Special Collection: Computational Chemistry

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Chemists know well the value of an experimental or a theoretical result, but what is the value of a computational result? Simulation is neither theory nor experience, nor a mere calculation tool, but a genuine way of approaching reality that is transforming the scientific method. In some cases, it offers explanations to observations or experiments that seem incomprehensible because they are too complex. In this case, the computation serves as a relief. An experiment that converges with a certain computation has more scientific value than an experiment that does not converge with anything at all. In other cases, contribution of computational chemistry is essential because there is no experimental manner to determine what happens during a chemical process; for instance, in the path from reactants to products in (fast) reactions. Now, computational chemistry provides additional information that is not possible to obtain from experiments, so it is a valuable complement to them. Indeed, fruitful synergy between computation and experiment has led to the approach of theory-driven experimentation. Finally, computational chemistry helps to legitimize models or theories that have little opportunity to be contrasted with reality. In this situation, computational chemistry is not experience, but it does substitute it in relation to theory. In the present special collection, we have examples of the different ways computational chemistry helps chemists to interpret the electronic and molecular structure of molecules and their reactivity.

Computational chemistry is an important and dynamic research field within chemistry. Covering the full spectrum of the molecular and material sciences from an in silico perspective, it remains at the forefront and maintains huge importance in the latest developments in chemistry. The latest Special Collection at *ChemistryOpen* gathers a series of works that give a good idea of the current state-of-the-art in computational chemistry.

In their Review, Pan et al. describe the bonding between two noble elements, a noble metal (M) and a noble gas (Ng). The authors start from the discovery in 1977 of the AuNe$^+$ compound through mass spectroscopy and they thoroughly analyze all M–Ng compounds discovered to date. They emphasize the importance of computational chemistry and the synergy between experimental and computational chemists for the development of this relatively young field. Computational chem-

ists provided essential insights into the structure, stability, nature of the chemical bond, and barrier for the decomposition of noble gas compounds.

In this issue, three papers discuss aspects related to the quantum theory of atoms-in-molecules (QTAIM). In their Full Paper, Symons et al. develop an interpretation of the intra-atomic deformation energy of interacting quantum atoms (IQA) as a quantitative description of steric energy. The authors show that through-space compression of atomic volume experienced by approaching topological atoms causes an exponential increase in the intra-atomic energy of those atoms, the kinetic energy being the main responsible of this effect. In a subsequent paper, Nishide et al. perform a QTAIM dual functional analysis (QTAIM-DFA) to elucidate the dynamic and static nature of various neutral hydrogen bonds (nHBs). The authors classify the nHBs studied as van der Waals, typical HB with covalency or no covalency, and charge transfer HBs. Finally, in his work, Jabłoński casts doubt about the QTAIM concepts of bond paths as chemical bonds or as privileged exchange channels. He shows that, in general, bond paths have nothing in common with dominant interactions between distant atoms. He also reports bond paths that violate the concept of privileged exchange channels.

Aromaticity is a property that cannot be measured directly by any physical or chemical experiment because, as many other fundamental concepts in chemistry, it is not a well-defined magnitude. Three contributions in this issue are related to this topic. First, Szczepanik and Solà investigate the formal number of π electrons, d-orbital conjugation topology, π-electron delocalization, and aromaticity in d-block metallacycles in the context of recent findings concerning the correlation of π-HOMO topology and the magnetic aromaticity indices in these

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species. They conclude that some of the metallacycles studied cannot be classified exclusively as Hückel or Möbius because they have a hybrid Hückel-Möbius or even quasi-aromatic nature. Second, Pino-Rios et al. introduce the bifurcation analysis of the induced magnetic field to interpret the aromatic or antiaromatic character of a series of monocycles, as well as a set of polycyclic aromatic hydrocarbons (PAHs). They identify the presence of ring-shaped reducible domains that, in the case of PAHs, agree with the expectations from Clar's π-sextet theory. Third, Szatylowicz et al. discuss the substituent effect on electronic properties and aromaticity of 1-, 2-, and 9-anthrols. In contrast to the classical substituent constants, they find that electron accepting/donating properties of a given substituent depend on the position of this substituent in anthrol moieties.

Miquel Solà (1964) is full professor in the Universitat de Girona since 2003. He was awarded with the ICREA Academia Prize two times, in 2009 and 2014. In 2013, he got the Physical Chemistry prize awarded by the Spanish Royal Society of Chemistry. He is coauthor of about 30 book chapters and 350 scientific papers and has supervised 19 doctoral theses. He is a theoretical and computational chemist working on aromaticity, chemical bonding, and reaction mechanisms.

