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Solvay Workshop on “Conceptual quantum chemistry: present aspects and challenges for the future”

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Learning New, and Old, Chemical Concepts from Data

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Can machine-learning methods reveal chemical rules-of-thumb? Consider, for example, the concept of acidity. If A is a stronger Lewis acid than B, then A will accept electrons from B. Similarly, if B is a stronger Lewis acid than C, then B will accept electrons from C. The concept of acid/base strength indicates that A will also accept electrons from C. (Of course, there are numerous exceptions to this rule, which chemists excuse by asserting that acid/base strength is not always the dominant effect in a chemical reaction.) By viewing acid/base reactions as a "competition for electrons," we deduce the acid/base strength of different reagents. This provides an alternative scale for Lewis acidity. Similarly, by viewing reactions with multiple products (e.g., different conformations of a molecule; hard/soft acid/base reactions) as "competitions" between the various products, we can discover new conceptual descriptors for conformational stability and chemical reactivity.

Theory of Chemical Bonding and Reactivity: Quantitative Orbital and Activation Strain Models

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The aim of this talk is to convey a way of understanding the factors that determine bonding and reactivity, in general, and the activity and selectivity of transition-metal catalysts in bond activation and cross-coupling reactions, in particular [1]. I will discuss the effect of varying the metal M along the d^{10} metals of groups 9, 10 and 11, in combination with varying the number as well as the type of ligands, using relativistic density functional theory (DFT) [2] and the activation strain model (ASM) [1].

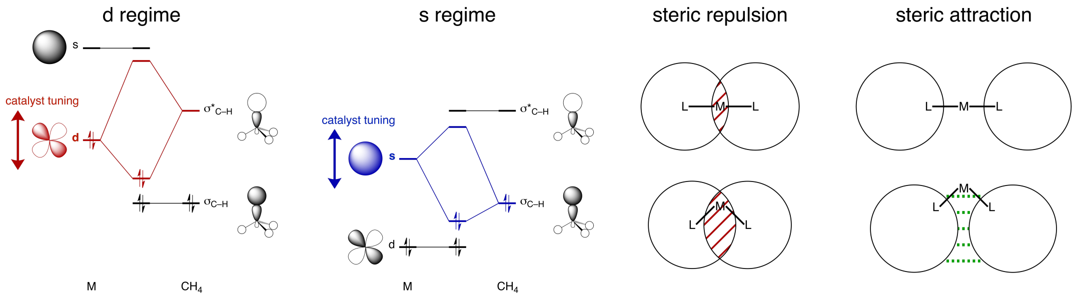

Figure 1. Schematic illustration of concepts presented in this lecture.

Three concepts for tuning a catalyst's activity emerge: (i) d-regime catalysts; (ii) s-regime catalysts; and (iii) bite-angle flexibility (see Figure 1, left). These concepts explain why the effect of one and the same ligand on a catalyst's activity can be completely different, even opposite, for catalysts from different electronic regimes. Furthermore, I will point out why not the bite angle itself, but its flexibility is decisive for the catalyst's activity. Finally, I show how the latter is influenced not only by steric repulsion but also by what we designate "steric attraction" (see Figure 1, right).

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Deciphering Multi-Center Bonding in Chemistry

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Canonical Molecular Orbitals (CMO) obtained by either the Hartree-Fock method or by Density Functional Theory are completely delocalized over the whole chemical system. When systems are getting larger it is hard to interpret CMOs. Chemists on the other side prefer to use localized bonding based on Lewis model, which operates with lone pairs and two-center two-electron bonds. When Lewis model works, interpretation of chemical bonding is simple. However, more and more new chemical systems cannot be represented by Lewis model. The resonance description may be used in those cases, but it becomes very challenging for structurally complex chemical species. We recently introduced two new theoretical methods Adaptive Natural Density Partitioning (AdNDP)[1] and Solid State Adaptive Natural Density Partitioning (SAdNDP)[2], which allow to express chemical bonding in terms of localized (1c-2e and 2c-2e) and delocalized (multi-center nc-2e) bonds. We initially search for all lone pairs, core electrons and 2c-2e bonds with good occupation numbers. In the ideal Lewis model occupation numbers correspond to 2 (an electron pair). If we cannot completely describe chemical bonding by a single Lewis structure we look for multicenter bonds, still trying to use as small number of centers as possible, though in principle delocalized bonds can be delocalized over the whole chemical system. In my talk I will show how AdNDP and SSAdNDP methods allow us to use both localized and delocalized bonding elements simultaneously for rationalization of chemical bonding in difficult cases of organic molecules, bare and embedded clusters, two-dimensional sheets and solids. AdNDP and SSAdNDP both provide a very efficient and visual approach to represent chemical bonding and could be used for research and for teaching chemistry.

This research was supported by the National Science Foundation (CHE-1361413).

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Chemical response functions in degenerate states and extended systems

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A system in a spatially (quasi-)degenerate ground state responds in a qualitatively different way to a change in the external potential. Remarkably, for degenerate states, the functional derivatives of the energy with respect to the external potential do not exist, and must be replaced by the weaker concept of functional variation. The resultant reactivity indicators depend on the specific perturbation. Therefore, degenerated states is a case in which the chemical (DFT-)reactivity cannot be thought as an intrinsic property. The cases of the Fukui function, the molecular electrostatic potential and charges of atoms in molecules will be discussed in detail. The ideas of chemical reactivity descriptors in degenerated ground states as a guiding principle to describe reactivity of extended systems will be also addressed.

The Symmetry of the Periodic System

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The periodic system of the chemical elements is one of the icons of modern science. The *overall* structure is best described by the Madelung Rule, which implies a doubling of periods of length $2n^2$, i.e.: 2, 2, 8, 8, 18, 18, 32, (32). With the recent IUPAC assignments of new elements up to Z=118, the final period now counts 30 elements.

While the length of the periods is still 'hydrogenic', their composition is not described by the standard algebra of the hydrogen spectrum. Instead a non-linear algebra is established which provides an Elementary Particle Approach to the periodic table. [1] It contains the period doubling as a natural ingredient. The generic model of a multi-electronic atom will be discussed.

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VISUAL DESCRIPTIONS OF ELECTRONIC STRUCTURE FROM MODERN VALENCE BOND THEORY: O_3 AND SO_2.

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We outline how spin-coupled theory (also known as the full generalised valence bond approach) can provide highly visual direct descriptions of molecular electronic structure, including the electronic rearrangements that accompany bond breaking and bond formation [1]. Then, using the ground states of O_3 and SO_2 as examples, we compare (and combine) qualitatively rather different descriptions of the bonding that can turn out to be fairly close in energy [2,3].

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Non covalent interactions: achievements and unsolved challenges of topology

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Along this contribution I will focus on the topological description of non-covalent interactions. I will highlight the state of the art, the achievements made in the last decade, but specially focus on the challenges that still need to be solved.

The characterization of very weak interactions from topological grounds was somehow deficient. We will illustrate this fact and show how it can be overcome. Analysis of the underlying gradient formulae in non covalent interactions shows that NCI critical points can be classified in two types: those that match with the critical points of the electron density (AIM-CPs), and those that are precluded by zeros of the one-electron potential (Non-AIMCPS), and therefore by transitions from classically allowed to classically forbidden regions. This typically corresponds to very weak interactions to which AIM was blind.

Still, one of the obvious link that is still missing in topology is energetics. We will point in some fruitful directions. The quantity {bose}({\vec{r}, which is a measure of the bosonic kinetic energy, corresponds to the second term in the ELF core and it is able to visually reveal covalent, ionic and non-covalent interactions at a time \cite{tbose}. The basis of NCI, the reduced density gradient, $s(\vec{r})$, being proportional to the square root of {bose}(\vec, inherits this same physical interpretation.

