstates in ascending order are $1\sigma, 1\pi, 1\delta, 2\sigma$, and so on.

2.2.4. Hollow cylinder model

Figure 2.12 displays the geometrical parameters that define a hollow cylinder model (HCM).



Figure 2.12. Hollow cylinder model. The hollow cylinder's height is L, radius is R, inner radius is R_0 , and outer radius is R_1 . Particle's movement is limited from R_0 to R_1 , with $R_0 = R - r$, $R_1 = R + r$ where r is called the active radius of the hollow cylinder.

In cylindrical coordinates, the Schrödinger equation for a particle of mass μ moving in this hollow cylinder is expressed by the equation (2.66):

$$\left(\frac{\partial^2}{\partial\rho^2} + \frac{1}{\rho}\frac{\partial}{\partial\rho} + \frac{1}{\rho^2}\frac{\partial^2}{\partial\theta^2}\right)\psi(\rho,\theta,z) + \vartheta^2\psi(\rho,\theta,z) = 0$$
(2.77)

where

$$\boldsymbol{\vartheta}^{2} = \frac{2\mu}{\hbar^{2}} \left(E - V(\rho, z) \right) \tag{2.78}$$

for a potential depending on the radial coordinate ρ and z. Here, $V(\rho, z)$ is a step potential depending on the radial coordinate ρ and the height z:

$$V(\rho, z) = \begin{cases} 0, & \text{if } R_0 \le \rho \le R_1 \text{ and } 0 \le z \le L \\ \infty, & \text{otherwise} \end{cases}$$
(2.79)

The solutions for equation (2.79) were previously proposed by Gravesen and coworkers [102]. According, the wavefunction $\psi(\rho, \theta, z)$ can be written as:

$$\psi(\rho, \theta, z) = P(\rho)\Theta(\theta)Z(z)$$
(2.80)

with:

$$\Theta_l(\theta) = \frac{1}{\sqrt{2\pi}} e^{il\theta} \tag{2.81}$$

and

$$Z_k(z) = \sqrt{\frac{2}{L}} \sin\left(\frac{k\pi}{L}z\right)$$
(2.82)

and

$$\rho^2 \frac{\partial^2 P}{\partial \rho^2} + \rho \frac{\partial P}{\partial \rho} + (\vartheta_{ln}^2 \rho^2 - l^2)P = 0$$
(2.83)

and $\boldsymbol{\vartheta}^2 = \vartheta_{ln}^2 + \left(\frac{k\pi}{L}\right)^2$.

The $Z_k(z)$ function responds to the boundary conditions at two surfaces z = 0and z = L in such a way that the rational quantum number k must be a positive integer (k = 1, 2, 3, ...). In addition, the $\Theta_l(\theta)$ function must satisfy the periodic number l which for its part must be an integer ($l = 0, \pm 1, \pm 2, \pm 3, ...$). States with nonzero values for l will be 2-fold degenerate.

The general solution to the Bessel equation (2.83) is:

$$P(\rho) = AJ_l(\vartheta_{ln}\rho) + BY_l(\vartheta_{ln}\rho)$$
(2.84)

where A, B are numbers and J_l , Y_l are Bessel functions of order l of the first and second kinds, respectively. A solution of the $P(\rho)$ equation with the vanished boundary conditions at inner and outer radii positions ($\rho = R_0$ and $\rho = R_1$) is a Bessel function, which is written in equation:

$$J_l(\vartheta_{ln}R(1+\varepsilon))Y_l(\vartheta_{ln}R(1-\varepsilon)) - J_l(\vartheta_{ln}R(1-\varepsilon))Y_l(\vartheta_{ln}R(1+\varepsilon)) = 0 \quad (2.85)$$

There are three parameters in equation (2.85): l, $\vartheta_{ln}R$, and ε . J_l and Y_l are the Bessel functions of order l with the first and the second kind, repsectively.

 $\varepsilon = r/R$ is the pseudo-radius of the hollow cylinder. Determination of the $\vartheta_{ln}R$ parameter allows the energies of the equation (2.77) to be derived as given:

$$E = \frac{\hbar^2}{2\mu R^2} \left[(\vartheta_{ln} R)^2 + \left(\frac{k\pi}{L^f}\right)^2 \right]$$
(2.86)

in which $L^f = L/R$ is called pseudo-height of the hollow cylinder.



Figure 2.13. The variation of function $f(\vartheta_{ln}R)$ in equation (2.85) according to $\vartheta_{ln}R$ with $\varepsilon = 0.5$ and $l = \pm 1$ or $l = \pm 2$.

If the pseudo-radius ε and the rotational quantum number l are known, we can then plot the $f(\vartheta_{ln}R)$ and thereby determine the value of $\mathcal{S}_{ln} = \vartheta_{ln}R$ for which $f(\vartheta_{ln}R) = 0$. An example of the variation of function $f(\vartheta_{ln}R)$ in equation (2.85) according to $\vartheta_{ln}R$ with $\varepsilon = 0.5$ and $l = \pm 1$ or $l = \pm 2$ is shown in Figure 2.13. This implies that equation (2.85) can be solved by numerical method at the n = 1, 2, 3, ... is the order of the solution.

In such a context, the energies in the HCM are characterized by three quantum numbers including a rational (k = 1, 2, 3, ...), a rotational ($l = 0, \pm 1, \pm 2, \pm 3, ...$), and a radial (n = 1, 2, 3, ...) quantum number. Accordingly, the energy in an ascending ordering is changed following any change of the values of ε or L^{f} .

Determination of the value S_{ln} brings us to the explicit form of the wavefunction $\psi(\rho, \theta, z)$ in eqn (2.80):

$$\psi(\rho,\theta,z) = C \sin\left(\frac{k\pi}{L}z\right) e^{il\theta} \left(J_l\left(\mathcal{S}_{ln}\frac{\rho}{R}\right) - \frac{J_l\left(\mathcal{S}_{ln}(1+\varepsilon)\right)}{Y_l\left(\mathcal{S}_{ln}(1+\varepsilon)\right)} Y_l\left(\mathcal{S}_{ln}\frac{\rho}{R}\right) \right)$$
(2.87)

Chapter 3. RESULTS AND DISCUSSION

In this chapter, a selection of the results obtained during the doctoral study is reported, illustrating the different models of aromaticity in atomic clusters, whose backgrounds are described in Chapter 2. These include i) the mixed silicon-boron clusters for the ribbon model, ii) the boron clusters B_{70}^{2-} for the disk model, iii) the lithium doped boron clusters for the disk-cone model, and iv) the multiply doped boron clusters for the hollow cylinder model.

3.1. The Hückel rule and the ribbon model: The cases of B₂Si₃^q and B₃Si₂^p clusters.

The main content in this section is taken from the published paper entitled "Boron Silicon $B_2Si_3^q$ and $B_3Si_2^p$ Clusters: The Smallest Aromatic Ribbons", by **Long Van Duong**, Nguyen Ngoc Tri, Nguyen Phi Hung, and Minh Tho Nguyen, in the Journal of Physical Chemistry A, vol. 126, no. 20, pp. 3101–3109, May 2022.

3.1.1. Motivation for the study

As stated in Chapter 2, the selection of appropriate functionals and basis sets for study of specific properties of particular chemical systems tends to go beyond the knowledge of a practical computational quantum researcher. In such cases, statistical benchmark studies for various types of functionals and basis sets have proven to be more effective, creating a database that enables scientists to develop accessible methods for improving theoretical approaches. A good benchmark should be initiated with small structures and accompanied by, where available, experimental data to arrive at reliable conclusions. Based on this notion, the research conducted computations on boron or boron doped clusters that had been analysed through experiments, and incidentally discovered a discrepancy with the results reported by Lu and co-workers [103] concerning the $B_2Si_3^-$ isomers. Figure 3.1 illustrates that a missed isomer by these authors, upon proper identification, emerges as the global minimum, whereas the reported isomer is higher than the missing isomer by ~2.0 kcal/mol in relative energy.



Figure 3.1. Photoelectron spectra of $B_2Si_3^-$ clusters recorded with 266 nm photons

[103].



Figure 3.2. (a) Comparison of IR-UV2CI spectrum of B₂Si₃ with IR absorption spectra calculated for the low-energy structures **3.2a-e** [104]. (b) Relaxed **3.2.a** isomer was obtained using the CCSD method or different DFT functionals [105].

In the neutral state, the resonant infrared-ultraviolet two-color ionization (IR-UV2CI) spectroscopy of B_2Si_3 , as provided by Truong *et. al.* [104], serves as an excellent reference for benchmark calculations. A benchmarking survey previously conducted by Koukaras [105] reveals that the most stable isomer **3.2.a**, reported by Truong, adopts a perfect planar structure through optimization using CCSD computations and certain DFT functionals, while some other DFT functionals suggest instead a quasi-planar structure (cf. Figure 3.2).

The isomer **3.2.a** (cf. Figure 3.2.a), also referred to as **B₂Si₃.a** in Figure 3.3, has 2 π electrons and 2 σ delocalized electrons, which suggests it to exhibit a double aromaticity by the Hückel (4n + 2) rule with n = 0. Another isomer, **B**₂**Si**₃**.b** (cf. Figure 3.3) with higher symmetry, has the same electron configuration as the **B**₂Si₃.a. Additionally, replacing a Si atom with a B^- atom leads to a similar electron configuration in the B_3Si_2 structure. All three structures can be optimized by various functional methods, resulting in either a perfect planar or quasi-planar conformation, as shown in Figure 3.3. Generally, structures exhibiting a double aromaticity tend to have high thermal stability, high symmetry, and a planar shape for small molecules. Figure 3.3 also provides examples of B₃Si⁻ and B₄Si structures [106], that possess a double aromaticity and maintain a planar conformation regardless of the optimization method used. This raises some significant doubt about whether the structures **B₂Si₃.a**, **B₂Si₃.b**, and B_3Si_2 are indeed double aromatic or if other aromatic characters influence them. To clarify this uncertainty, a systematic investigation of $B_2Si_3^q$ with the charge q going from -2 to 2 and $B_3Si_2^p$ with the charge p going from -3 to 1 structures is conducted and presented below.



Figure 3.3. An illustration of clusters with 2 π electrons and 2 σ delocalized electrons.

3.1.2. The benchmarking tests

The global equilibrium structures and some lower-lying isomers of the B₂Si₃^{*q*} with the charge *q* going from -2 to 2 and B₃Si₂^{*p*} with the charge *p* going from -3 to 1 are presented in Figure 3.4 and 3.5. In these figures, the relative energies are obtained by single point electronic energy computed at the (U)CCSD(T)/CBS level based on TPSSh/6-311+G(d) optimized geometries, all with ZPE corrections [obtained by TPSSh/6-311+G(d) harmonic vibrational frequencies without scaling]; the relative energies from TPSSh/6-311+G(d) + ZPE are also given in parentheses, and the relative energies obtained by single-point CASSCF/CASPT2 computation are given in brackets. From here, the (U)CCSD(T)/CBS energy is referred to as CBS energy for brevity. Relative energies between isomers given in the following sections are obtained from CBS + ZPE computations, unless otherwise noted, which is used to name the isomer as **X.A**, where **X** = **I**, **II**, **III**, ... indicates the increasing order of relative energy, and **A** is the name of the cluster under consideration. The DFT calculations (using TPSSh and other functionals as listed below) are



Figure 3.4. Shapes of low-lying isomers of $B_2Si_3^q$ clusters with q going from -2 to +2. Geometry optimizations are carried out using the TPSSh/6-311+G(d) level of theory. Relative energies (kcal/mol) are computed using three different methods and will be elucidated in the text.

performed using the Gaussian 16 program [36]. The ORCA package [69] is utilized to calculate the CBS energy which is extrapolated from the aug-cc-pVxZ basis sets, where x = D, T, and Q. The multi-configurational perturbation theory calculations, using a completely active space wave function as references CASSCF/CASPT2, are performed using the ORCA program package. For species with even and odd

electron numbers, the CASSCF(12,12) and CASSCF(11,12) wavefunctions are constructed, respectively.



Figure 3.5. Shapes of low-lying isomers of $B_3Si_2^p$ clusters with p going from -3 to +1. Geometry optimizations are carried out using the TPSSh/6-311+G(d) level of theory. Relative energies (kcal/mol) are computed using three different methods and will be elucidated in the text.

As outlined in the "motivation of the study" section, a benchmark calculation is conducted to demonstrate the theoretical suitability of the TPSSh/6-311+G(d) method for optimizing structures containing boron and silicon. The global energy minimum structure of each charged state of the series $B_2Si_3^q$ and $B_3Si_2^p$ (cf. Figures 3.4 and 3.5), except for the trianion $B_3Si_2^{3-}$ (which is a structure with a high spin contamination), are reoptimized employing DFT with several widely used functionals in conjunction with either the 6-311+G(d) or the def2-QZVPP basis set. The density functionals employed for these optimizations include the HSE06 [107] and PBE0 [62] which are the two best functionals according to Koukaras' study [105], B3LYP [108] and TPSS-D3 [109], which have been used in studies where experimental results are available [103, 104], and the hybrid functional TPSSh [67]. Geometries produced by each DFT functional are evaluated by performing single-point electronic energy computations at these optimized geometries using the high-accuracy coupled-cluster (U)CCSD(T)/CBS method. The lowest CBS energy obtained is referred to as the reference energy, E_{ref} . The single-point energy deviation from E_{ref} is denoted as δE , that are shown in Table 3.1. The root mean square (RMS) can then be calculated as:

$$RMS = \sqrt{\frac{1}{n} \sum \delta E^2}$$
(3.1)

where n = 9 in considering 9 isomers. The RMS values as provided in the last column of Table 3.1, can serve as a universal metric for assessing the accuracy of optimized geometries. In spite of the fact that it is much less time-consuming to use than the def2-QZVPP basis set, the 6-311+G(d) counterpart consistently leads to significantly better results, as their RSM values are close to zero for the functional PBE0 or HSE06 or TPSSh. Thus, the functionals PBE0, HSE06, and TPSSh in conjunction with the 6-311+G(d) basis set are proved to be quite reliable approaches to investigate the geometries of stable mixed B–Si clusters in different charge states.
optimized geometry	B ₃ Si ₂ ²⁻	B ₃ Si ₂ -	B ₃ Si ₂	B ₃ Si ₂ ⁺	B ₂ Si ₃ ²⁻	B ₂ Si ₃ -	B ₂ Si ₃	B ₂ Si ₃ ⁺	B ₂ Si ₃ ²⁺	RSM
B3LYP/6-311+G(d)	0.06	0.14	0.04	0.06	0.44	0.39	0.22	0.19	0.53	0.29
B3LYP/def2-QZVPP	0.14	0.21	0.12	0.14	0.21	0.20	0.15	0.14	0.44	0.22
PBE0/6-311+G(d)	0.02	0.01	0.03	0.07	0.02	0.02	0.00	0.03	0.15	0.06
PBE0/def2-QZVPP	0.11	0.09	0.11	0.17	0.17	0.09	0.05	0.09	0.13	0.12
HSE06/6-311+G(d)	0.02	0.00	0.03	0.07	0.02	0.01	0.00	0.03	0.13	0.05
HSE06/def2-QZVPP	0.11	0.08	0.11	0.17	0.14	0.07	0.04	0.09	0.11	0.11
TPSSh/6-311+G(d)	0.00	0.07	0.00	0.00	0.00	0.01	0.00	0.00	0.03	0.03
TPSSh/def2-QZVPP	0.02	0.10	0.02	0.05	0.05	0.01	0.61	0.02	0.00	0.21
TPSS-D3/6-311+G(d)	0.07	0.22	0.04	0.00	0.06	0.10	0.71	0.09	0.08	0.26
TPSS-D3/def2-QZVPP	0.01	0.19	0.01	0.01	0.00	0.00	1.24	0.04	0.00	0.42

Table 3.1. Deviations of single-point (U)CCSD(T)/CBS total energies of the considered structures computed using geometries optimized by different DFT levels.