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Hydrogen bonds (HBs) are fundamentally important in all fields of chemical and biological sciences. They are the subject of three studies in this issue. The first uses QTAIM-DFA and, as such, it has been discussed in the QTAIM section of papers. In the second, Yang et al. study the structures and interaction energies of water clusters with ring stacking motifs using ab initio calculations. The structures of the water clusters are constructed by stacking either single rings or multi-rings of tetramer, pentamer, and hexamer. They find that, in the single-ring-stacking motif, the most stable isomers exhibit an alternative clockwise-anticlockwise stacking pattern. They also show that four-layer single-ring-stacking isomers are not energetically favorable in comparison with those of two-layer multi-ring-stacking isomers. The relative stability of the isomers is also analyzed in terms of HB strength and elastic distortions of the water molecules. In the third, Petelski and Fonseca Guerra use dispersion-corrected density functional theory (DFT) in combination with energy decomposition analysis to examine the hydrogen-bonded self-assembled rosettes of melamine and ammeline. The authors found that ammeline is a much better building block than melamine for the fabrication of cyclic complexes based on HBs. Interestingly, they prove that the mechanism of the cooperativity in melamine and ammeline rosettes is the same as that in guanine and N-halo-guanine quartets.

Computational chemistry has contributed enormously to the understanding of chemical reactivity. In this issue the reader can find several examples. The first two refer to the Diels–Alder (DA) reactions. In their Full Paper, Yu et al. describe the physical factors that control the DA reactivity of hetero-1,3-butadienes using activation strain analyses. They show how and why replacement of carbon atoms by heteroatoms in 1,3-butadiene (CCCC) dramatically influences the DA reactivity of hetero-1,3-butadienes with ethylene. On the other hand, Larrañaga and de Cózar, using the same methodology, analyze the DA reaction of cyclopentadiene with acrylonitrile, methylacrylate and their α-methylated counterparts to understand the excellent exo-selectivities observed experimentally in the latter due to the presence of the methyl substituent. According to the authors, the exo preference in methacrylonitrile and methyl methacrylate can be explained by the lower Pauli repulsion or higher electrostatic interactions rather than more stabilizing orbital interactions. Next, Tiezza et al. analyze the metal-catalyzed [2+2+2] cycloaddition of acetylene to give benzene and of acetylene/acetonitrile to give 2-methylpyridine for different metal catalysts. The authors discover a relationship between the extent of variation in the geometrical slippage along the reaction of the metal relative to its aromatic ligand in group 9 metal half-sandwich complexes and their catalytic activity in the [2+2+2] cycloaddition. Lu and Lai employ the hybrid quantum mechanics/molecular mechanics (QM/MM) methodology to fully analyze the reaction mechanism of the cleavage of the central double bond of stilbenes to two phenolic aldehydes catalyzed by NOV1, a stilbene cleavage oxygenase, using a four histidine Fe(II) center and dioxygen. Their QM/MM results support the dioxygenase mechanism involving

a dioxetane intermediate, whereas the mechanism involving an epoxide intermediate is a high-energy pathway and can, therefore, be ruled out. Finally, Deraet et al. provide a benchmark study of both the thermodynamics and kinetics of the hydride reductions of 2-substituted cyclohexanones using both density functional approximations and wavefunction methods. They conclude that, depending on the substituent, both the torsional strain and dispersion interactions affect the stereochemical outcome of this reaction.

Computational chemistry is a powerful tool to predict the physicochemical properties of molecules. In this Special Collection, we have gathered five examples. First, De Souza et al. calculate ^{1}H NMR chemical shifts of the antioxidant and anticancer flavonoid rutin in DMSO solution. Comparison between the experimental and theoretical ^{1}H NMR chemical shift profiles offers a powerful fingerprint criterion to determine the predominant molecular structure of flavonoid rutin in solution. Second, the electronic spectra of 2-mercapto-3-phenyl-2,3-dihydro-1H-quinazolin-4-one and the product obtained after its treatment with acetylacetone are determined by Hamada, based on time-dependent DFT calculations in three different solvents. Third, Dronskowski and co-workers report the crystal structure of $Ba(CN_3H_4)_2$. They show how the refinement of its molecular structure can be greatly aided by DFT calculations. Moreover, the infrared and Raman spectra of $Ba(CN_3H_4)_2$ are compared with DFT-calculated phonon spectra to identify the vibrational modes. Fourth, Estrada et al. apply, for the first time, computational chemistry (in particular, molecular dynamics) to identify a series of polymers that can be used as removing agents for pesticide remediation in water and soils with the aim of avoiding spring water contamination. Esterhuysen and co-workers investigate the importance of, and interplay between, steric and electronic effects in determining the strength of the coordination bond in cationic and neutral gold N-heterocyclic carbene complexes.

A correct description of electron correlation is a central issue for the physicochemical description of the electronic structure of molecules. In their work, Matito and co-workers analyze the Coulomb hole of Ne from highly accurate correlated wave functions using optimized even-tempered basis sets. They confirm the existence of a shoulder in the short-range region of the Coulomb hole of the Ne atom, which is attributed to an internal reorganization of the K-shell caused by electron correlation of the core electrons. The feature is not exclusive to Ne; it turns out to feature in most of the second-row atoms.

As Guest Editors, we are very grateful to all the authors who have contributed to this Special Collection and we consider that the resulting issue provides a good account of the current state-of-the-art in computational chemistry. Hopefully, the works published in this collection will be a source of inspiration for many.