The relationship of $t_{bose}({\vec{r})$ with other descriptors, such as LOL, ELF and t_{LOL}(r), will be highlighted. All of them are able to disclose atomic shells, bonding and lone electron pairs. They reveal non-covalent interactions as saddle points, thereby being more suited to visualize covalent bonds. $t_{bose}({\vec{r})$ behaves similar to $t_{LOL}({\vec{r})$ in covalent bonds. However, $t_{bose}({\vec{r})$ is the only one able to reveal not only ionic and covalent features, but also non covalent interactions.

It has been shown[2] that the several interaction types from the s22 set can be classified in terms of the kinetic energy density at a given isosurface of the reduced density gradient. By analyzing the deviation of $t_{bose}({\vec{r})$ from a reference monorbital density we try to get insight into this relationship.

Understanding the relationship in 3D of energy and electron density is among the greatest challenges that topology has faced, and is facing.

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On the many facets of analyzing (non-)covalent interactions

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We will discuss a density-dependent molecular scalar field that distinguishes between one-electron-like regions (e.g., core electrons and tails) from high-overlap bonding regions.[1] The utility of the approach will be illustrated through the analysis of visual and numerical DORI signatures associated with distinct chemical situations The attractive characteristics of this density overlap regions indicator (DORI) also make it a suitable ingredient of various type of density functionals.[2] Alternatively, we illustrate the current capability and challenges of an intramolecular variant of Symmetry adapted perturbation theory (SAPT).[3]

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A different approach to understand and control reactivity

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The recently introduced activation strain model (ASM) of reactivity has allowed us to gain more insight into the intimacies of different fundamental processes in chemistry.[1] In combination with the energy decomposition analysis (EDA) method,[2] we have nowadays a very useful tool to quantitatively understand the physical factors that govern the activation barriers of reactions within organic and organometallic chemistry.

In this lecture, we shall first present an illustrative example of the application of this methodology to a particular class of pericyclic reactions known as Double Group Transfer Reactions.[3] Then, the Diels-Alder reactivity of polycyclic aromatic hydrocarbons including fullerenes and endohedral metallofullerenes will be analyzed (Figure 1).[4] Finally, examples in organometallic chemistry will be described as well.[5]

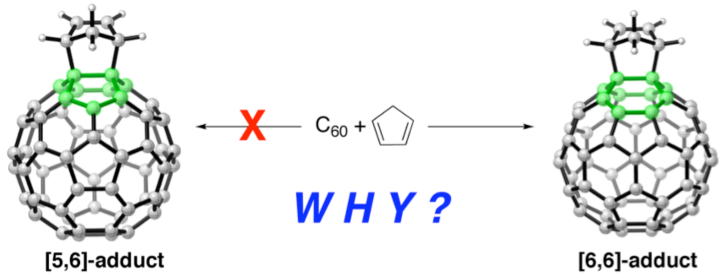

Figure 1

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Molecules With Unusual Bonding Situations - A Challenge for Chemical Bonding Models

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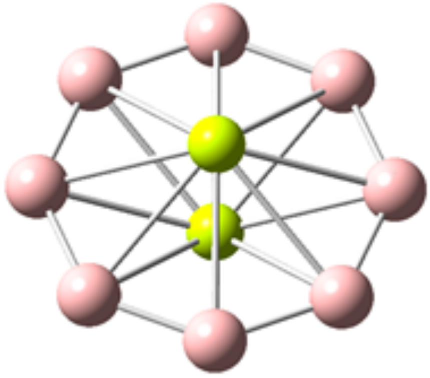
The lecture focuses on the bonding situation in molecules which are not easily described with standard Lewis structures. For example, the discus shaped molecule Be_2B_8 has a record-short Be-Be distance of 1.910 Å but there is no bond between the beryllium atoms. Further examples are discussed which show that a genuine understanding of chemical bonding requires sophisticated quantum chemical methods.



Be_2B_8

On the concepts of electron donor and electron acceptor systems

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In the context of Density Functional Theory of chemical reactivity we review various attempts to introduce mathematical equations to define some very well known empirical chemical concepts like acid and bases, electrophilicity and nucleophilicity. From a theoretical point of view it sounds more general to talk about electron donor and electron acceptor molecules. In this presentation we will show the derivation of an index, which could represent in a reasonable way the concept of nucleophilicity or bases, both better described as electron donor.

Temperature in density functional theory of chemical reactivity

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The Taylor series expansion of the energy as a function of the number of electrons and the external potential, around an isolated chemical species, has been the basis of the density functional theory of chemical reactivity. The response functions that appear through this approach describe the inherent or intrinsic chemical reactivity, which may be used to infer the behavior of a molecule when it interacts with different families of reagents. Most of the work done in this framework has been developed at zero temperature, and although it has provided very important results, it also presents some difficulties, mainly associated with the piecewise-continuous straight-line behavior of the energy as a function of the number of electrons. By making use of the Hohenberg-Kohn-Mermin formalism in the grand canonical ensemble, it is found that at temperatures different from zero, the derivatives of the average energy and the average electronic density with respect to the average number of electrons exist to all orders and can be evaluated analytically [1,2]. Thus, we will present this analysis together with the application of the temperature dependent expressions to charge transfer processes [3].

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Some Advances in Energy Decomposition Analysis of Electronic Structure Calculations

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Intermolecular interactions are central to the formation of clusters, supramolecular interactions, and many aspects of the behavior of molecules in condensed phases. The relevant forces are well understood: permanent and induced electrostatics, Pauli repulsions, attractive dispersive interactions, and charge-transfer interactions. However, they are only uniquely defined at long range. Similar issues arise in understanding the chemical bond, where the components and net interaction are even larger.

Electronic structure theory calculations can accurately calculate the net interaction, but what are the key contributions? To address this need, many intermolecular energy decomposition analysis (EDA) methods have been developed which seek to define these contributions. Examples include natural bond order (NBO) methods, Morokuma analysis and its many variants, symmetry-adapted perturbation theory (SAPT), the block-localized wavefunction (BLW) EDA, and the absolutely localized molecular orbital (ALMO) EDA. All of these useful methods have demonstrable weaknesses and formal limitations. Often these different EDAs yield results that disagree amongst themselves. Since they have different weaknesses, it may be difficult for a non-specialist to assess which, if any, are reliable for a given problem.

The purpose of this talk is to discuss some recent progress on several key issues associated with making a well-defined EDA based on modern density functional theory (DFT) calculations. An EDA typically divides an intermolecular interaction into the sum of three components: a frozen energy (which includes permanent electrostatics, Pauli repulsion and dispersion), a polarization energy, and a charge-transfer energy. I will discuss the following:

1) How should the so-called frozen energy be evaluated? With frozen orbitals, or should relaxation at constant density be included? If so, with any other constraints? How do these choices affect chemical conclusions?

2) How should the dispersion, permanent electrostatics and Pauli repulsion contributions to the frozen energy be disentangled? Can this be done in a fully quantum manner? If so, how do the results differ to so-called classical electrostatics and Pauli repulsion?

3) The BLW-EDA and the ALMO-EDA separate polarization (i.e. induced electrostatics) from charge transfer in a way that depends on the use of atomic orbital basis sets and lacks a well-defined complete basis set limit. Can these formal limitations be lifted, and if so, how are results changed?

If time permits, I will discuss some of the interesting challenges that arise in extending successful EDAs for intermolecular interactions to described bonded interactions.