Table 3.2. Comparison of two PES peaks of $B_2Si_3^-$ ([103]) to calculate VDEs and ADEs (eV) using different functionals with 6-311+G(d) basis set and CCSD(T)/aug-cc-pVTZ for both anionic isomers **I.B₂Si₃⁻** and **II.B₂Si₃⁻**.

Isomer		B3LYP	PBE0	HSE06	TPSSh	TPSS-D3	CCSD(T)	Expt. ^a
$I.B_2Si_3^-$	VDE	2.63	2.80	2.78	2.78	2.76	2.63	2.64 ± 0.08
	ADE	2.60	2.76	2.75	2.74	2.71	2.61	
II.B ₂ Si ₃ -	VDE	2.40	2.56	2.55	2.56	2.56	2.41	2.64 ± 0.08
	ADE	2.33	2.49	2.48	2.50	2.50	2.35	

^{*a*} The VDEs are taken from ref. [103].

Table 3.3. Comparison of IR-UV2CI spectra of B_2Si_3 (ref. [104]) with harmonic vibrational frequencies calculated at the DFT/6-311+G(d) and CCSD(T)/aug-cc-pVTZ levels.

		v_{cal} (cm ⁻¹)					
Isomer	v_{expt} (cm ⁻¹) (ref. [104])	B3LYP	PBE0	HSE06	TPSSh	TPSS-D3	CCSD(T)
I.B ₂ Si ₃	491	500	517	515	497	470	498
	698	697	726	723	708	696	702

In their assignment of the experimental photoelectron spectrum of the anion B_2Si_3 , Lu *et al.* [103] used the PBE0/aug-cc-PVDZ results as references to evaluate the values obtained by other functionals employed and concluded on a good performance of their B3LYP/6-311+G(d,p) results. Accordingly, the calculated adiabatic and vertical detachment energies (VDE and ADE) of the isomer **II.B₂Si₃**⁻ (labelled as isomer **3A** in ref. [103]) amount to 2.46 and 2.16 eV by using both PBE0 and B3LYP functionals. However, our present computations using the PBE0/aug-cc-PVDZ point out that these VDE and ADE values are larger, being 2.57 and 2.50 eV, respectively. It is apparent that these authors misquoted their results because the values of 2.46 and 2.16 eV are actually the experimental photoelectron spectroscopy (PES) data. In any case, they cannot be regarded as reference values as proposed in ref. [103], simply because these authors failed to identify the lowest-lying isomer of the B₂Si₃⁻ anion.

As stated above, the isomer **I.B**₂**Si**₃⁻ is located to be the global energy minimum of the anion B₂Si₃⁻ (cf. Figure 3.4). The VDE and ADE values for both isomers **I.B**₂**Si**₃⁻ and **II.B**₂**Si**₃⁻ determined using several density functionals and the 6-311+G(d) basis set along with the CCSD(T)/aug-cc-pVTZ level are presented in Table 3.2 and compared to available PES experimental results [103]. Surprisingly, in addition to the relevant CCSD(T) results, the B3LYP functional yields values much closer to experiment. The calculated results further enable a new assignment for the PES of the B₂Si₃⁻ anion. In fact, while the first PES peak having VDE = 2.46 eV and ADE = 2.16 eV are due to the isomer **II.B**₂Si₃⁻ (cf. Figure 3.1). In other words, both anionic isomers, having an energy gap of ~2–3 kcal/mol (Figure 3.4), are most probably present in the molecular beam of the PES experiment, even with a much smaller proportion of the higher energy isomer. The lowest-lying anionic isomer **I.B**₂Si₃⁻ apparently generates a higher VDE peak.

Using the resonant infrared-ultraviolet two-color ionization spectroscopy, Truong *et al.* [104] observed two clear vibrational bands peaking at 491 and 698 cm⁻¹ for the B_2Si_3 and then assigned them to the coupled Si–B and B–B stretch modes. Harmonic vibrational frequencies of **I.B₂Si₃** are carried out at both DFT/6-311+G(d) and CCSD(T)/aug-cc-pVTZ levels and listed in Table 3.3. These calculated vibrational modes confirm the above assignment. Again, both B3LYP and CCSD(T) levels provide us with the most consistent vibrational frequencies with respect to the experiment.

The benchmark results in this study highlight the issue of a DFT functional not being universally suitable for all properties of certain atomic species. It becomes essential to know which DFT functional to use for a specific purpose. Specifically, the TPSSh, HSE06 and PBE0 functionals are well-suited for optimizing the geometric structures of molecules containing B and Si, and the conclusions regarding the relative energies of the isomers from these calculations are highly reliable. However, when reproducing experimental results such as photoelectron spectroscopy or harmonic vibrational frequencies, the B3LYP functional yields superior outcomes. Indeed, this conclusion should be further corroborated by additional benchmark calculations in the future, whenever possible.

3.1.3. Ribbon aromaticity model versus the Hückel electron count

The lowest-lying isomers of the $B_3Si_2^{3-}$ trianion include the global minimum, which is the linear $I.B_3Si_2^{3-}$ and the second lowest-lying isomer which is the ribbon $II.B_3Si_2^{3-}$ and being 3.7 kcal/mol higher in relative energy. Figure 3.6 indicates that both dianionic isomers $I.B_2Si_3^{2-}$ and $II.B_2Si_3^{2-}$ are formed upon replacement of a B⁻ unit in the trianion $II.B_3Si_2^{3-}$ at different positions by an Si atom. This replacement can be done without significantly altering the electronic structure because each of both B⁻ and Si units contains four valence electrons. Indeed, Figure 3.7 illustrates that the isomers $I.B_2Si_3^{2-}$, $II.B_2Si_3^{2-}$ and $II.B_3Si_2^{3-}$ all possess 4 π electrons and 2 σ delocalized electrons. According to Hückel rule, these isomers are categorized as π antiaromaticity and σ -aromaticity, making them susceptible to distortion from their planar conformation. Nevertheless, irrespective of the functional used, the results consistently indicate that these isomers adopt a planar configuration. This suggests that they do not possess π -antiaromaticity characteristics. Upon revaluation of the electron configurations of these isomers, it becomes evident that they satisfy the *ribbon aromatic* rule $\pi^{2(n+1)}\sigma^{2n}$ [26] with n = 1.

To demonstrate the influence of the ribbon model on these structures, the bond lengths, bond orders [55, 56], net atomic charges [55, 56], the ELF maps [44] analyses were employed. The results of these analyse (isosurface of ELF = 0.8) including with the electronic configurations for the $B_3Si_2^p$ ribbon isomer with p going from -3 to 1+ are shown in Figure 3.8. A *self-lock* phenomenon [26], an indicator of structures influenced by the ribbon model, is observed in the model species **II.B_3Si_2^3** following a shortening of the terminal B^a-Si^d and B^b-Si^e (cf. Figure 3.7 for atom labelled) bonds with bond lengths of ~1.93 Å.



Figure 3.6. A pathway illustrating the evolution leading to the $B_2Si_3^q$ from the trianionic ribbon **II.B₃Si₂³⁻** in which a B⁻ unit is replaced by an isovalent Si atom at two different positions leading to two isomeric types, namely ribbon (R) and Hückel (H).

As presented in the section 2.2.2, a *self-lock* is a phenomenon in which the terminal bonds become significantly shortened. For ease of visualization, Figure 3.9 presents the significant shortening of the B-B bonds at the terminal bonds compared with the rest of the B-B bonds in the ribbon structures including $B_7H_2^-$ [110], B_8H_2 [111], $B_9H_2^{3-}$, $B_9H_2Li_2^-$ [98] and $B_{10}H_2^-$ [98] structures in different charged states. Although more electrons are added in these systems, the B-B length at the terminal

bonds increases, a general picture is that the bond length at the terminal bonds is shorter than the remaining bonds. A *self-lock* phenomenon is hardly recognized in the trianion $II.B_3Si_2^{3-}$ because of its small size and the redundancy of up to 3 electrons. The electron excess leads to an increase in the average bond length and tends to decrease the dimensionality of the structure. The latter effect explains the significantly stronger stability of the 1D isomer $I.B_3Si_2^{3-}$ than the 2D $II.B_3Si_2^{3-}$ by DFT calculations, as well as explains the negative frequencies observed in the ribbon form of the trianion $B_9H_2^{3-}$.



Figure 3.7. Delocalized π and delocalized σ CMOs of a) II.B₃Si₂³⁻, b) I.B₂Si₃²⁻ and
c) II.B₂Si₃²⁻ isomers. The atom positions are labelled by a, b, c, d and e.

Such a charge effect is eliminated when two electrons are replaced by two Li atoms, forming an aromatic ribbon $B_9H_2Li_2^-$ structure [98] or the $B_3Si_2Li_2^-$ (cf.

Figure 3.10). The ribbon $B_{12}Si_2^{2-}$ [26] includes the B-Si terminal bond length of ~1.89 Å and the remaining B-B bond lengths in range of 1.59 - 1.74 Å. In general, these bonds have an increased length in the many-electron excess structure of **II.B₃Si₂³⁻** with the B-Si terminal bonds amounting to 19.3 Å and the B-B bonds to 1.62 and 1.72 Å.

A consequence of the *self-lock* phenomenon is that the Coulombic repulsion between the nuclei of the two atoms at the terminal bond of the ribbon significantly increases, which is expected to lead to a substantial increase in the potential energy barrier between the two terminals of the structure, facilitating a suitable movement of delocalized electrons in a one-dimensional box model [26]. In the ribbon model, the π electrons and the σ delocalized electrons are considered to be free to move in an one-dimensional box of width l_{π} and l_{σ} , respectively. Results reported in ref. [26] has clearly indicated that these widths can be determined if at least two CMOs of an electron species are occupied. In the case of **II.B₃Si₂³⁻**, the width of l_{π} can be easily calculated as 3.93 Å, which is very close to the distance between two Si atoms (4.09 Å).

The *self-lock* phenomenon appears to increase the nuclear repulsion energy in the ribbon species and thus the electrons need to have a special distribution to compensate for such a disadvantage. Such a special distribution indicates a strong overlap of π CMOs at terminal bonds (cf. the ELF_{π} map of **II.B₃Si**₂³⁻ and **I.B₂Si**₃²⁻ in Figure 3.11), whereas the σ delocalized electrons cause the B^a-B^b bond shortened to ~1.61 Å. Loss of one π electron from the trianion **II.B₃Si**₂³⁻ leads to the dianion **I.B₃Si**₂²⁻ with slightly longer terminal B^a-Si^d and B^b-Si^e bonds (1.94 Å) and shorter B-B bond (1.58 Å). The electron removed from **I.B₃Si**₂²⁻ can be either a remaining π electron on the SOMO leading to **I.B₃Si**₂⁻ (C_{2v}) having an imaginary frequency, or a σ electron on the SOMO – 1 resulting in the triplet anion **II.B₃Si**₂⁻. In **I.B₃Si**₂⁻ (C_{2v}), the terminal B^a-Si^d and B^b-Si^e bond distances amount to ~1.96 Å and the B^a-B^b bond to 1.55 Å. Comparable effects are thus observed upon successive removal of π electrons in going from the trianion **II.B₃Si**₂³⁻ to the dianion **I.B₃Si**₂²⁻ and then the anion $I.B_3Si_2^-$ (C_{2v}) (cf. Figure 3.8). Overall, most of the species considered above follow a *self-lock* phenomenon concerning their terminal bonds.

In addition to the changes in bond length, the changes in bond order are more obvious when different electrons are removed from a structure. The bond order of B^a -Si^d and B^b -Si^e bonds rapidly decreases from 1.75 to 1.50, then to 1.22 upon removal of 1 π electron from **II.B**₃Si₂³⁻ giving **I.B**₃Si₂²⁻ and then to **I.B**₃Si₂⁻, whereas removal of that electron induces no appreciable effect on the order of other bonds. From the ribbon model viewpoint [26, 98, 111], the trianion **II.B**₃Si₂³⁻ is characterized as an aromatic structure because its electron configuration of 4 π electrons and 2 σ delocalized electrons fully satisfies the electron shell of a ribbon, namely $\pi^{2(n+1)}\sigma^{2n}$ with n = 1. The *self-lock* phenomenon which ensures the working of ribbon model, is represented by bond order difference of B^a-Si^d and B^b-Si^e bonds with respect to the rest of the bonds present in the structure.

As $II.B_3Si_2^{3-}$ is characterized as a *ribbon aromatic*, $I.B_3Si_2^{2-}$ can be considered as a *ribbon semi-aromatic* structure where the *terminal–locks* remain strong enough to keep both the π and σ delocalized electrons moving in a similar way as in the model of a free particle moving in the one-dimensional ribbon [26]. Removal of a π electron also implies a reduction in the influence of the π electrons set and allows the effects of σ electrons to become more pronounced.

The unusual shortness of the B^a-B^b bond (1.55 Å) in the anion **I.B**₃**Si**₂⁻ (C_{2v}) which is due to an enhancement from σ delocalized electrons after removal of two π electrons, causes a distortion to form the stable **I.B**₃**Si**₂⁻ structure with C_2 symmetry. Therefore, **I.B**₃**Si**₂⁻ (C_{2v}) is a *ribbon antiaromatic* species with the electron configuration of $\pi^{2(n+1)}\sigma^{2n}$ involving 2 π electrons and 2 σ delocalized electrons.

In this way of classification of ribbon types, the triplet ribbon $B_{10}Si_2^{2-}$ structure [26] can be classified into a *ribbon triplet aromatic* class with an electronic configuration $\pi^{2(n+1)}\sigma^{2n}$ involving 3 π electrons and 1 σ delocalized electrons. In this context, the triplet isomer **II.B₃Si₂** is assigned as a *ribbon triplet aromatic* cluster.



Figure 3.8. **a-f**) Ribbon structures of $B_3Si_{2^p}$. **i**) Bond lengths (Å) and bond order (given in brackets) by blue numbers and net atomic charges are given by red numbers. ELF isosurfaces of ELF = 0.8 under **ii**) top view and **iii**) side view. **iv**) Electron configurations. Energy levels with green arrow(s) belong to π and σ delocalized CMOs whereas energy levels with grey arrows point out localized CMOs.



Figure 3.9. The representation of the self-locking phenomenon in the ribbon structures of B₇H₂⁻, B₈H₂, B₉H₂³⁻, B₉H₂Li₂⁻, and B₁₀H₂⁻. B-B bond lengths are assigned by colour range from red to blue: 1.50 Å to 1.80 Å. Nimag indicates the number of negative frequencies of the structure.





The calculated net atomic charged (NAC) of the atoms given in Figure 3.8 show that Si atoms lose more electron than B atoms when removing electrons one by one from $B_3Si_2^{p}$. The strength of the *locks* in these ribbons can clearly be observed from the monosynaptic basin of the centres Si^d and Si^e in their ELF maps (cf. Figure 3.8.ii and Figure 3.8.iii). These monosynaptic basins possess their own lone pair electrons of Si atoms; the p_z electrons contribute to the π -MOs, and p_x and p_y electrons contribute to σ -MOs. The decreasing number of electrons in these basins is consistent with the gradually positive charges observed in Si atoms. Because the width of the $3p_z$ orbital in Si is much larger than that of the $2p_z$ orbital in B, the ELF_{π} maps (cf. Figure 3.11) from the 2 π -MO do not fully observe the $3p_z$ of Si. The ELF maps from the side view (cf. Figure 3.8.iii) emphasize that the *z*-

width extension of these basins decrease when the π electron is removed from **II.B**₃**Si**₂³⁻ to form **I.B**₃**Si**₂²⁻ and from **I.B**₃**Si**₂²⁻ to form **I.B**₃**Si**₂⁻ (*C*_{2v}). This corresponds to a gradual loosening of the terminal locks and thus the ribbon aromaticity character changes from *aromatic* to *semi-aromatic* and to *antiaromatic*. The *z*-width extension of these basins does not seem to change when a σ electron is removed from **I.B**₃**Si**₂²⁻ to form **II.B**₃**Si**₂²⁻ to form **II.B**₃**Si**₂⁻ are strong enough to guarantee a ribbon triplet aromaticity character.



Figure 3.11. ELF_{π} maps for **II.B₃Si₂³⁻** and **I.B₂Si₃²⁻**.

