Aix*Marseille université — Ecole Doctorale des Sciences Chimiques ED250 — Contrats Doctoraux **2022**

PhD proposal: **Localized wave functions and aromaticity**

Lab: **Institut des Sciences Moléculaires de Marseille**

Team: **Chimie ThéOrique et Modèles (CTOM)**

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Description of the proposal:

Electronic delocalization in hydrocarbons and more specifically in cyclic systems possibly leads to aromaticity (and/or anti-aromaticity). This delocalization confers most interesting structural and electronic properties. There are many cases where such a delocalization leads to uncommon properties. Well known cases include charge transfer due to aromatization in the ground state, as in fulvenes and indacenes for instance. Another important class of molecules in which electron delocalization and aromaticity confer a particular stability to high temperatures and UV radiation is the class of benzenoid molecules: they belong to the Polycyclic Aromatic Hydrocarbons (PAH) family and consist only in fused 6 carbon atom rings and hydrogens. Some of them cannot be represented schematically by Kekulé structures, i.e by mesomeric forms in which the π electrons are grouped together in pairs and made up of an alternating arrangement of single and double carbon-carbon bonds (Fig. 1); at least one carbon atom carries a single electron: they are called “non-Kekulean” benzenoids, for example the two compounds belonging to the triangulene family (Fig. 2). Until very recently, these compounds were not characterized experimentally; only in 2019 the first synthesis of small non-Kekulean benzenoids was carried out and their characterization is now possible, in particular for their electronic and magnetic properties.[1,2].

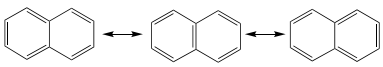


***Fig. 1**: The 3 Kekulé structures of naphthalene*

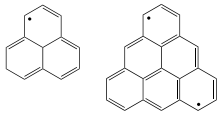


***Fig. 2**: Two non-Kekuléan benzenoids represented by one possible mesomeric form*

The goal of this project is on the one hand to study the electronic and magnetic properties of some non-Kekulean benzenoids using quantum chemistry methods (ab initio or DFT), and on the other hand to characterize the aromaticity of these compounds by approximate methods and compare it to other cases, with and without charge transfer.[3] The candidate should show good knowledge in quantum/theoretical chemistry and a strong motivation for this discipline. Knowledge in programming and / or linux system would be a plus. A part of the project will use our (HuLiS) program and there will be room to actively participate to its development.[4]

Context:

Our lab is interested in aromatic systems and related applications.[5] We also use and define localized methods for ground and excited states.[6,7] Our freeware HuLiS is a unique tool based on the simple Hückel approximation. It helps to describe electronic delocalization in terms of localized structures (with weights of the structures and trust factor).

References:

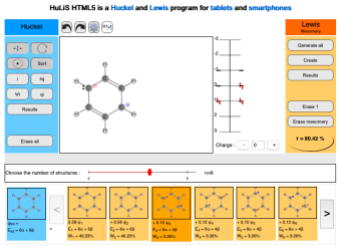
[1] S. Mishra et al, *Synthesis and Characterization of π-Extended Triangulene,* J. Am. Chem. Soc., **2019**, 141, 10621–10625.
[2] J. Su et al, *Atomically precise bottom-up synthesis of π-extended [5]triangulene*, Sci. Adv., **2019**, 5, eaav7717.
[3] M. Randić, *Benzenoid rings resonance energies and local aromaticity of benzenoid hydrocarbons,* J. Comput. Chem., **2019**, 40, 753–762.
[4] (a) Y. Carissan, D. Hagebaum-Reignier, N. Goudard, S. Humbel, *Hückel-Lewis-Projection Method: A “Weights Watcher”* J. Phys. Chem. A. **2008**, 112, 13256–13262. (b) Y. Carissan et al. In *Applications of Topological Methods in Molecular Chemistry* **2016**; Vol. 22, 337–360.
[5] M. Roy et al., *Stereoselective Syntheses, Structures, and Properties of Extremely Distorted Chiral Nanographenes Embedding Hextuple Helicenes* Angew. Chem. IE, **2020**, 59, 3264-3271.
[6] J. Racine, M. A. Touadjine, A. Rahmouni, S. Humbel, “*Methylenecyclopropene: local vision of the first $^1B_2$ excited state*” J. Mol. Mod., **2017**, 23, 22.
[7] J. Racine, D. Hagebaum-Reignier, Y. Carissan, S. Humbel, *Recasting wave functions into Valence Bond Structures: a simple projection method to describe excited states* J. Comp. Chem **2016**, 37, 771-779.

Details for the application:

Requirements:
A master/academic degree in Physical Chemistry, Physics or Chemistry with at least merit, or distinction (passing grade >= 12/20 in the french system) and a correct quantum chemistry background.

Appointment:
For a period of three years starting in October 1st 2022.

Application and deadlines:
• Contact the team before **Monday May 2nd** by sending a pdf file to stephane.humbel@univ-amu.fr including a cover letter, CV, copies of certificates and a short abstract of the Master thesis. Additionally, we ask you for names and contacts of two scientific referees to supply recommendation letters.
• Complete your application form by **Friday May 20th** (ask Stéphane for the form)
• Shortlisted candidates will take an interview at the School of Chemical Sciences (Ecole Doctorale des Sciences Chimiques) on Monday May 30th & Tuesday 31st (Zoom-like interview is possible)



Salary:
1975 €/month before taxes (net salary: about 1540 € / month including standard medical care and taxes)
For french native-speaking or fluent in French candidates, a possibility of teaching (64h) will increase the net salary by about 200 €.

HuLiS: www.hulis.free.fr
Hückel-**L**ewi**S** is a code where the Hückel Hamiltonian and the related wavefunction is used to describe the resonance between localized electronic structures (as Lewis structures). At the moment we have two released versions (java and javascript), plus our "private" (unreleased) development version where new ideas are implemented. Anyone can freely download the java executable from the www website. The access to the javascript version (m.hulis.free.fr) is also totally free.
We plan to release soon the "Block" delocalization option in the java code. In this "Block" approach, N electrons can delocalize on M atoms. It includes the notion of lone pair (N,M)=(2,1) and the notion of bond (2,2), but extends to aromatics (6,6) and antiaromatics.

Location:
The lab is located at unit 561, Campus St Jérôme, Marseille North. It possesses a significant computing facility (about 600 cores on its own + an access to the campus nodes). Teaching might involve to go (by bus for instance) to other scientific campus (Marseille Luminy, Marseille St Charles, Aix-en-Provence).
Marseille is located in France, on the Mediterranean coast and has a large national park "Les Calanques" where hiking for instance can be done in an outstanding panorama.