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Characterization and Identification of Molecular Electrides

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Electrides are among the most intriguing species lately discovered. These ionic compounds, postulated and synthesized by J. L. Dye [1], have electrons occupying the anionic positions of solids. They eluded room temperature stability until the group of Hosono produced $[Ca_{24}Al_{28}O_{68}]4e^{-}$, the first stable electride [2]. Thereupon, these compounds have found a plethora of applications ranging from an electron emitter [5] to a reversible H_2 storage device [6]. Despite many attempts just eleven electrides have been synthesized, only four of them being stable at room temperature [1,2,4]. Thus far, only a few studies attempted the analysis of the electronic structure of these compounds and none featured the possibility of electrides beyond the solid lattice, where the electron is hosted in an empty cavity [7] We herein provide a computational means to distinguish electrides from similar species, proving the existence of some electrides in the gas phase [8]. We also put forward a recipe to design new electrides.

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Some insights into the nature of ground and excited states from real space descriptors

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Real space descriptors are widely used in theoretical and computational chemistry thanks to their invariance under orbital transformations and their ability to capture chemical concepts independently of the electronic structure method underlying a given calculation. Within the Interacting Quantum Atoms approach,[3] atomic and inter- atomic energetic quantities may also be understood as viable indices, that considerably enlarge our descriptor toolbox. Here we show how a combined used of IQA energetic quan- tities together with other standard real space indices, like localization or delocalization measures, may be used to shed light into the nature of ground and excited states[?] of simple molecules.[?]

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“Is conceptual chemistry ready to work on open systems?”

Andreas Savin

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The maximum probability domains (MPDs) define a region of space for which the probability to find a given number of particles is maximal. They were applied mainly to electronic systems, and showed a good agreement with the intuitive pictures of chemistry for the ground state of an isolated system. One may ask, however, what happens if this system interacts with an external field.

Only very simple systems will be analyzed. After a short formalization of the problem, and a presentation of an example of an MPD for an excited state, it will be shown how the MPDs evolve in time. Also, a simple example will show how the role of boundary conditions becomes less important, as the size of the system increases: different forms of embedding produce similar results.

The Hidden Physics Behind the Periodic Table and New Aspects of Valence, Oxidation State and Charge and Correlation Numbers

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Periodic Tables (PT) of Elements were first invented in the 1860s.[1] The break-through came with Meyer's curves of elemental properties (e.g. atomic volume) *vs* atomic weight, showing pronounced peaks from halogens to alkali metals. Since Bohr's explanation of the atomic shell structure in the 1920s, 'all' textbooks note the periodicity with respect to the filled p^6 noble gas (Ng) shells. Some chemists wonder why filled shells s^2 of the alkaline earth metals, or d^{10} of Ni, Pd, Pt, Ds do not behave like Ng shells. Now we know the reason. (i) The core electron shielding effect increases with the valence electron's angular momentum ~ ℓ^2, resulting in large AO energy gaps just above the 1s and 2p to 6p NG shells. (ii) The AO energies and their order vary with nuclear charge and ionic charge for different valence ℓ values in characteristic manners.[2]

The first PTs were ordered according to the highest valence or oxidation numbers, which caused problems for what we now call the later d and f elements. For the atoms from the middle of the PT (for instance Fe, Co, Ni, Cu and their heavier homologs) it costs much energy to fully ionize the valence shell, which cannot always be compensated by ionic counter-ions attraction and covalent AO-overlap stabilization. According to the balance of these three energy contributions, the highest valence and oxidation numbers at first increase along the periods, then decrease and then increase again.[3-7]

Depending on the AO overlap values, the amount of covalence and its character may change quite a bit. We discuss the Fe·4O isomers. Unexpectedly though with reason, open shell $[Fe^{II-V}]$ – open shell $[O^{1-½}]$ species can be better approximated by single-particle models (including DFT) than the apparently closed-shell isomer $[Fe^{VIII}\text{-}3d^0](O^{2-})_4$, which has strong open-shell spin-singlet $3d^1$-$6p^5$ bonding contributions, which are not uncommon among transition metal compounds.[8]

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Connecting hydrocarbon and boronhydride chemistries and bidimensional and three-dimensional aromaticities

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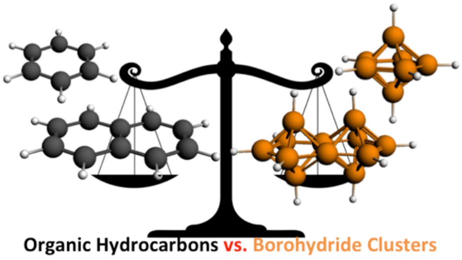
In the first part of the lecture, a link between the hydrocarbon and boronhydride chemistries will be established by showing that hydrocarbons and boronhydrides have a common root regulated by the number of valence electrons in a confined space [1]. Application of the proposed electronic confined space analogy (ECSA) method to archetypal hydrocarbons leads to well-known boronhydrides but, more importantly, it allows the design of new interesting boron-containing molecules that can be a source of inspiration for synthetic chemists. In the second part, we apply the ECSA method to archetypal polycyclic aromatic hydrocarbons (PAH) to conclude that the 4n+2 Wade-Mingos rule for three-dimensional closo boranes is equivalent to the (4n+2)π Hückel rule for bidimensional PAHs [2,3].



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Four concepts to characterize the mechanisms of chemical reactions

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Chemical change is driven by the tendency of atoms and molecules to rearrange themselves in order to maximize their thermal energy, this rearrangement takes place through a set of chemical events that drive the course of the reaction and define its mechanism. In this presentation four key concepts that permits characterize reaction mechanisms are presented, they are: ***i)*** The reaction force that defines a framework for the study reaction mechanisms by dividing the reaction coordinates into reaction regions where different mechanisms might be operating. ***ii)*** Partition of activation and reaction energies into structural and electronic contributions, this allows to describe the physical nature of activation and equilibrium processes. ***iii)*** The reaction electronic flux (REF) that permits characterize the electronic activity taking place in the course of a chemical reaction. ***iv)***. The reaction force constant that provides a fingerprint of the kinetic mode of the reaction. Illustration and discussion of these four concepts are provided with the analysis of different kind of chemical reactions such as proton transfer, adsorption on catalytic surfaces, complex rearrangements in organic chemistry, polymerization reactions, etc.

Hydrogen Bond – π-Conjugation Coupling in Enzyme Catalysis: Making "Weak Acids" Strong Proton Donors

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Enzymes can alter the acidities of specific active site residues to facilitate many valuable reactions, but how Nature achieves this remains elusive. For example, imidazole (pKa = 14) and phenol (pKa = 10) (the side chains of neutral histidine and tyrosine) are considered to be "weak acids," but act as the general acid catalyst in the triosephosphate isomerase (TIM), citrate synthase (CTS), photoactive yellow protein (PYP), and ketosteroid isomerase (KSI). We show that "H-bond–π-conjugation coupling"[1,2] may increase the proton donating abilities of imidazole and phenol at these enzyme active sites. Strongly electrostatically-stabilized H-bonding interactions can polarize the ring π-electrons of imidazole and phenol, increase their π-conjugation energies, and stabilize the corresponding residue-substrate complexes by 10-20 kcal/mol, beyond the inherent electrostatic interactions present. Block-localized wavefunction computations document the energetic impact of this cooperative effect in several model enzyme-substrate systems and other biologically relevant H-bonded heterocycles.

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Contributed Talks Abstracts

On the topology of the reduced density gradient

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Non-covalent interactions (NCI) play a key role in many areas of science, ranging from biochemistry to condensed matter. In this regard, the NCI index, has come up as a new tool to identify and characterise weak interactions of various strengths as chemical intuitive reduced density gradient (RDG) isosurfaces that reveal both stabilising (hydrogen bonding and van der Waals interactions) and destabilising interactions. The success of the NCI index rests on the nature of RDG, which is closely connected to kinetic energy densities, and may be understood as an indicator of the bosonic character of a chemical systems. Therefore, not only NCI, but also covalent interactions may be visualised as RDG isosurfaces .This unique feature makes RDG a promising tool for developing a universal chemical bond indicator that encompasses all interaction types. Beyond qualitative analysis, the electron population of NCI isosurfaces are in good agreement with the hydrogen bonding potential energy surfaces. Recently Saleh found a good linear correlation between stabilising energies and kinetic energies integrated on the main NCI isosurfaces. These results empirically connect the topology of RDG with energetics.