Bond orders of the B^a-Si^d and B^b-Si^e bonds of the B₃Si₂ and B₃Si₂⁺ ribbon structures that approach the value of 1, indicate that the *self-lock* phenomenon is no longer present in these structures. Indeed, the monosynaptic basins of Si centres are small and their terminal locks become too weak in such a way that the ribbon model no longer applies to these species. **I.B₃Si₂**⁺ can then be considered as π aromatic, whereas **I.B₃Si₂** is both π and σ aromatic, all assigned by the Hückel model.



Figure 3.12. **a-f**) Nanoribbon structures of $B_2Si_3^q$. **i**) Bond lengths (Å) and bond order (given in braces) are given by blue numbers and net charges are given by red numbers. ELF isosurfaces of ELF = 0.8 under **ii**) top view and **iii**) side view. **iv**) Electron configurations. Energy levels with green arrow(s) belong to π and σ delocalized CMOs while energy levels with grey arrows point out localized CMOs.



Figure 3.13. a-e) The Hückel type of B₂Si₃^q i) Bond lengths (Å) and bond order (given in braces) are given by blue numbers and net charges are given by red numbers. ELF isosurfaces of ELF = 0.8 under ii) top view and iii) side view. iv)

Electron configurations. Energy levels with green arrow(s) belong to π and σ delocalized CMOs while energy levels with grey arrows point out localized CMOs.

Although both $I.B_2Si_3^{2-}$ and $II.B_2Si_3^{2-}$ are ribbon aromatic species, the C_{2v} symmetry of $I.B_2Si_3^{2-}$ suggests that it is closer to the ribbon model than the $II.B_2Si_3^{2-}$. At the same time, the ELF map (Figure 3.12.a.ii and Figure 3.13.a.ii) of

II.B₂Si₃²⁻ shows that the three monosynaptic basins of three Si centres are distributed roughly in a circular pattern around the structure, in such a way that the Hückel model on **II.B**₂Si₃²⁻ appears more pronounced than that in **I.B**₂Si₃²⁻. In possessing 2 σ and 4 π electrons, both **I.B**₂Si₃²⁻ and **II.B**₂Si₃²⁻ are considered as having in the meantime a σ aromaticity and a π antiaromaticity according to the classical Hückel rule. Thus, a geometry closer to the ribbon motif of **I.B**₂Si₃²⁻ and a more circular geometry of **II.B**₂Si₃²⁻ seem to lead to a higher aromaticity character for **I.B**₂Si₃²⁻ than **II.B**₂Si₃²⁻, and as a result, **I.B**₂Si₃²⁻ turns out to be more stable than its next isomer **II.B**₂Si₃²⁻ by ~5 kcal/mol. To facilitate the competitive characterization for the stability of such isomers, the superscript R (ribbon) and H (Hückel) are added to the structures derived from **I.B**₂Si₃²⁻ and **II.B**₂Si₃²⁻, respectively (cf. Figure 3.6).

Figure 3.6 shows that the $Si^{d}B^{c}Si^{e}$ bond angle marginally decreases from 168° to 165° and then to 161° when an electron is successively removed from the dianion ^HII.B₂Si₃²⁻ to the anion ^HII.B₂Si₃⁻ and to the neutral ^HI.B₂Si₃. A small decrease of this bond angle corresponds to a larger transformation of the structure into a circular shape, implying that it could become different from a ribbon. This is evidenced by a reduction of the relative energy between ^RI.B₂Si₃⁻ and ^HII.B₂Si₃⁻ to only ~2 kcal/mol, and a reversed energy ordering in the neutral state, with ^HI.B₂Si₃ being ~4 kcal/mol more stable than ^RIII.B₂Si₃ (*C*_{2v}).

Let us note that in neutral isomers, either **RIII.B**₂**Si**₃ (C_{2v}) or **HI.B**₂**Si**₃ has 2 π and 2 σ electrons, implying that it can be considered as doubly aromatic according to the Hückel electron count. This is expected to give the planar structure a higher thermodynamic stability. CCSD(T)/aug-cc-pVTZ calculations verify it for **HI.B**₂**Si**₃ by the lowest harmonic vibrational frequency of ~100 cm⁻¹. For **RIII.B**₂**Si**₃ (C_{2v}), influence of the ribbon antiaromaticity appears to be stronger than the Hückel aromaticity, and the C_{2v} ribbon motif becomes less stable. This structure has a small lowest harmonic vibrational frequency (60 cm⁻¹) at the CCSD(T)/aug-cc-pVTZ level, but it is distorted to a C_2 point group at the TPSSh/6-311+G(d) level.

3.1.4. Concluding remarks

The study successfully achieved its initial objective, which was to conduct a benchmark to demonstrate the suitability of the TPSSh/6-311+G(d) theoretical method for exploring stable structures of clusters containing B and Si. Nevertheless, when replicating experimental results like photoelectron spectroscopy or harmonic vibrational frequencies, the B3LYP functional consistently outperforms the others.

More important is the corresponding model for aromaticity this study proposed to account for the geometry and stability. The ribbon aromaticity model is categorized into different sub-classes including *aromaticity*, *semi-aromaticity*, *antiaromaticity*, and *triplet-aromaticity* when the electronic configuration of $[...\pi^{2(n+1)}\sigma^{2n}], [...\pi^{2n+1}\sigma^{2n}], [...\pi^{2n}\sigma^{2n}], and [...\pi^{2n+1}\sigma^{2n-1}]$ are involved, respectively.

The isomers $\mathbf{II}.\mathbf{B}_{3}\mathbf{Si}_{2}^{\mathbf{3}}$, $\mathbf{I}.\mathbf{B}_{2}\mathbf{Si}_{3}^{\mathbf{2}}$ and $\mathbf{II}.\mathbf{B}_{2}\mathbf{Si}_{3}^{\mathbf{2}}$ are assigned as ribbon aromatic species whereas the $\mathbf{I}.\mathbf{B}_{3}\mathbf{Si}_{2}^{\mathbf{2}}$, $\mathbf{I}.\mathbf{B}_{2}\mathbf{Si}_{3}^{\mathbf{3}}$ and $\mathbf{II}.\mathbf{B}_{2}\mathbf{Si}_{3}^{\mathbf{3}}$ are ribbon semi-aromatic species. The ribbon antiaromatic character of $\mathbf{I}.\mathbf{B}_{3}\mathbf{Si}_{2}^{\mathbf{2}}$ (C_{2v}) and $\mathbf{III}.\mathbf{B}_{2}\mathbf{Si}_{3}$ (C_{2v}) is assigned because it leads them to a distortion to a lower symmetry (C_{2}). Although the neutral $\mathbf{I}.\mathbf{B}_{2}\mathbf{Si}_{3}$ has a ribbon antiaromaticity, it has a more pronounced π aromatic nature according to the conventional Hückel rule. Because it is effectively characterized by both models but going in opposite directions, one antiaromatic and one aromatic, the distortion of the $\mathbf{I}.\mathbf{B}_{2}\mathbf{Si}_{3}$ structure when optimized by several DFT functionals is understandable. In general, each small geometrical change due to an addition or a removal of electron from both ribbon \mathbf{R} and Hückel \mathbf{H} type structures is also manifested in an increase or decrease in the degree of aromaticity corresponding to either the ribbon or the Hückel model.

The competition between the application of the Hückel model and the ribbon model on the isomers can be summarized in Figure 3.6 and Table 3.4.

Table 3.4 Summary of the aromatic characters of the species considered. The abbreviations: R = ribbon, $H = H\ddot{u}ckel$, S = strong, W = weak, A = aromatic, AA = antiaromatic, SA = semi-aromatic, TA = triplet aromatic.

Electronic configuration	Aromaticity character					
	II.B ₃ Si ₂ ³⁻	$\mathbf{I}.\mathbf{B}_{2}\mathbf{Si}_{3}^{2-}$	II.B ₂ Si ₃ ²⁻			
$[\pi^4\sigma^2]$	R: ^S A	R: ^S A	R: ^S A			
	H: none	Η: ^w π-AA; ^w σ-A	Η: ^s π-AA; ^s σ-A			
	I.B ₃ Si ₂ ²⁻	I.B ₂ Si ₃ ⁻	II.B ₂ Si ₃ ⁻			
$[\pi^3\sigma^2]$	R: ^S SA	R: ^S SA	R: ^W SA			
	H: none	Η: ^w π-AA; ^w σ-A	Η: ^s π-AA; ^s σ-A			
	I.B ₃ Si ₂ ⁻ (C _{2ν})	I.B₂Si₃ (C _{2ν})	I.B ₂ Si ₃			
$[\pi^2 \sigma^2]$	R: ^W SA	R: ^W AA	R: ^W AA			
	H: none	Η: ^w π-A; ^w σ-A	Η: ^S π-A; ^S σ-A			
	II.B ₃ Si ₂ ⁻	IV.B ₂ Si ₃				
$[\pi^3\sigma^1]$	R: ^S TA	R: ^S TA				
	H: none	Η: ^w π-AA; ^w σ-A				
	I.B ₃ Si ₂	II.B ₂ Si ₃ ⁺	I.B ₂ Si ₃ ⁺			
$[\pi^2 \sigma^1]$	R: none	R: none	R: none			
	Η: ^w π-A; ^w σ-A	Н: ^w π-A; ^w σ-A	Η: ^s π-A; ^s σ-A			
	I.B ₃ Si ₂ ⁺	IV.B ₂ Si ₃ ²⁺	$\mathbf{I.B_2Si_3^{2+}}$			
$[\pi^2 \sigma^0]$	R: none	R: none	R: none			
	Н: ^W π-A	Н: ^W π-A	Н: ^S π-A			

3.2. The disk aromaticity on the quasi-planar boron cluster $B_{70}^{0/2}$ -

The main content in this section is reproduced from the published paper entitled "A topological path to the formation of the quasi-planar B₇₀ boron cluster and its dianion", by Pinaki Saha, Fernando Buendia Zamudio, **Long Van Duong** and Minh Tho Nguyen, in *Physical Chemistry Chemical Physics*, Advance Article, 2023.

3.2.1. Motivation of the study

Topological principles play an important role in the search, design and study of nanostructures [112]. Topology refers to the mathematical study of shapes and their properties, and in the context of nanostructures, it is used to describe the connectivity and spatial arrangement of atom within a molecular system. By using topological principles, we can design and also manipulate the structure of nanostructures in a precise and controlled manner, leading to the creation of new materials with tailored and unique properties and functions. In addition, computational methods such as density functional theory (DFT) calculations can be used to predict and analyse the properties of these nanostructures, allowing us to explore their potential applications in fields such as catalysis, electronics, energy and medicine.

The topological *leapfrog principle* is a specific approach for searching the structures having new shapes, designing a specific shape for a chemical species, and studying their structural properties of a molecules, all based on topology. This principle involves several steps, first starting with a small known structure, and then using a set of operations to systematically add or remove atoms in a topologically controlled manner to generate a new structure.

The generation of a structure using a leapfrog search involves three operations: dual, capping, and omni-capping. In the first step, the initial guess cluster structure is subjected to a dual operation which involves swapping faces and vertices followed by perpendicular rotation at each edge of the parent geometry. The second step is a capping operation in which all new hexagons are capped. Finally, an omni-capping operation transforms the structure into a triangular tessellated geometry. On this generated structure, geometric optimizations are then performed to obtain the final structure for the cluster. The goal of this approach is to create new nanostructures with unique properties and functions, based on the underlying topology of the original structure. For example, formation of the quasiplanar B_{50} [113] and B_{56} [114] boron clusters were established using a topological leapfrog approach from the stable elongated B_{10}^{2-} and B_{12} , respectively.

In this study, the topological leapfrog algorithm is used to probe the formation of the B_{70} quasi-planar structure from a B_{16} form with 13 vertices as shown in Figure 3.14. Besides, a stable structure search algorithm, the Mexican Enhanced Genetic Algorithm (MEGA) [115] which has been implemented within the Vienna *ab initio* simulation package (VASP) [116], is used to generate other isomers of B_{70} .



Figure 3.14. A quasi-planar structure consisting of 70 boron atoms was generated using the topological leapfrog algorithm starting from an initial B₁₆ form with 13 vertices (the atom with yellow glow).

In the storyline explaining the stability of clusters based on their geometric shapes, the quasi-planar shape of $B_{70}^{0/2-}$ is very suitable because its electron configuration follows the disk model [101, 117]. This study will also establish a general electron counting rule, encompassing both the Hückel and Barid rules.

3.2.2. The quasi-planar $B_{70}^{0/2}$ -

Figure 3.15 shows a depiction of the geometric structures of the energetically lowest-lying isomers. The figure displays several quasi-planar (QP) isomers labelled as **QP.n** with n = 1, 2, 3, ..., which vary from each other by the position of the hexagonal holes. Isomer **QP.1** is the lowest-lying quasi-planar isomer and is characterized by a triplet ground state, while the other structures have a singlet ground state. Previously, the global minimum structure of B₇₀ was assigned to the bilayer structure **3D.1**. Calculations from this study support this finding, as the energy of bilayer **3D.1** is found to be 1 kcal/mol lower than that of the tubular **3D.2**. However, under certain growth patterns, the tubular structure **3D.2** may be experimentally obtained.

In order to gain a better understanding of the quasi-planar isomer **QP.1** shown in Figure 3.15, which is marginally less stable than its bilayer **3D.1** and tube **QP.2** counterparts, a detailed analysis will be conducted. As shown above, its planar structure is derived from the leapfrog algorithm applied to an initial B_{16} unit (Figure 3.11). This initial guess structure is formed by combining three hexagonal B_6 structures, as depicted in Figure 3.11. The resulting structure undergoes dual operations followed by successive capping and omni-capping operations. The final structure contains 61 boron atoms. In contrast to carbon fullerenes, where the leapfrog process includes omni-capping and dual operations, an additional boron cap must be applied to boron systems due to the electron deficit of the boron atom. This process eliminates all the dangling bonds, resulting in a planar B_{70} structure. Subsequent geometry optimization of that structure inevitably leads to the quasiplanar structure **QP.1** shown in Figure 3.15.



Figure 3.15. The selection of energetically favourable isomers of B_{70} . The abbreviation "**3D**" refers to three-dimensional isomers, while "**QP**" denotes quasiplanar isomers. The numbers, represented by " $\mathbf{n} = 1, 2, 3, ...,$ " indicate the relative energy order of each **3D** or **QP** isomer.

As previously mentioned, the lowest triplet state of **QP.1** is ~2 kcal/mol energetically more favourable than its closed-shell singlet counterpart. This suggests that the corresponding dianionic quasi-planar B_{70}^{2-} structure, in which the two open shells of the neutral structure are now filled, could become a stabilized closed-shell structure. Anionic species of boron clusters are commonly observed in experimental studies using photoelectron spectroscopy. Therefore, the size of B_{70} could potentially be detected experimentally through its anion and dianion structures using PES.

The quasi-planar isomer **QP.1** is characterized by a remarkably low vertical ionization energy, IE_v (**QP.1**) = 5.3 eV, as well as a substantially large vertical twoelectron affinity (TEA), which is the energy difference between the dianion and neutral states, with TEA (**QP.1**) being approximately 5.6 eV. Therefore, it can be expected that the dianionic state of **QP.1** will be more thermodynamically stable.

In fact, our calculations for the dianionic B_{70}^{2-} isomers indicate that the quasi-planar dianion **QP.1** is more stable, with a lower energy state that is ~ 3 kcal/mol lower than the corresponding bilayer dianion **3D.1**. The tubular dianion **3D.2**, on the other hand, is located much higher in energy.

3.2.3. Disk model and electron count rule

The π MOs of B₇₀²⁻ can be assigned according to the spectrum of levels in the disk aromaticity model (DM) as shown in Figure 3.16. The wave functions of the levels in the DM are derived from a solution of the Schrödinger equation for a particle moving in a disk, which is characterized by two quantum numbers: the radial quantum number n = 1, 2, 3, ... and the rotational quantum number $l = \sigma, \pi, \delta, \phi, \gamma, ...$ The lowest eigenstates in ascending order are $1\sigma, 1\pi, 1\delta, 2\sigma$, and so on (cf. Chapter 2, section 2.2.3). The eigenstates with zero rotational quantum number (l = 0) are non-degenerate, while the wave functions with non-zero rotational quantum numbers $(l \neq 0)$ are doubly degenerate levels. As a result, the electron count for a DM follows the (4N + 2M) rule, where N is the number of energy levels with $l \neq 0$ and N is the number of non-degenerate (with l = 0) energy levels. The ground eigenstate is the 1σ -orbital, so $N \ge 1$. For smaller sizes, there are fewer non-degenerate orbitals, and the DM rule reverts to the classical 4N + 2 Hückel rule when M= 1.

The B_{70}^{2-} dianion has 50 π electrons thus satisfying the DM rule for N = 11 and M = 3 (cf. Figure 3.16). The correspondence of the π MOs denoted as MO122, MO130 and MO163 with the levels 1σ , 2σ and 1σ is shown in Figure 3.17. Although there is a separation from double degeneracy into two pseudo-degenerate levels at levels 1ϕ and 2ϕ , it does not affect the aromaticity of the structure when all the pseudo-degenerate and double degeneracy levels are fully occupied. The SYSMOIC package [47] was used to calculate and visualize the magnetic current density maps. The B₇₀²⁻ dianion enjoys a π disk aromatic character according to the DM rule, as evidenced by the diatropic current flows (clockwise arrows) over the outer ring of the structure highlighted by the red circle in Figure 3.18.



Figure 3.16. Correspondence between the calculated π -MOs of the B₇₀²⁻ dianion with the energy levels of the disk model.



Figure 3.16. (continued).





Figure 3.18. Total magnetic current density maps of **a**) the B₇₀²⁻ dianion, and **b**) the triplet **QP.1** B₇₀. Vectors are plotted on a surface at 1 Å above the framework of the structure with the external magnetic field perpendicular to the molecular plane directed towards the reader.

Figure 3.18 illustrates that there is no significant difference between the ring current maps of the B_{70}^{2-} dianion and the neutral B_{70} triplet, indicating that **QP.1** also exhibits a triplet aromaticity. A more accurate way to count electrons for the stable disk-shaped structure in the triplet state is 4N + 2M - 2. Similar to the rule for singlet species, as the structure becomes smaller and the number of electrons decreases, the number of non-degenerate states remains M = 1, that is the above rule reverts back to Baird rule of 4n.

3.2.4. Concluding remarks

The triplet state of **QP.1** is the most stable isomer among structures close to the planar form of B_{70} , whereas the dianion state of **QP.1** has high thermodynamic stability and could be eventually identified from photoelectron spectra. The (4N + 2M - 2) electron count rule is suitable for the neutral triplet ground state, while the (4N + 2M) rule explains the stability of the B_{70}^{2-} dianion. The (4N + 2M) and (4N + 2M - 2) electron count rules are general electron counting rules for disk-like structures in the singlet and triplet states, respectively. These rules revert to the Hückel and Baird rules when the molecule is small enough in size.

3.3. Binary boron lithium clusters B₁₂Li_n with n = 1–14: the disk-cone model for the B₁₂Li₄ cluster

The main content in this section is reproduced from the published paper entitled "The binary boron lithium clusters $B_{12}Li_n$ with n = 1-14: in search for hydrogen storage materials", by **Long Van Duong**, Nguyen Thanh Si, Nguyen Phi Hung, and Minh Tho Nguyen, in *Physical Chemistry Chemical Physics*, vol. 23, no. 43, pp. 24866–24877 (2021).

3.3.1. Motivation of the study

The current global warming caused by the use of fossil fuels and the gradual depletion of these resources is one of the humanity's top concerns. Research on green energy sources not only addresses the issue of energy scarcity but also

promotes sustainable development, halting the aggravated global warming. Of the green energy sources, hydrogen energy has received significant attention due to its reaction producing water, while generating a high amount of heat. However, this high heat generation also poses safety challenges in its usage. Therefore, studies on safe hydrogen storage continue to attract considerable interest.

High molecular hydrogen adsorption capacity is one of the critical criteria in designing materials for hydrogen storage. This criterion focuses on the material's ability to adsorb and store a substantial amount of hydrogen gas relative to its mass or volume. The higher the hydrogen storage capacity, the more hydrogen the material can hold, making it more efficient for practical hydrogen storage applications. To achieve a high hydrogen storage capacity, the material must possess numerous hydrogen adsorption centres for hydrogen molecules to physically adsorb onto the material's surface. This process is commonly known as physisorption. Additionally, the material's surface should possess high adsorption strength, meaning that the hydrogen molecules can be strongly attracted and retained. This ensures that a significant amount of hydrogen is held on the material, even at moderate pressures and temperatures. In search for materials satisfying these criteria, this study investigates the mixed-phase Li-B clusters because both B and Li are light elements and Li has a high potential to become effective hydrogen adsorption centres.

The B_{12} cluster is an interesting cluster due to its ability to undergo geometric transformations under various influences. The octahedral B_{12} is the building block to form the solid phase of boron [118, 119]. However, in its cluster form, B_{12} transforms into a quasi-planar structure with high thermal stability [15]. Recently, Dong *et al.* [120] revealed that doping one, two, or three Li atoms into B_{12} leads to shape changes from quasi-planar to tubular and to cage-like structures, respectively. The $B_{12}Li_3$ cage form has also been studied for its hydrogen storage potential [121]. However, the thermal stability of the $B_{12}Li_3$ radical is not very high, in part due to its open-shell configuration. Therefore, this study systematically investigates the

stability of $B_{12}Li_n$ clusters with n = 0 - 14 to identify the most promising candidate for hydrogen storage materials among these clusters.

The results obtained from this study have exceeded expectations as $B_{12}Li_8$ was found to be a promising candidate that satisfies numerous criteria for a hydrogen storage material. Additionally, the cone-shaped structure of $B_{12}Li_4$ exhibits an exceptionally high thermal stability. In the narrative of this dissertation, greater emphasis is placed on explaining the stability of the cone-shaped $B_{12}Li_4$ structure using the disk model.

3.3.2. The growth pattern of $B_{12}Li_n$ with n = 0 - 14

The geometry of the most stable clusters of $B_{12}Li_n$ with n = 0 - 14 is shown in Figures 3.19 and 3.20. These structures were optimized at the TPSSh/6-311+G(d) theoretical level, and single-point energy calculations (U)CCSD(T)/cc-pVTZ + ZPE were performed to validate the DFT calculations. A benchmark was conducted in this study to demonstrate the suitability of the TPSSh theoretical level for investigating the stability of the mixed B-Li clusters. However, it is not presented here as it is not the main focus of the dissertation, and a similar analysis has already been provided in section 3.1.2.

As for a convention, each isomer structure given hereafter is labelled by nX, in which **n** is the number of lithium atoms and **X** being **A**, **B**, **C**, ... indicating an increasing relative energy ordering. Accordingly, the **nA** isomer invariably refers to the lowest-lying isomer of the size n. The red labels given in figures point out the lowest-lying isomer(s) of each size within a range of 3 kcal/mol determined at the (U)CCSD(T)/cc-pVTZ + ZPE level.

The optimized shapes of the $B_{12}Li_n$ clusters with n = 0 - 6 are displayed in Figure 3.19. Firstly, the thermodynamically stable quasi-planar pure B_{12} (n = 0) [15, 122] is shown as **0A**, followed by isomers of $B_{12}Li$ **1A** (n = 1) and $B_{12}Li_2$ **2A** (n =2); these sizes were previously well described in ref. [120]. For $B_{12}Li_3$ (n = 3), with respect to results reported in ref [120], we find a new lowest-lying isomer of $B_{12}Li_3$ and this is now displayed as **3A**. The B_{12} framework of **3A** is a quasi-3D structure in



Figure 3.19. Geometry, point group and relative energy (kcal/mol, (U)CCSD(T)/cc-PVTZ + ZPE) of $B_{12}Li_n$ with n = 0 - 6. Relative energies at TPSSh/6-311+G(d) + ZPE are given in parentheses. TPSSh/6-311+G(d) optimized geometries are used.

which an B atom is placed on one side of an elongated B_{11} . The other side of the elongated B_{11} is coordinated by a Li atom and the other two Li atoms are located on the other plane of the elongated B_{11} . Although this isomer is more stable than the cage-like structure **3B** reported by Dong and co-workers [120] by ~5 kcal/mol by DFT calculations, UCCSD(T) results show that both structures, along with three other structures, have relative energies smaller than 3 kcal/mol, still in favour of **3A**.

Because the relative energy ordering between isomers is expected to be modified with respect to the computational methods employed, even their absolute differences remain small, all 3A - 3E isomers (Figure 3.19) can be considered as quasi-degenerate in terms of energy.

The global minimum **4A** of $B_{12}L_{i4}$ has a pyramidal shape with three Li atoms around the apex and one Li atom placed in the inner side of the pyramid. The second **4B** and the fourth **4D** isomers are formed resulting from a displacement of the Li atom in **4A**. The first cage of the B_{12} frame appears at **4C** with ~9 kcal/mol higher. This cage comes from a distortion of a T_d symmetry structure **4C-T_d** which has three degenerate negative frequencies.

The B₁₂Li₅ size (n = 5) has an energy ordering reversal between the two isomers **5A** and **5B** from DFT and UCCSD(T) calculations. While **5B** has a coordination of Li atoms around a quasi-planar form of B₁₂, **5A** has a caged B₁₂ framework. Both isomers are energetically quasi-degenerate with a relative energy of < 3 kcal/mol.

The three lower-lying isomers **6A**, **6B** and **6C** of $B_{12}Li_6$ (n = 6) also compete to become its global minimum. Geometries of these three structures arise from an arrangement of Li atoms around a quasi-planar B_{12} framework with a B_4 rhombus deviated from the plane.

The optimized shapes and characteristics of the following $B_{12}Li_n$ series with n = 7 – 10 are displayed in Figure 3.20. The global minimum of $B_{12}Li_7$ is expected to be one of the four isomers **7A**, **7B**, **7C** and **7D** that again possess a comparable energy content. Among these isomers, **7A**, **7B** and **7C** result from addition of a Li atom to the $B_{12}Li_6$ structures **6A**, **6B** and **6C**. A 3D form of the boron framework returns in **7D**.

The $B_{12}Li_8$ structures (n = 8) turn out to be completely different from the previous sizes (Figure 3.20). A fullerene 3D framework of B_{12} in **8A** is in fact not present in smaller $B_{12}Li_n$ sizes. Structure **8A** which is also much more stabilized,

being ~ 13 kcal/mol lower than the second isomer **8B**, will be examined in more detail in a following section.

Four isomers **9A**, **9B**, **9C** and **9D** of $B_{12}Li_9$ (n = 9) are generated upon addition of a Li atom to the $B_{12}Li_8$ **8A** (Figure 3.20). They are again close in energy having relative energies of < 1.5 kcal/mol.



Figure 3.20. Geometry, point group and relative energy (kcal/mol, (U)CCSD(T)/cc-PVTZ + ZPE) of $B_{12}Li_n$ with n = 7 - 10. Relative energies at TPSSh/6-311+G(d) + ZPE are given in parentheses. TPSSh/6-311+G(d) optimized geometries are used.

The $B_{12}Li_{10}$ size (n = 10) becomes more specific with a competition of two structures **10A** and **10B** having quite different geometries from each other (Figure 3.20). While the B_{12} frame of **10A** is a 3D unit, that of **10B** exhibits the shape of a long boat with a hexagonal hole at the centre. Such a hexagonal hole is somehow fixed by two Li atoms located above and below the plane, three Li atoms symmetrically arranged at the end of the long boat **10B**. With a difference of only ~0.3 kcal/mol, both **10A** and **10B** are effectively the degenerate global minimum of $B_{12}Li_{10}$.

Optimized geometries of the following sizes $B_{12}Li_n$ with n = 11 - 14 are displayed in Figure 3.21. There is a strong competition between both 2D and 3D forms of the B_{12} moiety in $B_{12}Li_{11}$. Both **11C** and **11D** with a quasi-planar B_{12} frame have a higher energy than the 3D **11A** by < 4 kcal/mol at the UCCSD(T) level but < 1 kcal by DFT method. The 3D isomer **11B** arises from a single change in the position of a Li atom as compared to **11A** with an increase of ~2 kcal/mol in relative energy. Structure **11B** also begins to show a Li–Li bonding that occurs when several Li atoms are added. The $B_{12}Li_{12}$ **12A** contains a quasi-planar semicircular shape, whereas the second isomer **12B**, which is the lowest-lying isomer from DFT computations, is at ~3 kcal/mol higher. **12B** has a 3D B_{12} frame by a connection between a B_{10} cage and a B_4 rhombus through 2 joint B atoms. The mixed 2D-3D isomers of **12C** and **12D** can be found with Li atoms added to the edges, at both above and below the B_{12} frame.

13A is generated upon addition of a Li atom to the quasi-planar semi-circular **12A**. The $B_{12}Li_{13}$ size includes more Li–Li bonds in **13B**, **13C** and **13D** isomers, especially in **13B**. Thanks to these additional bonds, **13B** turns out to be energetically degenerate with **13A** in DFT calculation.

Three isomers 14A, 14B and 14C are again energetically degenerate with a difference of only ~2 kcal/mol. The Li atoms in 14B are attached around a quasiplanar B_{12} frame at the edges situated above and below the plane. The C_i symmetry of 14C is the result of a geometry relaxation from a higher T_h symmetry structure, named as 14C-T_h, which is characterized by three tiny negative frequencies (34*i* cm⁻¹). Interestingly, 14C-T_h is formed by 14 Li atoms distributed around the ubiquitous icosahedral B_{12} present in solid state [123–126]. Each of the group of 8 Li atoms caps an equilateral triangle, and each of the other group of 6 Li atoms connect making a short diagonal (2 B atoms) of a B₄ convex rhombus. 14C-T_h

appears as an ideal structure to be used for a building-block in crystalline structure if the right linker is found such as the synthesized $Li_2B_{12}C_2$ and $LiB_{13}C_2$ crystals [127].



Figure 3.21. Geometry, point group and relative energy (kcal/mol, (U)CCSD(T)/cc-PVTZ + ZPE) of $B_{12}Li_n$ with n = 11 - 14. Relative energies at TPSSh/6-311+G(d) + ZPE are given in parentheses. TPSSh/6-311+G(d) optimized geometries are used.

In general, the grown pattern of boron B_{12} clusters mixed with lithium atoms are varied and rather unpredictable. The sudden appearance of the smallest tubular boron $B_{12}Li_2$ structure [120] is a prime example for such a behaviour. Or even doping the first Li atom into B_{13} leads to a novel cone-shaped $B_{13}Li$ structure [128] which has never been seen before. However, the simple formation of B_nLi_{m+1} structure from addition of a Li atom to B_nLi_m structure indicates that the dominant form of B_nLi_m structure is associated with high thermodynamic stability. The three lowest-lying $B_{12}Li$ isomers all form by adding a Li to the well-known stable planar B_{12} structure in agreement with the stability of the latter [15, 122]. The **8A** isomer becomes the most interesting size because it is a highly stable structure bearing the most distinct geometry.

Isomers **9A**, **9B** and **9C** with completely indistinguishable energies are formed from addition of a Li atom to **8A** at different positions, thus taking advantage from the high thermodynamic stability of **8A**. Structure **8A** accumulates many of the most important properties to become a hydrogen storage material, namely, a high thermodynamic stability, being substantially large relative energy as compared to the second isomer, a fullerene B_{12} framework decorated by Li atoms with free space around the Li atoms to increase hydrogen capture.