In this work we analyse the topology of RDG for several chemical representative systems, such as N$_2$, F$_2$, H$_2$O, ethanediol or the ferrocene dimer among others, and we tryto connect it with energetics.

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Group and fragment electronegativities from constrained SCF methods

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Constrained SCF computations are used to include additional restrictions to the energy minimization procedure in electronic structure codes. The effect of constraining the electronic population in one or more atoms, or even fragments, leads to an additional term in the Euler-Lagrange equations. This additional terms can be interpreted as an attracting/repulsive potential located around the constrained sites and it modifies the molecular electron distribution. Previously it has been shown that electronegativity equalization parameters can be obtained by restricting the Mulliken's population in the atoms of a molecule. In this work, constraints are applied to functional groups in a molecule and to molecules in hydrogen-bonded simple complexes. Group and fragment electronegativies can be directly obtained, but a new model is needed to get the value of the other parameters.

When two is better than one: the seniority scheme as a new tool to build wave functions

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Strong quantum correlation is one of the unsolved problems of electronic structure theory. It was recently observed [1] that the seniority scheme offers a much better partitioning of the Hilbert space than the conventional particle-hole scheme to capture strong static correlations. This scheme organizes the electron configurations into electron pairs, rather than in single-particle excitations on top of a reference state. It was found that full Configuration Interaction (fCI) calculations limited to the fully paired space only (or Doubly-Occupied Configuration Interaction), were able to describe bond-breaking processes with very high accuracy. Unfortunately, as a fCI method, the computational scaling of DOCI remains exponential, and hence impractical for large systems.

The mean-field picture associated with electron pairing is known as the theory of Antisymmetric Product of Interacting Geminals[1] (APIG). This ties in with the intuitive Lewis picture of chemical bonding, however the exponentially scaling computational cost of an APIG wavefunction hardly trumps DOCI. A recent breakthrough in APIG theory came with the connection with Richardson-Gaudin (RG) integrable systems [2, 3], in which we have identified a new family of APIG states with mean-field like computational cost and the same accuracy as DOCI.

In this presentation, I will discuss recent progress on the seniority scheme, APIG theory and its connection to Richardson-Gaudin integrability.

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[1] Geminus: [Latin] double, paired (substantive) one who is a twin.

Beyond the three state ensemble model, Chemical Reactivity Theory for the general case

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The ensemble model composed by the three nearest fundamental states has constituted the fundamental framework in the development of practical calculation schemes for the conceptual chemical reactivity descriptors [1]. For example, the working equations of the electronic chemical potential and the Fukui function, have been formulated in this way. Therefore, in the vast majority of the studies, it is implicitly considered that the excited neither the highly ionized electronic states contributes to the chemical reactivity of the electronic systems. To our knowledge, there is no a formal exploration about the situations in which such species can contribute to the conceptual chemical reactivity indexes, neither to the amount of such contributions.

In the present study we make a systematical analysis about the contributions coming from both the highly ionized as well as the excited electronic states, to the chemical reactivity of the species by working in the framework of the Grand Potential as unique functional of the equilibrium electron density at finite temperatures. In the first stage, we have developed the analytical working equations for the most widely used chemical reactivity response functions, the electronic chemical potential, the Fukui function and the global, local and linear softness, considering the general case of an ensemble constituted by any number of fundamental and excited states with different number of electrons. Consequently, we build several ensemble models constituted by different numbers of fundamentals and excited states, in order to evaluate the contribution of each of these states to the electronic chemical potential and the Fukui function using the Copper atom as a representative example.

Regarding the softness based reactivity functions, we found that these descriptors display a divergent behavior for some values of the electrons number at low temperatures (as room temperature) [2, 3]. Nevertheless, using our formulation, conjunctly with the extension of some of the well-known relationships between these reactivity indexes to the non-zero temperature condition previously reported by us [2], we are providing new insights about how these descriptors can be used in practice without invoking to any of the widely used interpolation schemes in the electrons numbers [3].

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Application of Charge Sensitivity Analysis to Improve the Accuracy of the Fragmentation Based Methods of Electronic Structure Calculations

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Huge progress in computer technology brings about conditions for *ab initio* computational methods to be of practical value in chemistry, biochemistry and material science. However, the application of Hartree-Fock (HF), Kohn-Sham (KS), and post-HF computational methods to huge molecular systems is limited due to undesired scaling behavior. The expense of a given method is usually expressed as βN^{α}, where N, α, and β are the number of basis functions applied in the calculations, scaling exponent, and scaling prefactor, respectively. In this presentation we would like to describe the elongation (ELG)[1] and elongation/cutoff (ELG/C)[2,3] methods and their scaling behavior.

The ELG and ELG/C methods belong to fragmentation techniques. They are based on concept of locality and take into account the sparsity of HF and KS matrices in regionally localized molecular orbital basis sets.[1,4] In this presentation, a recent progress in ELG (ELG/C) method is summarized.[2,5] Namely, a simple way of including long-range polarization into ELG (ELG/C) methods is presented. The modified ELG method includes a simplified electrostatic field resulting from point-charge distribution of the system's environment.[6,7] The field attenuates during the ELG process to eventually disappear when the final structure is reached. The point-charge distributions for each ELG step are obtained from Charge Sensitivity Analysis (CSA) in force-field atoms resolution.[8,9] The presence of the intermediate field improves the accuracy of ELG calculations. The errors in total energy and its kinetic and potential contributions are reduced by at least one-order of magnitude.

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Towards the first theoretical scale of the trans effect in octahedral complexes

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The Dual Descriptor [1] is one of the local reactivity indicators defined in the density functional theory of chemical reactivity[2,3]. It is mathematically defined as the second derivative of the electron density with respect to the number of electrons:

$$f^{(2)}(r) = \Delta f(\vec{r}) = \left(\frac{\partial^2 \rho(\vec{r})}{\partial N^2}\right)_{v(\vec{r})} = \left(\frac{\delta \eta}{\delta v(r)}\right)_N$$

It has been shown that its sign is an indicator of the electrophilicity/nucleophilicity of a reactive site within a molecule [4,5]. This feature has been extensively applied in organic chemistry [6,7].

Very recently, new physical bases have been given to the DD [8] by expanding the electron density of a perturbed ground state through excited densities [9]. Besides, an efficient algorithm has been proposed to partition real space into domains of univocal reactivity and to accurately characterize their properties [10]. The main goal of this talk is to present these new tools as well as their applications.

More precisely, part of the talk will focus on the trans effects in octahedral complexes. It will be shown that it can primarily be related to differences in the ability, for a given ligand, to cede electron density to the metal cation under the influence of the ligand on the trans position. Using the DD and its counterpart in the Grand-Canonical ensemble, a set of representative octahedral complexes has been investigated. A numerical trans-effect scale is finally proposed that retrieves the experimental trans orienting series [11].

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Towards reliable electron dynamics across molecular wires and nanostructures

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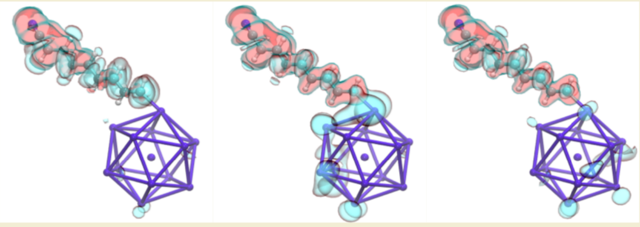
Relative density function $\delta\rho(t) = \rho(t) - \rho(0)$ of Na_{13}-$(C_2H_2)_4$-CN



t = 0.5 fs t = 5.0 fs t = 6.0 fs

Red: depletion of e^- density Cyan: gain of e^- density

Accurate first-principles modeling of electron dynamics is a challenging area of research. To follow the dynamics of molecular electronic density one has to solve the time-dependent electronic Schrödinger equation (TDSE). Straight-forward extensions of common quantum chemistry methods to the time-dependent domain reveal density functional theory (DFT), or even the coupled cluster theories to be extremely unsuited for this purpose. In a series of studies, we have demonstrated linear equations of motions to be one of the fundamental requirements to reliably model electronic wavepacket dynamics, or coherent controlled state-to-state excitation. To this end, we have developed one of the most efficient implementations of the time-dependent configuration-interaction (TDCI) methodology to solve the TDSE. Our implementation has been successfully applied to follow the electron transport across molecular wires and nanostructures terminating in a small metal cluster or a model gold surface. When combined with imaginary time propagation, or other variational schemes TDCI can be utilized also to perform time-independent task of computing the bound states. The present talk will provide an overview of the TDCI methodology and summarize the results of some recent applications.

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Qualitative Insights into Molecular Transmission: A Curly Arrow Approach

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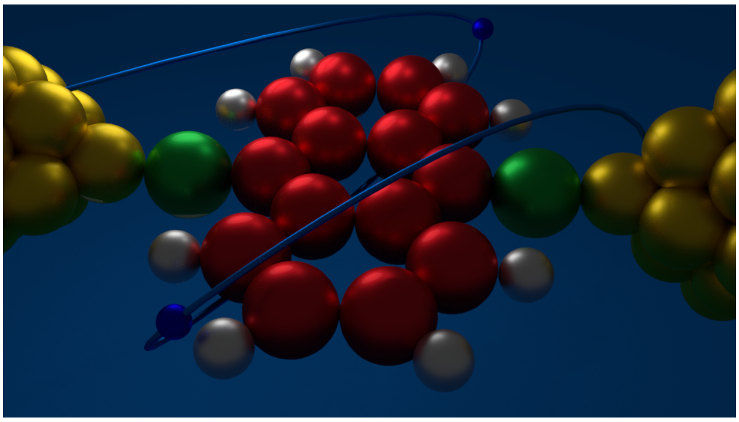
Over the past decades, the amount of research in the field of molecular electronics soared.[1] An ever-increasing number of experimental[2] and theoretical papers[3] have been published, studying the transport properties of organic molecules containing π-conjugated systems under small bias and considering possible applications for the resulting molecular electronic devices. Most of the theoretical calculations in these studies were performed at high level of theory, but such calculations do not always lead to simple, e.g. pictorial, insight. In response, the advances in the field have inspired the formulation of several simple rules to rationalize the experimental results and to obtain chemical insight into the relationship between molecular structure and transmission and the presence/absence of quantum interferences.[3]

In order for these rules to be valid, the following conditions have to be fulfilled: (i) Only a small bias is applied (ii) The Fermi level of the metal contacts is located in between the HOMO and the LUMO of the isolated molecule (iii) A tight-binding (or Hückel) approach is suitable for the studied molecule (iv) The interaction between contacts and molecule is weak.[4]

These conditions are satisfied in most experimental studies in the field of molecular electronics up to date.[1,2,3] In the presented work, a new selection rule for molecular transmission is derived, based on curly arrow drawings in the Lewis structures of the considered molecules. The use of curly arrows opens up a connection to the widely used concept of resonance effects in organic chemistry. This new selection rules bridges the gap between transmission conductance and reactivity.



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Electron density and reactivity: A synergetic DFT-CDFT-QTAIM approach

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The electron density is a cornerstone both in experimental and theoretical chemistries since it contains, by virtue of the first Hohenberg-Kohn theorem, all information required to determine the properties of any ground state system. Two challenges are actually underlying this real space function: its accurate determination and its interpretative analysis.

The first one can be achieved using Density Functional Theory (DFT), while the second issue, related to the extraction of descriptors that are chemically relevant, can be tackled from the complementary conceptual DFT (CDFT)[1] and atoms-in-molecules (QTAIM)[2] theories.

We will at first show how a synergetic DFT-CDFT-QTAIM approach, based on a fruitful dialogue between these three frameworks sharing the same founding ingredient, leads to the conception of mixed DFT-QTAIM[3], CDFT-QTAIM[4], and DFT-CDFT[5] descriptors, which are able to quantify the intrinsic reactivity propensities of reactants[6] and to describe the interactions they establish along the reaction path, accounting for the outcome of a given chemical process and the height of the associated activation barrier.

We will finally illustrate the usefulness of these tools on real life organic chemistry reactions designed in our collaborators' laboratories[7].

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Constructing complete non-covalent force fields based on ab initio monomer densities

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When atomistic force-field simulations involving new porous materials or new ligands are carried out, carefully tuned non-covalent force-field parameters are not readily available. To avoid the expensive and daunting refinement of such parameters, it is common to take them from relatively old models, such as UFF or MM3. Recently, it was shown how one can refine such parameters using Symmetry-Adapted Perturbation Theory (SAPT) computations on a set of model dimers[1]. However, SAPT computations are still expensive and not simply applicable to large molecular systems. Furthermore, SAPT is not very accurate for short intermolecular distances[2].

In this work, we propose an efficient protocol to derive reliable non-covalent force fields from the ab initio densities of the isolated monomers involved[3]. These ab initio densities are typically obtained using Density Functional Theory. The first step of the procedure consists of an Atoms-in-Molecules (AIM) analysis with the Minimal Basis Iterative Stockholder method[4], which also yields a model of the valence electron density in terms of atom-centered Slater functions. In the second step, a van der Waals potential (for the Pauli, dispersion and induction interactions) is extracted from the partitioning data. The Slater functions and atomic charges are used directly to model the electrostatic interactions, including the penetration effect. Remarkably, the charge-transfer interaction is approximately proportional to the overlap of the same Slater functions, with a proportionality constant that is rather universal, i.e. the same for different types of molecular dimers. In the same vein, the model valence electron density is used to construct dispersion and Pauli repulsion terms. This finally leads to a force field with only 5 universal parameters that still need to be determined once and for all.

The proposed method was tested on the S66x8 database[5] of dimers. SAPT calculations were used to ensure physical parameters that reproduce the different components of the interaction energy correctly. After a final refinement of the parameters with respect to CCSD(T)/CBS reference energies, our force field shows an RMSD of less than 1kcal/mol with respect to these high-quality CCSD(T)/CBS values.

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Constrained CI calculations to investigate charge transfer and the effects of the integer nature of the electron

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A method is presented for constrained wave function calculations. This is done by adding a Lagrangian multiplier to the non-relativistic quantum chemical Hamiltonian. Results are shown for a set of constrained CI- calculations that impose different Mulliken charges on atoms of the NO^+ and BeH_2 molecules. Particularly interesting are the constrained full con- figuration interaction (FCI) calculations on strongly stretched molecules and atoms separated by an infinite distance. These calculations reveal derivative discontinuities of the energy and jumps of the chemical po- tential caused by the integer nature of electrons, those results provide a direct computational proof of the piece-wise linear behavior of the energy for fractionally charged atoms without the use of ensembles as predicted by Perdew et. al. [1]. It is shown how infinitesimal perturbations of the Hamiltonian can cause major changes in the electron density of the wave function. Improved understanding of those effects can lead to an extra criterion for the validation of new functionals for density functional theory (DFT), and other approximative methods. As an example several truncated CI methods are compared with the FCI results. It is shown that configuration interaction with single and double excitations from a reference (CISD) fails completely for the description of charge transfer at large bonds. This is in contrast with the doubly occupied configuration interaction (DOCI) wave function, which provides a qualitatively correct description of charge transfer, and a chemical potential which is quanti- tatively closer to the exact one.