3.3.3. Relative stabilities of clusters

Relative stabilities of clusters can usually be examined on the basis of the binding energy per atom (E_b) , dissociation energy (ΔE) , and second-order energy difference $(\Delta_2 E)$ considering the lowest-lying isomer of each cluster size. For the B₁₂Li_n (n = 0 – 14) these functions are defined as:

$$E_b[B_{12}Li_n] = (12E[B] + nE[Li] - E[B_{12}Li_n])/(12 + n)$$
(3.2)

$$\Delta E[B_{12}Li_n] = E[B_{12}Li_{n-1}] + E[Li] - E[B_{12}Li_n]$$
(3.3)

$$\Delta_2 E[B_{12} \text{Li}_n] = E[B_{12} \text{Li}_{n-1}] + E[B_{12} \text{Li}_{n+1}] - 2E[B_{12} \text{Li}_n]$$
(3.4)

in which E[X] is the total energy of the X unit at the (U)CCSD(T)/cc-pVTZ singlepoint calculation. The binding energy E_b diagram illustrated in Figure 3.22.a decreases when the size n increases. The B–Li bond is inherently much weaker than the B–B bond and addition of Li atoms further increases the number of B–Li bonds, invariably resulting in a continuing decrease in the average binding energy.

To account for the unusual decrease of E_b , the sum of bond orders (SBO) and net atomic charges (NAC) for each atom in are evaluated by using the DDEC6 bond order analysis program [56]. The SBO and the NAC for each atom of important isomer(s) of each B₁₂Li_n size are given in the Appendix along with the Cartesian coordinates of their optimized geometries. The SBO of B atoms in the planar C_{3v} B₁₂ [15, 122] have values in a range of 3.2 - 3.6. This range increases to 3.4 - 3.8after the first Li atom is added into and finally to 3.8 - 4.6 when all 14 Li atoms are added to the B₁₂ core. The SBO of Li in B₁₂Li [120] is equal to 0.4 with the largest bond order of B–Li bonds found to be 0.04. The SBO of Li atoms slowly increase upon addition of more Li atoms. The SBO of all Li atoms in B₁₂Li_n with n \leq 10 are < 1, which reflects a weak electron exchange following overlap between n[Li⁺] and [B₁₂ⁿ⁻] [56]. A more diffuse Li atom exhibits a larger SBO value which corresponds to a less positive value of its NAC (cf. Appendix). In general, SBO of Li atoms are very small as compared to those of B. Therefore, we here propose the average of the sum of the bond orders (ASBO) for a cluster size n as defined in the equation:

$$ASBO[B_{12}Li_n] = \frac{\sum SBO}{12+n}$$
(3.5)

Accordingly, the smaller the ASBO value, the more highly reactive the structure and the smaller the binding energy per atom. Therefore, a decrease of ASBO shown in Figure 3.22.b is in agreement with a decrease of E_b illustrated in Figure 3.22.a. All Li atoms are attached to the outer positions of the B₁₂ frameworks, transferring its valence electrons to the B₁₂ moieties and have a positive charge of < 1, due to reception of back-donated electron from boron atoms to the unoccupied p-AOs of

Li [129]. These Li ions readily participate in interaction or reaction, especially for the ability to capture hydrogen molecules.



Figure 3.22. a) Binding energy per atom; b) Average of sum of bond orders (ASBO) values; c) HOMO – LUMO gaps; and d) Dissociation energy (left y-axis) and second-order energy difference variation (right y-axis) of the binary B₁₂Li_n (n = 0– 14 clusters).

The frontier orbital (HOMO – LUMO) energy gap (HLG), ΔE , and $\Delta_2 E$ diagrams displayed in Figure 3.22.c and Figure 3.22.d follow a similar trend of alternating increase and decrease between closed-shell and open-shell systems and show the outstanding peak of B₁₂Li₄, followed by B₁₂Li₂, B₁₂Li₆ and B₁₂Li₈. These values tend to a certain saturation from B₁₂Li₁₁ onwards. The average HLG of B₁₂Li_n with n = 11 – 14 amounts to ~0.9 eV and these clusters advance to adopting metallic properties. Some Li atoms in these structures have the SBO values > 1 and the NACs close to 0, meaning that Li atom uses its covalent interaction instead of an ionic attraction.

3.3.4. Chemical Bonding

The **14C** (cf. Figure 3.21) in the T_h point group, denoted as **14C-T_h**, has 50 valence electrons and thus satisfies the Hirsch rule [130] of electron count 2(N+1)²
with N = 4. However, the spherical structure with a perfect electron number does not give **14C-T_h** a sufficient electronic configuration that could satisfy the filling of its electron shells. In fact, as shown by its MO_S depicted in Figure 3.23, the electronic configuration of $[1S^{2}2P^{6}1D^{10}2S^{2}1F^{8}2P^{6}1F^{6}2D^{6}1G^{4}3S^{0}]$ lacks 4 electrons for the 2D shell, and only 4 of 18 electrons occupy the 1G shell. Furthermore, the HOMO and HOMO-1 of **14C-T_h**, establishing the $[2D^{6}1G^{4}]$ shells, are antibonding MOs that can turn into bonding MOs following addition of a transition metal (TM) atom at its centre, such as the case of Cr@B₂₀Li₁₂, Ti@B₂₄Li₁₄, ... [131].



Figure 3.23. MO energy diagrams of the **4C**, **8A** and **14C-T**_h isomers. The line levels are full occupied MOs, and the dash line levels are unoccupied CMOs. The brown, red, blue, green, and black colour points out the S, P, D, F and G subshells, correspondingly.

In the present system, the spherical B_{12} appears to be too small to enclose such a TM atom. The early appearance of the 2D subshell before the 1G subshell, and the 3S subshell appearing as a LUMO, even though the 1G subshell is not filled yet, is the result of the phenomenological shell model (PSM) [132] when the impurity (Li) is less electronegative than the host atoms (B). The electron localization function (ELF) map plotted for $14C-T_h$ (cf. Figure 3.24) shows no B–B or B–Li basin but only basins that indicate electrons filling the empty sphere space (does not take core basins into account), meaning that B atoms are acting here as metallic elements. The small HLG of B₁₂Li₁₄ isomers (0.8 eV of $14C-T_h$ and 0.9 eV of 14A) agree well with the view that the bonds in B₁₂Li₁₄ are of metallic character.



Figure 3.24. The ELF map of 14C-T_h.
The red and yellow basins indicate the B and Li positions, respectively. The conventional covalent basins are coloured by green while the lone pair basins coloured by purple.

Elimination of antibonding MOs following structural distortion in such a way that antibonding MOs become bonding MOs is a consequence leading to more stabilizing structures. As a matter of fact, **14C** emerges as a lower-lying isomer derived from a symmetry lowering of **14C-T**_h. Formally **8A** can also be formed after removing six Li atoms from **14C-T**_h and subsequently deforming the sphere to a fullerene-like form. **8A** again with an emphasis on the 4-B-atoms binding motif of the Li atoms, which is a preferential motif over the 2-B-atoms bonding is a novel motif because such a structure has previously been found only with 3-B-atoms, 5-B-atoms or 6-B-atoms bond of the Li atoms, or a mixture of them [120, 129, 131, 133, 134]. Interestingly, the HOMO of the fullerene-like **8A** which is now a $2D_{z^2}$ subshell, because it is influenced not only by the PSM but also affected by the Clemenger–Nilsoon model [135, 136]. The 3S subshell remains as the LUMO of

8A, demonstrating that the PSM strongly governs the behaviour of the B_xLi_y complexes, in part due to the large electronegativity difference between Li and B elements (being 0.91 and 2.05, correspondingly). The $2D_{z^2}$ subshell (being the HOMO) turns out to be a strongly bonding orbital and thereby substantially enhances the thermodynamic stability of **8A**.



Figure 3.25. The ELF map of **8A**. The red and yellow basins indicate the B and Li positions, respectively. The conventional covalent basins are coloured by green while the lone pair basins coloured by purple.

The ELF map of **8A** (cf. Figure 3.25) includes the B–B bonding, lone pair B and core basins, indicating the conventional covalent bonding character in **8A**. What is remarkable about **8A** is that a decoration of Li atoms around the fullerene-like B_{12} makes it suitable and able to capture molecular hydrogen at the Li centres. Furthermore, relative energy between **8A** versus **8B** corresponds to the largest gap as compared to those between the most and second most stable isomers of other sizes in the series under investigation. This makes it plausible that **8A**, when it could be synthesized experimentally, is less prone to mixing with many other lower-lying isomers. With such advantages, the investigation of hydrogen storage capacity for **8A** indicates that this cluster can adsorb up to 40 H₂ molecules, corresponding to a gravimetric density of ~30% of hydrogen (cf. Figure 3.26).



Figure 3.26. Optimized adsorption configurations of **a**) **8A**-8H₂, **b**) **8A**-16H₂, **c**) **8A**-24H₂, **d**) **8A**-32H₂, and **e**) **8A**-40H₂ (wB97XD/6-311++G(2d,2p)).

3.3.5. A mixed cone-disk model

Now, the $B_{12}Li_4$ will be examined. Removal of four Li atoms from $B_{12}Li_8$ formally leads to $B_{12}Li_4$ which has 40 valence electrons. This is a magic number associated with a high thermodynamic stability of many spherical or subspherical, especially tetrahedral structures [137–140], and well defined by the PSM. In the present case, the most stable spherical structure found is the **4C** isomer with a C_3 symmetry after geometry relaxing from a structure with T_d symmetry having a three-fold negative frequency of 360*i* cm⁻¹. Its large HLG (3.2 eV) does not make **4C** the global minimum of $B_{12}Li_4$, but instead the conical **4A** does. This is a form

similar to its isoelectronic B_{13} Li [128] which is a new member of the tetrahedraltyped B_{13} ligand half-surround cluster (cf. structures given in Figure 3.27).



Figure 3.27. The lowest-energy structures of the isoelectronic $B_{13}Li$ and $B_{12}Li_4$ clusters.

Such a conical structure is far different from a spherical shape. Therefore, the electronic structure of **4A** cannot be explained in terms of spherical models as in the case of **4C** (cf. Figure 3.23). While the solution of the Schrödinger equation for a free particle moving in a cone is not yet available, the circular disk model (DM) [101, 117, 141] is the most adaptable for this cone-shaped structure. The DM eigenstates are usually classified according to $n\alpha$ with n and α being two principal quantum numbers, namely, n = 1, 2, 3... is a radial number, and $\alpha = 0, \pm 1, \pm 2, \pm 3$... and usually denoted by Greek letter as $\alpha = \sigma$, π , δ , ϕ , ... is a rotational quantum number. An eigenstate defined by a none-zero value for α is twofold degenerate. Both structures B₁₃Li and **4A** have similar MO shapes, in such a way that they are both suitable to be modelled by the DM. For the sake of convenience, the B₁₃Li structure is discussed in some detail here because it is more symmetrical than **4A** and therefore, the nodes in its MOs are more easily recognized and assigned.

The valence MOs and LUMO of **4A** are represented in Figure 3.28 including two different sets, namely, a) the σ set, and b) the π set of B₁₃Li. The 1 γ -orbital is

found to have only a single MO (HOMO-7) because it meets the maximum number of cylindrical nodes condition [141]. Accordingly, the latter consists of a perfect sign alternation in every atom of the outer ring of the cylinder. Although a molecular conical structure differs much from a perfectly planar disk structure in which the atoms are concaved from the centre out to the edge of the disk, the MOs observed in a cone also have such properties. Observation of the 2σ and 3σ -orbitals of the planar disk B_{20}^{2-} (ref. [142]) and B_{13} Li under the top view and side view as shown in Figure 3.30 can clearly emphasize this similarity. This transformation makes these MOs appear earlier in the corresponding electronic wavefunction. Specifically, the σ electronic configuration for the DM of B_{20}^{2-} is $[1\sigma^21\pi^41\delta^42\sigma^21\phi^42\pi^41\gamma^41\eta^42\delta^43\sigma^2]$, whereas that of B_{13} Li (cf. Figure 3.28) is $[1\sigma^21\pi^42\sigma^21\delta^42\pi^41\phi^43\sigma^21\gamma^23\pi^42\delta^4]$.



Figure 3.28. Valence MOs and LUMO of the B₁₃Li cluster assigned within the circular disk model. H stands for HOMO and L stands for LUMO.

For the sake of a clearer view, a look back at the π electron configuration of the bowl B₃₀, $[1\sigma^21\pi^41\delta^42\sigma^22\pi^41\phi^4]$ [117], is necessary, which was assigned as a disk aromatic species, even though it is also bowl or slightly conical with a wider angle than those of the B₁₃Li counterpart. Phenomenologically, a mixed cone-disk model can be proposed according to which the MOs spectrum changes the earlier appearance of the MOs with large radial and small rotational quantum numbers. The smaller the apex angle, the larger the change.





Figure 3.29. The total current density maps of a) $B_{13}Li$ and b) $B_{12}Li_4$ and the c) π and d) σ current density maps of $B_{13}Li$. External magnetic field vector is present by the blue arrow. Vectors are plotted on a surface having the cone shape at 1 Å inside B-cone framework.

Similarly, the electronic configuration of the π set for B₁₃Li is $[1\sigma^21\pi^42\sigma^2]$. In particular, the $2\sigma(\pi)$ -orbital is the HOMO of B₁₃Li. Because such an assignment for the HOMO can be confusing, we make a representation of the $2\sigma(\pi)$ -orbital from the disk model and compare it to the HOMO of B₁₃Li in a $C_{4\nu}$ symmetry; this is shown in Figure 3.28. Interestingly, the natural appearance of such HOMO has been observed in other stable structures such as the 5σ 1-orbital in the disk Ge₁₀⁴⁺, the tube B₁₄, the 6σ 1-orbital in B₁₂Si₂ by the cylinder model (cf. ref. [25]), and the (2 0 2)-orbital in NiB₁₄ and Ni₂B₂₀²⁻ (cf. ref. [143]), Li₂FeB₁₄ (cf. ref. [144]) by a hollow cylinder model [18]. This type of HOMO plays a role in the separation of two different electron shells in a molecule, which ultimately increases significantly the thermodynamic stability of that molecule.



Figure 3.30. 2σ and 3σ -orbitals of B_{20}^{2-} and B_{13} Li under the top view and side view.

The diatropic flows of the current density maps of $B_{13}Li$ and $B_{12}Li_4$ **4A** depicted in Figure 3.29 point out that they are strongly aromatic species. The sets of π and σ MOs of $B_{13}Li$ exhibit diatropic ring currents, implying that this structure is characterized by a double aromaticity character.

3.3.6. Concluding remarks

The **8A** isomer was discovered to exhibit a high thermodynamic stability, with energy lower than the second most stable isomer by up to 13.1 kcal/mol, making it an ideal candidate for synthesis with minimal competition from other isomers. The arrangement of Li atoms surrounding the fullerene-like B_{12} structure in **8A** creates an optimal environment for Li to act as a hydrogen adsorption site. Moreover, the presence of 8 Li atoms in **8A** significantly reduces the specific gravity and enhances the capacity for hydrogen adsorption, resulting in a remarkable maximum hydrogen storage capacity of up to gravimetric density of 30% of hydrogen in this study, representing a notable achievement at the time of publication.

The B₁₂Li₄ size is demonstrated as a magic cluster within the B₁₂Li_n series considered, in view of its superior thermodynamic stability as compared to other sizes. Such a high stability is shown by the binding energy per atom, average sum of bond order value, frontier orbitals energy gaps, dissociation energy, and secondorder energy difference variation. The high thermodynamic stability of the B₁₂Li₄ **4A** does not come from a magic number of 40 it formally possesses from the electron shell model, but rather from a satisfaction of the circular disk aromaticity model. As the **4A** isomer and the novel cone structure of B₁₃Li are similar in term of geometric shape and MO configuration, the disk aromaticity is equally presented for the B₁₃Li cone structure. Both HOMOs of B₁₃Li and **4A** are assigned as $2\sigma(\pi)$ orbitals from the circular disk model and they greatly contribute to the uncanny stability of these structures. The study would propose a mixed cone-disk electron shell model for this type of structures. They are both doubly aromatic species.

3.4. B₁₄FeLi₂ and the hollow cylinder model

The main content in this section is reproduced from the published paper intitled "The teetotum cluster Li₂FeB₁₄ and its possible use for constructing boron nanowires", by Ehsan Shakerzadeh, **Long Van Duong**, My Phuong Pham-Ho,

Elham Tahmasebi and Minh Tho Nguyen in *Physical Chemistry Chemical Physics*, vol. 22, no. 26, pp. 15013–15021 (2020).