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Poster Presentations Abstracts

Maximum Probability Domains

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The Lewis model of the chemical bond treats electrons as discrete pairs, localized in a certain region of space. On the other hand, the molecular orbital approach to quantum chemistry considers electrons as delocalized over the entire space. Many new ways to ex- tract Lewis-structural information from the wave function have been suggested, providing links between quantum and traditional chemistry.

One of these novel approaches is the use of maximum probability domains (MPDs) [1, 2]. This method statistically localizes electrons in domains, by determining those regions of 3D space for which the probability of finding a given number of electrons is maximal. This method has successfully been applied to interpret covalent and ionic bonding [3, 4]. However, MPDs have not yet been characterized by other chemical descriptors, which leaves their links with other conceptual quantities ill described. Furthermore, MPDs obtained from current implementations suffer from numerical inaccuracy, which clouds their properties [5].

In this poster, I will formulate the theory of MPDs for the Hubbard model in terms of projection operators. I will propose a fast MPD analysis procedure, which I will use to analyze numerical results for the Hubbard model. I will also present novel algorithms that can be used to obtain MPDs in real space efficiently and with improved numerical accuracy.

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On the topology of the reduced density gradient

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Non-covalent interactions (NCI) play a key role in many areas of science, ranging from biochemistry to condensed matter. In this regard, the NCI index, has come up as a new tool to identify and characterise weak interactions of various strengths as chemical intuitive reduced density gradient (RDG) isosurfaces that reveal both stabilising (hydrogen bonding and van der Waals interactions) and destabilising interactions. The success of the NCI index rests on the nature of RDG, which is closely connected to kinetic energy densities, and may be understood as an indicator of the bosonic character of a chemical systems. Therefore, not only NCI, but also covalent interactions may be visualised as RDG isosurfaces .This unique feature makes RDG a promising tool for developing a universal chemical bond indicator that encompasses all interaction types. Beyond qualitative analysis, the electron population of NCI isosurfaces are in good agreement with the hydrogen bonding potential energy surfaces. Recently Saleh found a good linear correlation between stabilising energies and kinetic energies integrated on the main NCI isosurfaces. These results empirically connect the topology of RDG with energetics.

In this work we analyse the topology of RDG for several chemical representative systems, such as N$_2$, F$_2$, H$_2$O, ethanediol or the ferrocene dimer among others, and we tryto connect it with energetics.

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Electronic Structure and Thermochemical Parameters of the Silicon-Doped Boron Clusters B_nSi, with n = 8–14, and Their Anions

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Keywords: boron clusters, silicon-doped boron clusters, aromaticity, ring current

We performed a systematic investigation on silicon-doped boron clusters B_nSi (n = 8–14) in both neutral and anionic states using quantum chemical methods. Thermochemical properties of the lowest-lying isomers of $B_nSi^{0/-}$ clusters such as total atomization energies, heats of formation at 0 K and 298 K, average binding energies, dissociation energies, etc. were evaluated by using the high accuracy G4 method. The growth pattern for $B_nSi^{0/-}$ with n = 8−14 is established as follows: i) $B_nSi^{0/-}$ clusters tend to be constructed by substituting B-atom by Si-atom or adding one Si-impurity into the parent B_n cluster with n to be even number, and ii) Si favors an external position of the B_n framework. Our theoretical results reveal that B_8Si, B_9Si^-, $B_{10}Si$ and $B_{13}Si^-$ are systems with enhanced stability due to having high average binding energies, second-order difference in energies and dissociation energies. Especially, by analyzing the MOs, ELF, and ring current maps, the enhanced stability of B_8Si can be rationalized in terms of a triple aromaticity.

Hydrogen production in [NiFe] hydrogenases and related biomimetic systems: Similarities and differences

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The [Ni(bdt)(dppf)][1](bdt = 1,2-benzenedithiolate, dppf = 1,1´-bis(diphenylphosphino)ferrocene) [$Ni^{II}L$]-catalyzed hydrogen formation proceeds through an ECEC pathway. The catalytic cycle involves intramolecular proton transfer from bdt sulfur to the metal center. The nickel center experiences multiple co-ordination environments during catalytic process and the large P-Ni-P bite angle of dppf ligand supports this change in the co-ordination environment. The change of the ligand from dppf to dppe results in shorter P-Ni-P bite angles and the resulting complex fails to survive the change in co-ordination environment around Ni-center, in-line with the experimentally observed lack of catalytic activity.

A comparative study between the Ni-centers of [$Ni^{II}L$], [NiFe] hydrogenase[2] and a structural mimic from the Ogo group[3] reveals that the ligand field plays a dominant role, in particular for the directionality of hydrogen evolution. Formation of a M-η^2-H_2 adduct is the first step for reversible hydrogen oxidation by [NiFe] hydrogenase. The low-spin, square-planar d^8 Ni-center in [$Ni^{II}L$] with a filled $d_z{}^2$ orbital prohibits η^1 and η^2 binding of H_2 along the axial direction, and in the case of proton reduction leads to immediate dissociation of H_2 following its formation from a di-hydride intermediate, giving rise to unidirectional catalytic activity of [$Ni^{II}L$] towards production molecular hydrogen.

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When two is better than one: the seniority scheme as a new tool to build wave functions

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Strong quantum correlation is one of the unsolved problems of electronic structure theory. It was recently observed [1] that the seniority scheme offers a much better partitioning of the Hilbert space than the conventional particle-hole scheme to capture strong static correlations. This scheme organizes the electron configurations into electron pairs, rather than in single-particle excitations on top of a reference state. It was found that full Configuration Interaction (fCI) calculations limited to the fully paired space only (or Doubly-Occupied Configuration Interaction), were able to describe bond-breaking processes with very high accuracy. Unfortunately, as a fCI method, the computational scaling of DOCI remains exponential, and hence impractical for large systems.

The mean-field picture associated with electron pairing is known as the theory of Antisymmetric Product of Interacting Geminals[1] (APIG). This ties in with the intuitive Lewis picture of chemical bonding, however the exponentially scaling computational cost of an APIG wavefunction hardly trumps DOCI. A recent breakthrough in APIG theory came with the connection with Richardson-Gaudin (RG) integrable systems [2, 3], in which we have identified a new family of APIG states with mean-field like computational cost and the same accuracy as DOCI.

In this presentation, I will discuss recent progress on the seniority scheme, APIG theory and its connection to Richardson-Gaudin integrability.

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IR and Raman phonon frequencies in Transition Metal Dichalcogenides (TMDC) heterostructures

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Unlike graphene, TMDC monolayers (e.g MoS_2, $MoSe_2$ WS_2 and WSe_2) have a direct band gap [1, 2] and spin and valley degrees of freedom [3]. This make them very attractive for applications as transistors, in optoelectronic, spintronic and valleytronic. Nowadays, in multilayer, the band gap becomes indirect and the spin and valley degrees of freedom are inaccessible to encode and manipulate informations [1]. Nevertheless, the van der Waals stacking of different TMDC offers new possibilities [4]. The TMDC heterostructures have on one hand the remarkable properties of monolayers and on the other hand new properties like interlayer exciton [5].