3.4.1. Motivation of the study

In 2014, Tam and co-workers [145] reported on an iron doped boron cluster, demonstrating that the B_{14} Fe cluster remains stable in the triplet state with a tubular arrangement of the B_{14} framework and the Fe atom is located at the center of the boron framework (cf. Figure 3.31). One question that arose was as to whether the magnetic properties of Fe could be completely suppressed through doping. The present study reveals that addition of two Li atoms effectively quenches the magnetic properties of Fe without affecting the stability of the B_{14} cluster in its double rings form. An explanation for the stability of B_{14} FeLi₂ using the hollow cylinder model is also a key aspect of the narrative in this dissertation.



Figure 3.31. The lowest-lying isomer of B₁₄Fe [145].

3.4.2. Stability of B₁₄FeLi₂ and its potential applications

Calculated results at the TPSSh/def2-TZVP + ZPE level point out that the low spin *teetotum* Li₂B₁₄Fe structure with a D_{7d} symmetry point group is its ground state. Some of the low-lying isomers are depicted in Figure 3.32. This structure composes of two B₇ strings which endohedral caped the Fe atom, whereas two Li atoms are attached to Fe at both sides along the symmetry axis. The B-B bond length in each B₇-string is 1.64 Å and between two strings is 1.81 Å. Previously, the most stable isomer of B₁₄Fe corresponds to a double ring (DR) composed of two seven-membered rings disposed in an anti-prism form and doped by the Fe atom at the centre of the cylinder.



Figure 3.32. Optimized structures of lower-energy isomers of $B_{14}FeLi_2$; ΔE values are in kcal/mol from TPSSh/def2-TZVP energies with ZPE corrections.

A high symmetry (D_{7d}) and high spin DR structure of B_{14} Fe (triplet state) turns out to be ~2 kcal/mol more stable than the low-spin counterpart. Addition of two Li atoms to the B_{14} Fe DR skeleton keeps its high symmetry. But the B_{14} FeLi₂ in a low-spin singlet state becomes more stable than the triplet structure by ~19 kcal/mol. Notably the B-B lengths within each string and between both B_7 strings are 1.62 and 1.76 Å, respectively. Thus, addition of Li atoms does not cause a large effect on the inter-ring distance, as two B7 strings go far further from each other by ~0.05 Å. Also, the B_{14} cylinder is slightly compressed upon approach of the Fe

atom. The Fe-B length amounts to 2.12 Å in B_{14} Fe, while it is about 2.05 Å in B_{14} FeLi₂.



Figure 3.33. Formation of MOs of B₁₄FeLi₂ from MOs of singlet B₁₄ skeleton and a contribution from *d*-AO of Fe atom. Some MOs of the singlet B₁₄ skeleton are assigned by hollow cylinder model.

The corresponding HOMO, LUMO and gap energies of this teetotum structure are calculated to be -5.1, -3.0 and 2.1 eV, respectively. Let us note that the SOMO-LUMO gap of the stable high spin tubular B₁₄Fe was computed to be 0.9 eV at the same TPSSh/def2-TZVP level. Thus, the frontier orbitals gap increases upon doping of Li atoms into B₁₄Fe. The vertical ionization energy of B₁₄FeLi₂ is IE(Li₂B₁₄Fe) = 6.5 eV computed as the energy difference between both teetotum

forms in the neutral and cationic states. The IE of $B_{14}Fe$ is $IE(B_{14}Fe) = 7.5$ eV, and thus addition of Li atoms reduces the IE by up to 1 eV.

Figure 3.33 indicates the formation of MOs of $B_{14}FeLi_2$ from the singlet B_{14} skeleton and a distribution from *d*-AO of the Fe²⁺ ion. Within this point of view, the Fe atom receives two electrons from two Li atoms. The triplet DR B_{14} skeleton is more stable than the singlet one by 2 kcal/mol (at TPSSh/def2-TZVP level), as well as the linear triatomic Li-Fe-Li unit in triplet state is lower in relative energy than the quintet and singlet by 2 and 86 kcal/mol, respectively. Therefore, the Li-(Fe@B₁₄)-Li teetotum is resulted from an interaction between the triplet B_{14} skeleton and the triplet Li-Fe-Li linear unit. Nevertheless, the MO diagram of the B_{14} singlet skeleton with only 2 kcal/mol higher energy than the triplet state can equally be used to have a better look for the formation of MOs of B_{14} FeLi₂.

The MOs of the singlet B₁₄ skeleton can be assigned by the hollow cylinder model (HCM) [18, 41]. Like in the case of $B_{14}Ni$ [143], significant contributions from 50% $3d_{xz}$ and $3d_{yz}$ of transition metal to the (1 ±2 2)-orbitals (the LUMO and LUMO') of the B_{14} skeleton form the HOMO – 3 and HOMO – 3' of B_{14} FeLi₂. Moreover, the HOMO -2 and HOMO -2' result from the $(2 \pm 1 2)$ -orbitals (the LUMO + 2 and LUMO + 2') and 51% $3d_{xy}$ and $3d_{x^2-y^2}$. The hybridization between the (3 0 1)-orbital (the HOMO – 3) of the B14 skeleton and the $3d_{z^2}$ forms a bonding HOMO - 9 and an antibonding HOMO - 1. The s-AO and p-AO of Fe also join into other MOs of Li₂FeB₁₄ which results in an electron configuration as follows: $[4s^{0.1} 3d^{8.36} 4p^{0.51} 5s^{0.26} 4d^{0.04} 5p^{1.16}]$ of Fe. Especially, the HOMO of B₁₄FeLi₂ is the (2 0 2)-orbital of HCM which can make a structure becoming highly thermodynamically stabilized such as the cases of Ni@B14, Ni2@B202-, and Ni₂@B₂₂ [143]. Insertion of a Fe atom inside the DR B₁₄ expands both peripheral B-B bonds and B-B bonds between two strings which results in a weakening of all B-B bonds. The (2 0 2)-orbital of HCM plays a role of shortening the peripheral B-B bonds which amount to 1.63 Å, whereas the B-B bonds between two rings are now 1.79 Å.



Figure 3.34. ACID map of Li₂FeB₁₄ from a) top view and b) side view.

Figure 3.34 shows the anisotropy of the induced current density (ACID) [54] maps of B₁₄FeLi₂ at the isosurface value of 0.05. The current density vectors plotted onto the ACID isosurface are highlighted by the clockwise arrows, which correspond to diatropic ring currents, and the anti-clockwise arrows correspond to paratropic ring currents. The external magnetic field vector is placed along the Oz axis with the direction out of the paper plane (Z+). The clockwise current density vectors are plotted on the ACID isosurface are highlighted by the arrows with red glow while the anti-clockwise current density vectors ones are highlighted by the arrows with orange glow. The right figures are the view of the left figures after an 80° rotation of Ox axis. It is interesting to note that current density vectors of B₁₄FeLi₂ show a weak diatropic current flow inside the B₁₄ border, and a strong diatropic current around the Fe atom, and strong paratropic currents at each B atom (three of them are highlighted). The contributions from three MOs sets defined by the hollow cylinder model (HCM) [18, 146] for boron DR clusters to the ACID maps are shown in Figure 3.35. The radial set (π set) reveals that Li₂FeB₁₄ is a π aromatic species as pointed out by the clockwise arrows around B atoms and around Fe atoms. The tangential set (σ set) just shows the clockwise arrows around Fe atoms, whereas the localized set (s-MOs set in HCM) causes the anti-clockwise arrows around each B atom.



Figure 3.35. ACID isosurface (isovalue = 0.05) of three valence MOs sets of B_{14} FeLi₂ on the view from Li-Fe-Li axis (Oz axis) including **a**) localized set, **b**) tangential set and **c**) radial set.

The time dependent density functional theory method (TD-DFT, TPSSh/def2-TZVP) is used to predict the optical absorption spectrum of Li₂FeB₁₄ for about 50 lower-lying excited states. This spectrum is displayed in Figure 3.36 The high symmetry of Li₂FeB₁₄ leads to several forbidden transitions. Although the frontier energy gap is ~2.1 eV, the UV-Vis spectrum shows the first major peak at 3.7 eV (~ 337 nm) due to a transition of HOMO – 1 \rightarrow LUMO + 2, and the second major peak at 4.2 eV (~ 298 nm) due to a transition of HOMO \rightarrow LUMO + 6. These two major peaks along with other minor peaks (at longer wavelengths) demonstrate that Li₂FeB₁₄ can absorb UV light but it is completely transparent with

respect to visible light. Accordingly, Li_2FeB_{14} can be regarded as a candidate material for visible-inert optoelectronic devices.



Figure 3.36. Predicted electronic absorption spectrum of the teetotum $B_{14}FeLi_2$ (TPSSh/def2-TZVP).

A pioneering feature of $B_{14}FeLi_2$ is its capability of introducing a linkage to construct some new boron-based nanowires. In fact, a nanowire can be designed using the stable $B_{14}Fe$ cylinder and $B_{14}FeLi_2$ teetotum motifs. This nanowire can be made of [Li- $B_{14}Fe$ -Li]-[$B_{14}Fe$]-[Li- $B_{14}Fe$ -Li]. The relaxed structure of this typical nanowire is also determined at the TPSSh/6-31+G(d) level (cf. Figure 3.37) leading to linear forms that are optimized as equilibrium structures. The HOMO-LUMO gap of such a structure is calculated to be 0.3 eV, which is significantly smaller than those of the isolated Li₂FeB₁₄ (2.2 eV) or $B_{14}Fe$ (0.9 eV). Therefore, combination of these motifs leads to a wire possessing a completely metallic character. It is noteworthy that the design of the nanowire in the other way of [$B_{14}Fe$]-[Li- $B_{14}Fe$ -Li]-[$B_{14}Fe$] is also examined, but no true minimum is observed for this approach. More interestingly, another wire is also predicted using the magnesium atom as linkage. The true energy minimum structures of $B_{28}Fe_2Li_2Mg$, $B_{42}Fe_3Li_2Mg_2$, $B_{56}Fe_4Li_2Mg_3$, and $B_{70}Fe_4Mg_4Li_2$ obtained at TPSSh/6-31+G(d) level, are displayed in Figure 3.38. Noticeably, two kinds of nanowire could be formed: the first one is an antiprism form, and the other form has a prism shape from two neighbour B_{14} DR. Both of them are calculated to be energetically degenerate. The $B_{28}Fe_2Li_2Mg$ nanowire is formed from two Li_2FeB_{14} motifs in such a way that the two middle lithium atoms in Li- $B_{14}Fe$ -Li ... Li- $B_{14}Fe$ -Li are replaced by one magnesium atom. Noticeably, the $B_{42}Fe_3Mg_2Li_2$ wire can be also obtained by assembling three $B_{14}FeLi_2$ motifs and replacing four middle lithium atoms by two Mg ones. Therefore, longer wires can be made by linking different numbers of $B_{14}FeLi_2$ units and substituting each two middle Li metals with a Mg one. This strategy is introduced herein for construction of boron-based wires using the innovative $B_{14}FeLi_2$ unit as follows:

$$n \text{Li}_2 \text{FeB}_{14} + (n-1)\text{Mg} \rightarrow \text{Li}_2 \text{Fe}_n \text{Mg}_{n-1} B_{14n} + (2n-2)\text{Li} \quad n \ge 2$$
 (3.6)

The overwhelming advantage of this strategy is to keep the (N 0 2)-orbital of the HCM being the HOMO of the wire having N B₇ rings, which is expected to keep the wire stable in a high symmetry. The HOMO-LUMO gaps of B₂₈Fe₂Li₂Mg, B₄₂Fe₃Li₂Mg₂, B₅₆Fe₄Li₂Mg₃ and B₇₀Fe₄Mg₄Li₂ are found to be 1.3, 1.2, 1.0 and 1.0 eV, respectively. By plotting these values versus the inverse numbers of Li₂B₁₄Fe units in each wire, a linear correlation with R² = 0.99 is obtained by a slope of unity, and an intercept of 0.8. Thus, it can be predicted that the energy gap of a nanowire with an infinite number of B₁₄FeLi₂ units has approached a value of ~0.8 eV.



Figure 3.37. Optimized structure of the designed [Li-B14Fe-Li]-[B₁₄Fe]-[Li-B₁₄Fe-Li] wire.



Figure 3.38. Optimized structures of (**I**) B₂₈Fe₂Li₂Mg, (**II**) B₄₂Fe₃Li₂Mg₂, (**III**) B₅₆Fe₄Li₂Mg₃, and (**IV**) B₇₀Fe₄Mg₄Li₂ nanowires in antiprism and prism forms.

3.4.3. Concluding remarks

In the present theoretical study, the effects of both Li and Fe dopants on the B_{14} cluster have been systematically studied. A teetotum form was found as the global minimum of the B_{14} FeLi₂ cluster, characterized by a low spin singlet state. The results obtained can be summarized as follows:

i) The HOMO of $B_{14}FeLi_2$ is characterized by the (2 0 2)-orbital of the hollow cylinder model, resulting in a highly thermodynamically stable structure. Therefore, insertion of a Fe atom inside the double ring B_{14} expands both peripheral B-B bonds and B-B bonds between two B-strings, which leads to a weakening of all B-B bonds. The (2 0 2)-orbital plays a role in shortening the peripheral B-B bonds of 1.63 Å, while the B-B bonds between both strings amount to ~1.79 Å.

ii) The high symmetry geometry of $B_{14}FeLi_2$ causes several forbidden electronic transitions according to TD-DFT calculations. The two major peaks along with other minor peaks illustrate that the teetotum $B_{14}FeLi_2$ can absorb UV light but it is completely transparent for visible light.

iii) Two different approaches are introduced for making boron-based nanowires using the Li₂FeB₁₄ as linkage unit. The [Li-B₁₄Fe-Li]-[B₁₄Fe]-[Li-B₁₄Fe-Li] sequence is optimized and showed that it has a metallic character with very small HOMO-LUMO gap of ~0.3 eV. Another nanowire is introduced on the basis on the magnesium (Mg) linkers, in such a way that that the two middle lithium atoms in the Li-B₁₄Fe-Li ... Li-B₁₄Fe-Li structure are replaced with one magnesium metal. Accordingly, the equilibrium structures of the B₂₈Fe₂Li₂Mg, B₄₂Fe₃Li₂Mg₂, B₅₆Fe₄Li₂Mg₃ and B₇₀Fe₄Mg₄Li₂ wires are obtained upon geometry optimizations. The (N 0 2)-orbital of the hollow cylinder model is determined to be the HOMO of the wire having N B₇ rings, which guarantees a nanowire stable in a high symmetry form. The HOMO-LUMO gap of a nanowire having an infinite number of B₁₄FeLi₂ units is extrapolated to be ~0.8 eV, implying its metallic character.

Chapter 4. GENERAL CONCLUSIONS AND FUTURE DIRECTIONS

4.1. General Conclusions

In this theoretical study, quantum chemical calculations were performed to determine the geometries, electronic structures, and bonding phenomena of several new pure and doped boron clusters with different impurities. During this doctoral study several important results have been achieved. The results obtained for the specific systems were reported in Chapter 3, but for the sake of overview, they are briefly summarized hereafter. More importantly, different aromaticity models were proposed and applied to these systems, depending on the geometry of each structure to account for its thermodynamic stability, and where possible, some of its physicochemical properties involved. The achieved results from these studies include:

i) In terms of methodology, the TPSSh functional is highly reliable for optimizing the geometric structures of clusters containing B atoms, as demonstrated in benchmark tests involving clusters comprising B and either Si or Li. When verification with experimental values related to VDEs or harmonic vibrational frequencies, the B3LYP functional achieves a better agreement for these clusters.

ii) The ribbon model: the study on $B_2Si_3^q$ with the charge q going from -2 to 2 and $B_3Si_2^p$ with the charge p going from -3 to 1 clarified the difference between the Hückel rule and ribbon model and showed how both models can be used to probe the stability of these clusters. The ribbon aromaticity model is categorized into subclasses including *aromaticity*, *semi-aromaticity*, *antiaromaticity*, and *tripletaromaticity* types when the electronic configuration of $[...\pi^{2(n+1)}\sigma^{2n}]$, $[...\pi^{2n+1}\sigma^{2n}]$, $[...\pi^{2n}\sigma^{2n}]$, and $[...\pi^{2n+1}\sigma^{2n-1}]$ are involved, respectively. To ensure a structure is classified into a ribbon, a *self-lock* phenomenon needs to be found in that structure. An alternating distribution between π and σ delocalized electrons will subsequently be found in the resulting aromatic ribbon structure.

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iii) The disk model: the investigation revisited the stable structure of B_{70} and discovered that the **QP.1** structure in the triplet state is the most stable quasi-planar form. The existence of the **QP.1** structure is in line with the topological leapfrog principle constrained structures. The QP form of the B_{70}^{2-} dianion becomes stabilized when two electrons are added to the neutral **QP.1** structure to fill the two open-shell SOMO levels of the neutral state. Ring current maps for **QP.1** in triplet neutral and singlet dianionic states both indicate an aromatic character. The generalized (4N + 2M) and (4N + 2M - 2) electron count rules are proposed for the disk model. These models revert to the Hückel or Baird models when the molecule size reduces to a non-degenerate level.

iv) The disk-cone model: a cone-disk electron shell model was proposed through the investigation of the stability of the cone-like $B_{13}Li$ and $B_{12}Li_4$ structures. With the electronic configuration $[1\sigma^21\pi^42\sigma^21\delta^42\pi^41\phi^43\sigma^21\gamma^23\pi^42\delta^4]$ of the σ electron set and $[1\sigma^21\pi^42\sigma^2]$ of the π electron set, both $B_{13}Li$ and $B_{12}Li_4$ are characterized by a double aromaticity. The systematic investigation of lithium doping into B_{12} revealed that $B_{12}Li_8$ is a promising cluster to serve as a desirable material for H_2 storage, with a gravimetric weight ratio of hydrogen is up to 30 wt%, and the interaction energy from the first H_2 to the 40th H_2 in the range of 0.15 to 0.08 eV, indicating a behavior being more than a physisorption but less than a chemisorption.

v) The hollow cylinder model: the teetotum $B_{14}FeLi_2$ is a stable structure that does not absorb visible light and is capable of extending into nanowires. When extended, they become conductors when the band gap is extrapolated to about 0.8 eV. Therefore, $B_{14}FeLi_2$ is considered as a material with potential applications in the field of photovoltaics. To account for the stability of this structure, the HCM has been effective in elucidating the formation of their MOs through the hybridization between the MOs of the B_{14} framework and the AO of Fe. The HOMO of $B_{14}FeLi_2$ is characterized by the (2 0 2)-orbital of the HCM is also one of the basic reasons which brings in a highly thermodynamically stable structure. Overall, the intensive work carried out during this doctoral study has led to the proposal of several novel models that account for aromaticity, which remains a fundamental concept in modern chemistry. The new models and electron count rules have been derived through a rigorous mathematical treatment involving the solutions of wave equations adapted for each type of geometry. Up to now, these models have demonstrated successful applications to various types of geometries. Moreover, the classical electron counts that determine the aromatic character have been revealed as the simplest cases within these models.

4.2. Future Directions

Although the aromatic models based on geometric shape including the ribbon model, disk model and hollow cylinder model, have been recognized within the scientific community through citations in many publications in prestigious international chemistry and physics journals, they still need to be used for a much larger set of atomic clusters and chemical compounds in order to confirm their validity and applicability. Besides, many known aromaticity models such as the spherical aromaticity [130, 147], the jellium model [148, 149], the elongated model [42],... need to be considered using the same rigorous treatment with the aim to clearly determine their suitability and complementarity for each structure considered.

The final purpose is that these models could routinely be used by chemists for understanding their compounds and materials. In this perspective, my future research direction is to continue to investigate the different classes of not only the boron clusters, but also those of other elemental clusters, to complete the picture of the shape – structure - bonding of these clusters, and through that, to understand their detailed properties and closely the role of aromaticity on their thermodynamic stability.

Furthermore, the current and potential applications of atomic clusters should also be considered and extended. From this doctoral study, the B₁₂Li₈ cluster has shown a superior hydrogen adsorption capacity as compared to many materials reported previously. Such a research work will be carried out in the following period. The subjects of interest are multiple as there are plenty of possible applications involving, among others, the use of clusters as building blocks for assembled materials in several fields, as catalysts for chemical transformations, as drug carriers for medical treatment etc... Briefly the future of atomic clusters looks quite bright and theoretical predictions are quite promising!

LIST OF PUBLICATIONS CONTRIBUTING TO THE DISSERTATION

- Boron Silicon B₂Si₃^q and B₃Si₂^p Clusters: The Smallest Aromatic Ribbons Long Van Duong, Nguyen Ngoc Tri, Nguyen Phi Hung, and Minh Tho Nguyen, J. Phys. Chem. A, vol. 126, no. 20, pp. 3101–3109, May 2022.
- A topological path to the formation of the quasi-planar B₇₀ boron cluster and its dianion

Pinaki Saha, Fernando Buendia Zamudio, Long Van Duong, and Minh Tho Nguyen, *Phys. Chem. Chem. Phys.*, Advance Article, 2023.

3) The binary boron lithium clusters $B_{12}Li_n$ with n = 1-14: in search for hydrogen storage materials

Long Van Duong, Nguyen Thanh Si, Nguyen Phi Hung, and Minh Tho Nguyen, *Phys. Chem. Chem. Phys.*, vol. 23, no. 43, pp. 24866–24877, 2021.

 The teetotum cluster Li₂FeB₁₄ and its possible use for constructing boron nanowires

Ehsan Shakerzadeh, **Long Van Duong**, My Phuong Pham-Ho, Elham Tahmasebi, and Minh Tho Nguyen, *Phys. Chem. Chem. Phys.*, vol. 22, no. 26, pp. 15013–15021, 2020.

List of conferences

Poster presentation in:

The Asia Pacific Association of Theoretical and Computational Chemistry (APATCC-10) at the International Centre for Interdisciplinary Science and Education (ICISE), Quy Nhon – Vietnam, February $19^{\text{th}} - 23^{\text{rd}}$, 2023.

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Appendix

Cartesian coordinates of some optimized structures computed at the TPSSh/6-311+G(d) level. The sum of bond orders (SBOs) and net atomic charges (NACs) of each atom are also given.

0A	(B ₁	2)

Atom	X	Y	Z	SBOs	NACs
В	-1.60165900	1.82554200	-0.18402700	3.19	-0.07
В	1.60165900	1.82554200	-0.18402700	3.19	-0.07
В	-2.38179500	0.47430700	-0.18402700	3.19	-0.07
В	2.38179500	0.47430700	-0.18402700	3.19	-0.07
В	-0.78013600	-2.29984900	-0.18402700	3.19	-0.07
В	0.78013600	-2.29984900	-0.18402700	3.19	-0.07
В	-1.75673700	-1.01425300	-0.04377200	3.23	0.06
В	1.75673700	-1.01425300	-0.04377200	3.23	0.06
В	0.00000000	2.02850500	-0.04377200	3.23	0.06
В	-0.84393500	0.48724600	0.41182600	3.55	0.08
В	0.84393500	0.48724600	0.41182600	3.55	0.08
В	0.00000000	-0.97449200	0.41182600	3.55	0.08

1A (B₁₂Li)

Atom	Х	Y	Z	SBOs	NACs
В	-0.17968600	2.32511300	-0.77140500	3.33	-0.13
В	-0.17968600	2.32511300	0.77140500	3.33	-0.13
В	-0.15230200	-0.45876100	-2.30339100	3.36	-0.12
В	-0.15230200	-0.45876100	2.30339100	3.36	-0.12
В	0.00546000	1.02607000	-1.71817100	3.43	-0.01
В	0.00546000	1.02607000	1.71817100	3.43	-0.01
В	-0.01297100	-2.14989300	0.00000000	3.45	-0.07
В	-0.14488200	-1.80585200	1.53383700	3.46	-0.14
В	-0.14488200	-1.80585200	-1.53383700	3.46	-0.14
В	0.67718500	-0.44673400	-0.84033500	3.57	0.01
В	0.67718500	-0.44673400	0.84033500	3.57	0.01
В	0.53000800	1.00368800	0.00000000	3.75	0.02
Li	-1.54764600	-0.22244600	0.00000000	0.35	0.82

2A (B₁₂Li₂)

Atom	Х	Y	Z	SBOs	NACs
В	0.00000000	1.60580600	0.76820000	3.65	-0.13
В	1.39066900	0.80290300	0.76820000	3.65	-0.13
В	-1.39066900	0.80290300	0.76820000	3.65	-0.13
В	1.39066900	-0.80290300	0.76820000	3.65	-0.13
В	-1.39066900	-0.80290300	0.76820000	3.65	-0.13
В	0.00000000	-1.60580600	0.76820000	3.65	-0.13
В	-0.80290300	1.39066900	-0.76820000	3.65	-0.13
В	0.80290300	1.39066900	-0.76820000	3.65	-0.13
В	-1.60580600	0.00000000	-0.76820000	3.65	-0.13
В	1.60580600	0.00000000	-0.76820000	3.65	-0.13
В	-0.80290300	-1.39066900	-0.76820000	3.65	-0.13
В	0.80290300	-1.39066900	-0.76820000	3.65	-0.13
Li	0.00000000	0.00000000	-2.30391600	0.52	0.77
Li	0.00000000	0.00000000	2.30391600	0.52	0.77

3A (B₁₂Li₃)

Atom	Х	Y	Z	SBOs	NACs
В	-0.10183700	-2.57871100	0.00000000	3.38	0.01
В	1.00496900	-1.12341800	0.00000000	3.45	0.08
В	0.03743600	-1.81313700	-1.34848800	3.58	-0.26
В	0.03743600	-1.81313700	1.34848800	3.58	-0.26
В	-0.19464500	2.42524100	-0.78209000	3.67	-0.15
В	-0.19464500	2.42524100	0.78209000	3.67	-0.15
В	0.20647200	1.26527000	-1.67986700	3.78	-0.41
В	0.20647200	1.26527000	1.67986700	3.78	-0.41
В	-0.56984600	0.86094100	0.00000000	3.87	-0.05
В	0.57202800	-0.29609000	-1.45080000	3.96	-0.21
В	0.57202800	-0.29609000	1.45080000	3.96	-0.21
В	-0.76227700	-0.84030800	0.00000000	4.06	-0.48
Li	-1.55668800	-0.17617300	-1.95252000	0.38	0.84
Li	-1.55668800	-0.17617300	1.95252000	0.38	0.84
Li	1.75739100	1.21722900	0.00000000	0.41	0.83

4A (B₁₂Li₄)

Atom	Х	Y	Z	SBOs	NACs
В	-1.32940600	-1.00877800	-1.51268000	3.60	-0.20
В	-1.32940600	-1.00877800	1.51268000	3.60	-0.20
В	2.23294800	-0.57202300	0.00000000	3.61	-0.18
В	0.09004700	-0.65700000	-2.02751100	3.76	-0.24
В	0.09004700	-0.65700000	2.02751100	3.76	-0.24
В	1.51621400	-0.37633700	-1.37345700	3.81	-0.30
В	1.51621400	-0.37633700	1.37345700	3.81	-0.30
В	-1.77863900	-0.77102300	0.00000000	3.83	-0.24
В	1.11420300	0.77267200	0.00000000	3.88	-0.03
В	-0.75203700	0.49279300	-0.91729400	4.14	-0.14
В	-0.75203700	0.49279300	0.91729400	4.14	-0.14
В	-0.20828300	1.74698600	0.00000000	4.41	-1.16
Li	0.29871400	-1.92754100	0.00000000	0.36	0.86
Li	-2.38387800	1.66684000	0.00000000	0.38	0.84
Li	0.70102900	1.73204500	-1.97563000	0.42	0.83
Li	0.70102900	1.73204500	1.97563000	0.42	0.83

4E (B₁₂Li₄)

Atom	Х	Y	Z	SBOs	NACs
В	0.00000000	1.85406700	-0.35538500	3.75	-0.20
В	1.60566900	-0.92703400	-0.35538500	3.76	-0.20
В	-1.60566900	-0.92703400	-0.35538500	3.76	-0.20
В	-1.07198800	-1.49657700	1.02110500	3.84	-0.45
В	-0.76008000	1.67665700	1.02110500	3.84	-0.45
В	1.83206800	-0.18008000	1.02110500	3.84	-0.45
В	-0.87470300	-0.36686000	-1.70269300	3.85	-0.30
В	0.75506200	-0.57408500	-1.70269300	3.85	-0.30
В	0.11964100	0.94094500	-1.70269300	3.85	-0.30
В	0.73299700	0.98678700	0.97153400	3.89	-0.12
В	0.48808400	-1.12818800	0.97153400	3.89	-0.12
В	-1.22108100	0.14140100	0.97153400	3.89	-0.12
Li	0.00000000	0.00000000	2.82640200	0.40	0.82
Li	-2.03102700	1.34092300	-0.83306900	0.46	0.81
Li	-0.14576000	-2.42938300	-0.83306900	0.46	0.81
Li	2.17678700	1.08845900	-0.83306900	0.46	0.80

5A (B₁₂Li₅)

Atom	Х	Y	Z	SBOs	NACs
В	-0.84892200	-2.02449100	-0.25792600	3.76	-0.18
В	2.11098500	-1.37640300	0.12142900	3.78	-0.25
В	-2.14547700	-1.20804500	0.07517800	3.82	-0.47
В	0.72093900	-2.05073000	0.03407900	3.84	-0.33
В	-0.41517700	0.86696000	1.06415000	3.88	-0.60
В	-1.44094200	1.58261900	-0.09934700	3.89	-0.55
В	2.51940600	0.08330400	-0.27469700	3.92	-0.32
В	-2.09757600	0.29267400	0.64467800	3.93	-0.21
В	1.65278200	1.31081900	-0.65436500	3.94	-0.56
В	0.01953400	1.23668400	-0.86038400	4.06	-0.25
В	-0.79105200	-0.20600200	-0.41770100	4.12	-0.07
В	0.83959400	-0.12786200	0.28714800	4.14	-0.11
Li	-2.79035000	0.51044400	-1.39353500	0.39	0.83
Li	1.02397500	-0.71294200	-1.84711600	0.40	0.84
Li	-0.58764400	-1.19484700	1.79613600	0.43	0.83
Li	0.27896500	2.98954400	0.29775100	0.55	0.72
Li	1.86822900	1.10859000	1.70969800	0.58	0.69

6A (B₁₂Li₆)

Atom	X	Y	Z	SBOs	NACs
В	2.56887300	0.48745100	-0.16765300	3.84	-0.20
В	0.95503300	0.06120700	0.35671600	3.87	0.04
В	-2.36761200	0.55685500	0.38032000	3.88	-0.36
В	2.23778600	-0.99434600	-0.43799900	3.91	-0.46
В	1.61836700	1.72641100	-0.01133400	3.97	-0.47
В	-1.54386800	1.83387000	0.01685700	4.00	-0.53
В	-0.89306900	0.26462700	-0.45715300	4.06	0.05
В	-0.71914400	-1.36778200	-0.89359700	4.14	-0.75
В	0.85453100	-1.76566100	-0.36232000	4.18	-0.33
В	-1.79674500	-0.96105800	0.46318600	4.24	-0.47
В	-0.15711600	-1.15169300	0.93858400	4.30	-0.78
В	0.04878300	1.70287100	-0.24728100	4.69	-0.59
Li	0.93858900	0.20163700	-1.87342500	0.39	0.85
Li	0.11118500	3.60689700	0.26375600	0.44	0.79
Li	-2.65706100	-0.66186400	-1.50866200	0.45	0.81
Li	-0.66147800	0.79124700	1.81356800	0.46	0.83
Li	1.83953100	-1.55713400	1.64539600	0.50	0.78
Li	-0.91379800	-3.03537100	0.36215700	0.50	0.80

7A (B₁₂Li₇)