Raman spectroscopy is one of the main characterization tools for the study of TMDC and their heterostructures [6]. The vibrational properties may also affect device performance through electron-phonon interactions. The aims of this research are the modelisation of phonons fréquencies, vibrational properties and Raman spectra in TMDC heterostructures. We also focus on influence of different parameters like stacking and strain. We have studied the heterobilayer $MoS_2 - WS_2$.

In order to do so, we have used electronic structure calculation with plane wave DFT and phonon calculation with DFPT. DFT and DFPT calculations were performed using Quantum Espresso package [7].

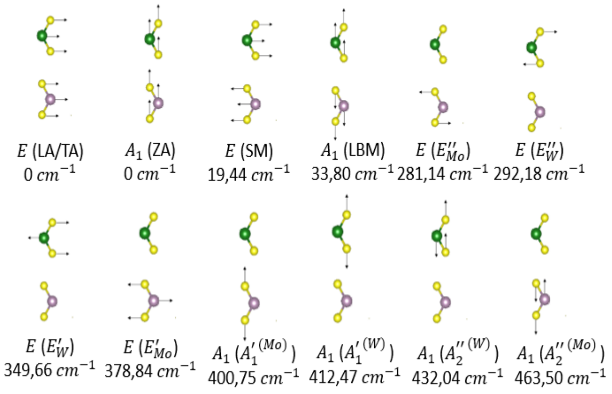

Figure 1: Normal modes at Γ of heterobilayer $MoS_2 - WS_2$; *Top layer:* $\boldsymbol{WS_2}$*, bottom layer:* $\boldsymbol{MoS_2}$

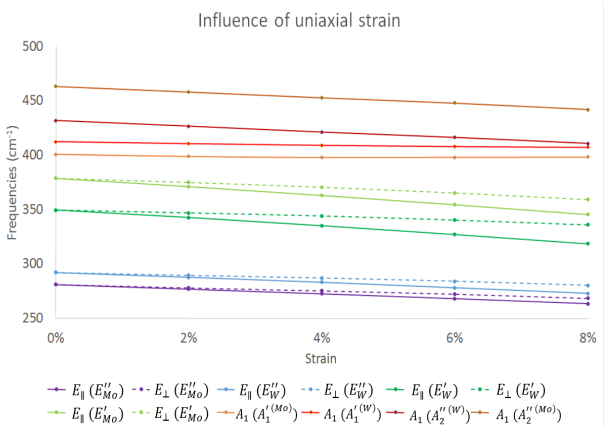

Figure 2: Influence of uniaxial tensile strain on frequencies of heterobilayer $MoS_2 - WS_2$ normal modes

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Energy Extrapolation using Local Range-Separation

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Prediction of reaction rates and chemical equilibria requires computation of very accu- rate energies, with errors no larger than a few kJ/mol at room temperature. It is difficult to systematically achieve this accuracy with existing computational methods. For example, methods that use a single Slater determinant as a wavefunction cannot directly describe electron correlation. Subsequent corrections by using additional Slater determinants fail to reproduce the exact wavefunction at short interelectronic distances unless enormous (and computationally inaccessible) basis sets are used. This is especially true of multireference methods like CASSCF and DMRG, which despite their extreme computational expense fail to describe dynamic electron correlation. One way to address these issues is to use R12/F12 methods to analytically describe the behavior of the wavefunction when electrons are close together. These approaches, however, require the evaluation of additional many- electron integrals, leading to considerable mathematical complexity and/or computational expense [1].

We propose an alternative, systematic way to describe the contributions from small interelectronic distances and to approach the basis-set limit without enormous basis sets. The electron-electron interaction is separated into short-range and long-range pieces [2]. The short-range piece is treated using a density functional model for the electron-electron cusp (like R12/F12 theory) and the on-top density (the probability of having two opposite- spin electrons at the same place, which is normally not directly modeled in R12/F12 methods) [3]. The long-range behavior is treated using an accurate wavefunction method. To obtain more accurate results with this approach, we can use a local range-separation parameter (as opposed to the usual global parameter), so that regions near the atomic nuclei are treated qualitatively differently than valence regions. In addition, exact re- sults (independent of the choice of basis set, the choice of density functional, and the choice of range-separation procedure) can be obtained by extrapolating the results of our calculations to the non-range-separated basis-set-limit full-CI result.

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Variational Approach to Hirshfeld Partitioning

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It is common to use the electron density to partition a molecular system into atomic regions. The necessity for such a partitioning scheme is rooted in the unquestionable role of atoms in chemistry. Nevertheless, atomic properties are not well-defined concepts within the domain of quantum mechanics, as they are not observable. This has resulted in a proliferation of different approaches to retrieve the concept of atoms in molecules (AIM) within the domain of quantum mechanics and *in silico* experiments based on various flavors of model theories.

One of the most popular families of models is the Hirshfeld, or stockholder, partitioning methods. Hirshfeld methods do not produce sharp atomic boundaries, but instead distribute the molecular electron density at each point between all the nuclear centers constituting the molecule [1, 2]. The various flavors of the Hirshfeld scheme differ mainly in how the atomic shares are computed from a reference promolecular density and how the reference promolecular density is defined [3-7].

We have developed a variational version of Hirshfeld partitioning method. The key idea in our approach is that we find the promolecular density that resembles the true density as much as possible. Then, using the information-theoretic approach to Hirshfeld partitioning [2], Hirshfeld-type atoms are retrieved by minimizing the information loss during the molecule formation. Our method has been tested on data sets of small drug-like molecules, inorganic compounds, and transition metal complexes. Atomic charges from our method accurately model molecular electrostatic potentials. Compared to other flavors of Hirshfeld analysis, our method performs better when dealing with highly charged atoms.

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Interaction of the first trans-membrane segment of NS2 protein with a popc lipid bilayer

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Non-structural protein 2 (NS2) plays a crucial role in hepatitis C virus (HCV) assembly. It has been supposed that NS2 is composed of three transmembrane (TM) segments. Molecular dynamics simulations is applied to investigate the position and orientation of the first transmembrane segment (TM1) as well as the interaction of TM1 with a zwitterionic POPC lipid bilayer, identifying several key residues that stabilize the position of TM1 within the membrane. The results reveal that TM1 induces the ordering of lipid and does not destabilize the lipid bilayer system. The hydrophobic mismatch in which the segment tilts an angle along the membrane normal is observed in this system. Free energy profile of TM1 in the membrane is also calculated and analyzed.

Modelling of the excitonic states of silicon quantum dots through DFT & TD-DFT methods.

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The potential applications of quantum dots (QDs) are numerous. Two of them are of particular interest to the future of computer technology: the single electron transistor and the use of exciton states for quantum computing. In both cases, the intervention of an external electromagnetic field is required and adds to the complexity of a theoretical model. The goal of this work is to understand the electronic dynamics of silicon QDs through the use of quantum control, i.e. the use of complex electromagnetic pulses to control phenomena at the pico- or even femtosecond time scale. This will for example allow us to populate a dark excitonic state like we did for dark vibrational levels in acetylene [1].

The first step of this work involves getting knowledge of the structural variables of interest for our system: excitonic levels, transition dipole moments, coupling matrix elements, etc. In order to do so, we use DFT and TD-DFT methods, both with atomic basis sets and plane wave basis set for the sake of comparison.

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Quantitative redox potentials from conceptual DFT charge transfer models

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The importance of redox reactions in biological processes, industry and in chemistry in general can hardly be overestimated. This, and the fact that they are often difficult to study experimentally, has motivated the search for theoretical tools to dissect them. Among the most popular techniques used today to study chemical reactions we have conceptual density functional theory (DFT),[1] which has proven of great success in rationalizing general acid-base reactions (e.g. charge transfer-driven reactions). However, even when redox reactions are classical examples of charge transfer processes, there have been only a few attempts to analyze them using conceptual DFT.