Atom	Х	Y	Z	SBOs	NACs
р	2 64822000	0 10029500	0.04295600	2 77	0.21
D	-2.04822000	-0.10028300	-0.04283000	5.77	-0.51
В	0.71779200	-2.04591800	-0.34337200	3.78	-0.22
В	-0.78361300	-2.19489600	0.14767900	3.79	-0.28
В	-2.20361300	-1.56082700	0.26787900	3.80	-0.29
В	-0.99076700	-0.32990000	0.39173300	4.05	-0.06
В	2.01475700	-1.16741500	-0.42190200	4.08	-0.51
В	0.61195100	-0.15436800	-0.47309100	4.09	0.03
В	-0.28037800	1.14852200	-1.16781100	4.12	-0.67
В	-1.74806000	1.20718300	-0.27539600	4.17	-0.45
В	2.21649400	0.36011500	-0.05949800	4.24	-0.63
В	1.11854000	1.55930300	-0.25971200	4.28	-0.53
В	-0.27560900	1.21566000	0.75325100	4.34	-0.82
Li	1.61142800	0.64296000	-2.21715000	0.41	0.84
Li	-1.21549900	-0.89288400	-1.74970300	0.44	0.82
Li	-2.08881800	0.94742700	1.88903700	0.49	0.78
Li	-0.51356600	3.05729700	-0.25463000	0.49	0.80
Li	3.49434500	-0.93432700	1.27734800	0.77	0.46
Li	0.74446100	-0.96955700	1.66087700	0.83	0.57
Li	1.71885900	1.58712800	1.86604800	0.90	0.47

8A (B₁₂Li₈)

Atom	X	Y	Z	SBOs	NACs
В	2.38813300	0.00000000	-0.33387000	4.01	-0.97
В	-2.38813300	0.00000000	-0.33387000	4.01	-0.97
В	-0.83607500	0.00000000	-1.17241500	4.02	-0.06
В	0.83607500	0.00000000	-1.17241500	4.02	-0.06
В	-1.29090000	-1.04274100	0.36441300	4.14	-0.24
В	1.29090000	-1.04274100	0.36441300	4.14	-0.24
В	-1.29090000	1.04274100	0.36441300	4.14	-0.24
В	1.29090000	1.04274100	0.36441300	4.14	-0.24
В	0.00000000	-1.48279800	-0.73350400	4.21	-0.82
В	0.00000000	1.48279800	-0.73350400	4.21	-0.82
В	0.00000000	-0.83592400	1.53401100	4.23	-0.74
В	0.00000000	0.83592400	1.53401100	4.23	-0.74
Li	1.90890700	0.00000000	2.15835500	0.44	0.84
Li	-1.90890700	0.00000000	2.15835500	0.44	0.84
Li	-2.08130100	-1.76207800	-1.54227800	0.56	0.75
Li	2.08130100	-1.76207800	-1.54227800	0.56	0.75
Li	-2.08130100	1.76207800	-1.54227800	0.56	0.75
Li	2.08130100	1.76207800	-1.54227800	0.56	0.75
Li	0.00000000	2.81901300	0.88778800	0.60	0.74
Li	0.00000000	-2.81901300	0.88778800	0.60	0.74

9A (B₁₂Li₉)

Atom	X	Y	Z	SBOs	NACs
р	2 48220500	0.0000000	0 10210600	2.01	0.04
D	2.46329300	0.00000000	0.10310000	2.01	-0.94
В	-2.48329500	0.00000000	0.10310600	3.91	-0.94
В	-1.31532500	-1.02610400	-0.46933300	4.11	-0.21
В	-1.31532500	1.02610400	-0.46933300	4.11	-0.21
В	1.31532500	-1.02610400	-0.46933300	4.11	-0.21
В	1.31532500	1.02610400	-0.46933300	4.11	-0.21
В	0.00000000	-1.46762800	0.66615900	4.17	-0.76
В	0.00000000	1.46762800	0.66615900	4.17	-0.76
В	0.00000000	-0.83988400	-1.57899400	4.23	-0.73
В	0.00000000	0.83988400	-1.57899400	4.23	-0.73
В	-0.89776600	0.00000000	1.06889200	4.36	-0.37
В	0.89776600	0.00000000	1.06889200	4.36	-0.37
Li	-1.86842500	0.00000000	-2.28877200	0.45	0.84
Li	1.86842500	0.00000000	-2.28877200	0.45	0.84
Li	0.00000000	-2.82587000	-0.93992300	0.60	0.73
Li	0.00000000	2.82587000	-0.93992300	0.60	0.73
Li	-2.19544000	-1.67250000	1.43293800	0.64	0.70
Li	2.19544000	-1.67250000	1.43293800	0.64	0.70
Li	2.19544000	1.67250000	1.43293800	0.65	0.70
Li	-2.19544000	1.67250000	1.43293800	0.65	0.70
Li	0.00000000	0.00000000	2.99065200	0.78	0.52

10A (B₁₂Li₁₀)

Atom	Х	Y	Z	SBOs	NACs
В	-1.28522900	-0.35876700	-0.92800300	3.99	-0.30
В	-1.28522900	-0.35876700	0.92800300	3.99	-0.30
В	0.06650200	-1.75993500	0.00000000	4.03	-0.03
В	1.66018400	-0.69242900	0.00000000	4.07	-1.03
В	-0.55179100	-1.68658700	-1.57411400	4.13	-1.01
В	-0.55179100	-1.68658700	1.57411400	4.13	-1.01
В	0.82697500	0.77209600	0.00000000	4.18	0.05
В	0.49532400	-0.35862500	1.39845800	4.41	-0.32
В	0.49532400	-0.35862500	-1.39845800	4.41	-0.32
В	-0.31395500	1.14501300	-1.34483500	4.45	-0.83
В	-0.31395500	1.14501300	1.34483500	4.45	-0.83
В	0.11752800	2.25162300	0.00000000	4.53	-1.16
Li	-1.98333300	-2.31268700	0.00000000	0.45	0.84
Li	-2.02673000	1.46206500	0.00000000	0.51	0.81
Li	2.06374700	1.10888600	-1.58479700	0.61	0.70
Li	2.06374700	1.10888600	1.58479700	0.62	0.70
Li	-0.78558100	-0.10363500	-3.06660600	0.62	0.73
Li	-0.78558100	-0.10363500	3.06660600	0.62	0.73
Li	1.52742700	-2.24275200	-1.58641800	0.63	0.72
Li	1.52742700	-2.24275200	1.58641800	0.63	0.71
Li	-0.26713400	3.28495800	-1.77081200	0.79	0.57

Li -0.26713400 3.28495800 1.77081200 0.79	0.57
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11A (B₁₂Li₁₁)

Atom	X	Y	Z	SBOs	NACs
	0.000000000	0.05500000	0.00000000	4.00	0.06
В	0.68237600	0.85708000	0.00000000	4.00	0.06
В	-1.27453400	-0.65549600	-0.92531000	4.00	-0.31
В	-1.27453400	-0.65549600	0.92531000	4.00	-0.31
В	0.23988700	-1.80246800	0.00000000	4.04	-0.02
В	-0.35156400	-1.84667600	-1.58499400	4.09	-1.01
В	-0.35156400	-1.84667600	1.58499400	4.09	-1.01
В	1.67092700	-0.53060900	0.00000000	4.10	-1.03
В	-0.55790500	0.98254300	1.32049000	4.36	-0.74
В	-0.55790500	0.98254300	-1.32049000	4.36	-0.74
В	0.47899100	-0.36609800	1.37444900	4.36	-0.29
В	0.47899100	-0.36609800	-1.37444900	4.36	-0.29
В	-0.39670200	2.13658900	0.00000000	4.42	-1.05
Li	-1.67889200	-2.70274800	0.00000000	0.42	0.85
Li	-2.34728200	0.99888600	0.00000000	0.48	0.82
Li	1.77761400	-2.09100600	-1.58380100	0.60	0.73
Li	1.77761400	-2.09100600	1.58380100	0.61	0.72
Li	-0.79583500	-0.30920900	-3.07367300	0.62	0.72
Li	-0.79583500	-0.30920900	3.07367300	0.62	0.72
Li	-0.72878300	3.05732200	-1.90285400	0.81	0.53
Li	-0.72878300	3.05732200	1.90285400	0.81	0.53
Li	2.06563300	1.09761300	-1.62925600	0.84	0.54
Li	2.06563300	1.09761300	1.62925600	0.84	0.54
Li	1.41147900	3.37919100	0.00000000	1.22	0.08

12A (B₁₂Li₁₂)

Atom	Х	Y	Z	SBOs	NACs
В	0.53342500	0.85024600	0.00000000	3.89	0.12
В	-1.31262900	-0.78379200	-0.92112900	3.98	-0.29
В	-1.31262900	-0.78379200	0.92112900	3.98	-0.29
В	0.29066500	-1.81877800	0.00000000	4.02	-0.02
В	-0.30585300	-1.91183600	-1.58839200	4.08	-1.03
В	-0.30585300	-1.91183600	1.58839200	4.08	-1.03
В	1.61286500	-0.45479100	0.00000000	4.15	-0.97
В	0.39947700	-0.37544500	1.36768200	4.34	-0.27
В	0.39947700	-0.37544500	-1.36768200	4.34	-0.27
В	-0.72772600	0.89626300	1.32519900	4.37	-0.79
В	-0.72772600	0.89626300	-1.32519900	4.37	-0.79
В	-0.59808900	2.07413700	0.00000000	4.40	-1.06
Li	-1.54255500	-2.87385900	0.00000000	0.43	0.85
Li	-2.49461900	0.80032600	0.00000000	0.47	0.82
Li	1.84290800	-1.98531400	-1.61760300	0.60	0.72
Li	1.84290800	-1.98531400	1.61760300	0.60	0.72
Li	-0.86272600	-0.41258100	-3.07911100	0.63	0.71
Li	-0.86272600	-0.41258100	3.07911100	0.63	0.71
Li	-1.06078100	2.99471400	-1.87114600	0.81	0.53
Li	-1.06078100	2.99471400	1.87114600	0.81	0.53
Li	1.49005500	1.40100900	-1.91905600	1.02	0.42
Li	1.49005500	1.40100900	1.91905600	1.03	0.42
Li	3.41667800	0.84769500	0.00000000	1.08	0.18
Li	1.22590800	3.39485700	0.00000000	1.27	0.07

13A (B₁₂Li₁₃)

Atom	Х	Y	Z	SBOs	NACs
В	-0.06751300	-0.62170500	0.29160500	3.96	-0.23
В	-0.84377400	-2.11164000	-0.40490600	4.02	-0.36
В	-1.45733800	0.50347400	0.30941600	4.12	-0.16
В	0.66188100	-2.26122400	-0.16547200	4.15	-0.54
В	1.43975200	0.29295000	0.31580200	4.17	-0.17
В	2.09534500	-1.52052100	-0.19867400	4.17	-0.31
В	-2.20141100	-1.25015800	-0.40600400	4.18	-0.34
В	3.01579500	-0.26389900	-0.06019000	4.27	-1.32
В	-3.06199800	0.01520500	-0.07451500	4.29	-1.36
В	0.05757200	0.88306300	-0.65720000	4.37	-0.54
В	-0.77365800	2.11897300	0.29046000	4.50	-1.07
В	0.95187700	2.04307600	0.30813400	4.59	-1.20
Li	4.29782200	-1.52495500	-0.98024300	0.54	0.74
Li	-4.54171200	-1.18459800	-0.71996400	0.55	0.73
Li	3.00365000	1.70776400	0.95968500	0.72	0.66
Li	-2.93841300	2.10653600	0.44412800	0.74	0.66
Li	0.18894800	3.87398300	0.99408200	0.74	0.62
Li	0.67220500	-0.90310200	-1.88784700	0.75	0.62

Li	-1.83988000	0.60234100	-1.86632200	0.76	0.62
Li	-0.00626600	0.96156500	1.95939700	0.83	0.60
Li	-0.43143500	-3.67008700	1.24938300	0.86	0.34
Li	-0.01252100	2.90318100	-1.59540000	0.88	0.52
Li	2.27901100	1.34143500	-1.44119400	0.89	0.56
Li	1.42615300	-1.40434400	1.88321600	0.92	0.47
Li	-1.79177800	-1.18904300	1.75365400	0.98	0.45

14A (B₁₂Li₁₄)

Atom	X	Y	Z	SBOs	NACs
В	-0.17465500	0.17098500	0.98572200	3.82	0.30
В	-0.17465500	0.17098500	-0.98572200	3.82	0.30
В	0.69158800	1.40712200	0.00000000	4.24	-1.06
В	-1.82138500	-0.06846200	1.52778200	4.37	-0.89
В	-1.82138500	-0.06846200	-1.52778200	4.37	-0.89
В	-1.35859600	-0.73352700	0.00000000	4.39	-0.71
В	0.94979800	-0.60276500	2.12172300	4.47	-0.99
В	0.94979800	-0.60276500	-2.12172300	4.47	-0.99
В	1.66833100	0.23879200	0.86787600	4.57	-0.59
В	1.66833100	0.23879200	-0.86787600	4.57	-0.59
В	-0.58911200	0.03186900	2.68161000	4.64	-1.08
В	-0.58911200	0.03186900	-2.68161000	4.64	-1.08
Li	0.68449800	1.79444200	-2.19088400	0.66	0.71
Li	0.68449800	1.79444200	2.19088400	0.66	0.71
Li	-0.87550000	-2.05091100	-1.79732800	0.70	0.67
Li	-0.87550000	-2.05091100	1.79732800	0.70	0.67
Li	0.60177800	-0.60871100	-4.26965200	0.72	0.61
Li	0.60177800	-0.60871100	4.26965200	0.73	0.61
Li	-1.52261200	1.73378500	0.00000000	0.75	0.65
Li	-2.42682400	0.82140800	-3.34024900	0.80	0.57
Li	-2.42682400	0.82140800	3.34024900	0.81	0.57
Li	-3.43090500	-0.19601500	0.00000000	0.86	0.55
Li	3.08349700	-0.97451000	-1.84784200	0.89	0.46
Li	3.08349700	-0.97451000	1.84784200	0.90	0.46
Li	2.87308300	1.84804500	0.00000000	0.90	0.49
Li	0.94729400	-1.70663600	0.00000000	0.93	0.54

14C (B₁₂Li₁₄)

Atom	Х	Y	Z	SBOs	NACs
В	1.01454500	0.16578600	-1.37795000	4.18	-0.52
В	-1.01454500	-0.16578600	1.37795000	4.18	-0.52
В	-0.65090800	0.79578900	-1.37810000	4.18	-0.52
В	0.65090800	-0.79578900	1.37810000	4.18	-0.52
В	0.36363800	0.96157500	1.37794900	4.18	-0.52
В	-0.36363800	-0.96157500	-1.37794900	4.18	-0.52
В	-1.07016900	1.30850400	0.27419700	4.20	-0.52
В	1.07016900	-1.30850400	-0.27419700	4.20	-0.52
В	0.59799800	1.58103000	-0.27419900	4.20	-0.52
В	-0.59799800	-1.58103000	0.27419900	4.20	-0.52
В	1.66814100	0.27259400	0.27411300	4.20	-0.52
В	-1.66814100	-0.27259400	-0.27411300	4.20	-0.52
Li	-0.00084900	-0.00124400	-3.32146200	0.80	0.55
Li	0.00084900	0.00124400	3.32146200	0.80	0.55
Li	-2.24354800	-2.01180600	-1.42444500	0.95	0.43
Li	-2.41687300	-1.79955100	1.42414200	0.95	0.43
Li	0.34883700	-2.99374700	-1.42247000	0.95	0.43
Li	-2.86488900	0.93568500	1.42274500	0.95	0.43
Li	0.62312300	-2.94871000	1.42278100	0.95	0.43
Li	-2.76741100	1.19247400	-1.42474600	0.95	0.43
Li	2.86488900	-0.93568500	-1.42274500	0.95	0.43
Li	-0.34883700	2.99374700	1.42247000	0.95	0.43
Li	2.76741100	-1.19247400	1.42474600	0.95	0.43
Li	2.41687300	1.79955100	-1.42414200	0.95	0.43
Li	-0.62312300	2.94871000	-1.42278100	0.95	0.43
Li	2.24354800	2.01180600	1.42444500	0.95	0.43