In this work we discuss previous attempts to predict redox potentials within conceptual DFT.[2] We show why these methods, despite their seemingly different characteristics, give very similar results. Then, we proceed to analyze the role of electronegativity in redox reactions, starting with a general discussion based on the maximum hardness principle. Afterwards, we present some quantitative models to predict oxidation potentials from the chemical potentials of the involved species. We highlight the importance of taking into account the perturbations of the molecular environment at the time of obtaining accurate results, and propose different ways to take these effects into account. Finally, we test the performance of the proposed models on a set of organic redox reactions occurring in different solvents, comprising multiple functional groups.

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Aromatic Sulfonation with Sulfur Trioxide: Mechanistic Insights from Molecular Dynamics

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Electrophilic aromatic sulfonation with sulfur trioxide is traditionally presented by a two-step S_EAR mechanism involving a s-complex Wheland intermediate. Recently, an alternative concerted pathway in apolar solvent was proposed from static calculations [1,2]. In this work, the sulfonation of benzene is studied with ab initio molecular dynamics simulations in gas phase and in explicit solvent. We investigate different possible reaction pathways, the number of SO_3 molecules participating in the reaction, and the influence of complexing and noncomplexing solvent. Our simulations confirm the existence of a low-energy concerted pathway with formation of a cyclic transition state with two SO_3 molecules (Fig. 1). The mechanism and kinetics of the reaction greatly depend on the polarity of the solvent. In addition, an alternative reaction pathway is proposed in polar solvent.

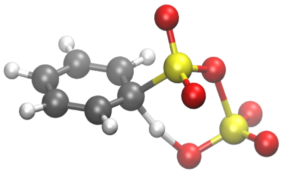

Figure 1. Sulfonation of benzene with two SO_3 molecules.

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Inverse Molecular Design of Diamondoids

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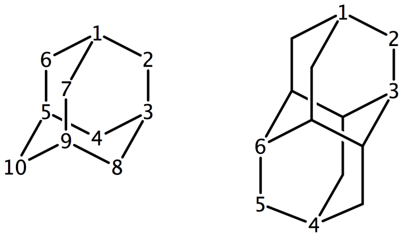
Nano-scale molecular diamonds, also called diamondoids, are cage-like hydrocarbon molecules with a diamond-like structure. They show great potential in a wide variety of electronic, mechanical and pharmaceutical applications due to their high thermal conductivity, hardness and thermodynamic stability. **[1]** These properties are strongly affected by substitution and doping.

An Inverse Design methodology **[2]** via the Best First Search algorithm **[3-5]** is applied to find modified diamondoids with improved electronic properties. In inverse design, one uses the computation of certain quantities or molecular descriptors to design molecules with an optimal target property. The design of molecules is translated to finding an optimal external potential of the system, generating a structure with the associated target property.

New compounds, based on adamantane and diamantane, i.e. diamondoids consisting of respectively 1 and 2 crystal cages (see figure), are designed with tuned band gap and ionization potential.



The structure and corresponding positions of the sites that are tuned: (a) adamantane and (b) diamantane

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Structure, Thermochemical Properties and Bonding of Earth-Alkali Mixed Silicon Trimers $Si_3M^{+/0/-}$ with M = Be, Mg, Ca

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The ground state geometries, electronic structures and thermochemical properties of earth-alkali binary alloy silicon clusters Si_3M with M = Be, Mg, Ca in neutral, cationic and anionic states were investigated using quantum chemical computations. Lowest-lying isomers of the clusters were determined on the basis of G4 energies. Along with total atomization energies, thermochemical parameters were estimated for the first time by means of the composite G4 and coupled-cluster theory with the complete basis set CCSD(T)/CBS approaches. The most favored equilibrium formation sequences for Si_3M clusters emerge as follows: all $Si_3M^{+/0/-}$ clusters are formed by attaching the M atom into the corresponding cation, neutral and anion silicon clusters $Si_3^{+/0/-}$, except for the Si_3Mg^+ and Si_3Ca^+ where the metal cations are bound to Si_3. The resulting mixed tetramers exhibit geometrical and electronic features similar to the pure silicon tetramer $Si_4^{+/0/-}$. Electron localization function (ELF) and ring current analyses point out that the σ-aromatic character of silicon tetramer remains unchanged upon substituting one Si atom by one earth-alkali atom.

Using the Non-covalent interaction index to probe H-bonding in proteins: AhpE as a case study

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Hydrogen bonds (H-bonds) in proteins are generally measured in molec- ular dynamics programs by comparing the distance between the hydrogen that is donated to the acceptor heavy atom to a set cut-off distance [1]. Although there are some variants on this, like using the distance between the donor heavy atom and the acceptor, including an angle restriction [2] or using pseudo-energetic cut-offs, they all have the same limita- tion [3]; This type of measured does not take into account the type of heavy atom that is either the donor or the acceptor.

We compared three of these methods to the newly developed non-covalent interactions (NCI) index [4] using the peroxiredoxin alkyl hydroperoxid reductase E (AhpE) [5]. The active site of these type of proteins is a thiolate cysteine. The comparison of the standard way of measuring H-bonds with the NCI index showed that when the either the acceptor or donor heavy atom changed from the standard oxygen or nitrogen atom that the methods can easily miss some important H-bonds.

As a result we adjusted the method of reference [1] so that the maximum cut-off distance between the hydrogen atom and the acceptor atom is dependent on the type of heavy atoms involved.

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Constrained CI calculations to investigate charge transfer and the effects of the integer nature of the electron

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A method is presented for constrained wave function calculations. This is done by adding a Lagrangian multiplier to the non-relativistic quantum chemical Hamiltonian. Results are shown for a set of constrained CI- calculations that impose different Mulliken charges on atoms of the NO^+ and BeH_2 molecules. Particularly interesting are the constrained full con- figuration interaction (FCI) calculations on strongly stretched molecules and atoms separated by an infinite distance. These calculations reveal derivative discontinuities of the energy and jumps of the chemical potential caused by the integer nature of electrons, those results provide a direct computational proof of the piece-wise linear behavior of the energy for fractionally charged atoms without the use of ensembles as predicted by Perdew et. al. [1]. It is shown how infinitesimal perturbations of the Hamiltonian can cause major changes in the electron density of the wave function. Improved understanding of those effects can lead to an extra criterion for the validation of new functionals for density functional theory (DFT), and other approximative methods. As an example several truncated CI methods are compared with the FCI results. It is shown that configuration interaction with single and double excitations from a reference (CISD) fails completely for the description of charge transfer at large bonds. This is in contrast with the doubly occupied configuration interaction (DOCI) wave function, which provides a qualitatively correct description of charge transfer, and a chemical potential, which is quantitatively closer to the exact one.

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Constructing complete non-covalent force fields based on ab initio monomer densities

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When atomistic force-field simulations involving new porous materials or new ligands are carried out, carefully tuned non-covalent force-field parameters are not readily available. To avoid the expensive and daunting refinement of such parameters, it is common to take them from relatively old models, such as UFF or MM3. Recently, it was shown how one can refine such parameters using Symmetry-Adapted Perturbation Theory (SAPT) computations on a set of model dimers[1]. However, SAPT computations are still expensive and not simply applicable to large molecular systems. Furthermore, SAPT is not very accurate for short intermolecular distances[2].

In this work, we propose an efficient protocol to derive reliable non-covalent force fields from the ab initio densities of the isolated monomers involved[3]. These ab initio densities are typically obtained using Density Functional Theory. The first step of the procedure consists of an Atoms-in-Molecules (AIM) analysis with the Minimal Basis Iterative Stockholder method[4], which also yields a model of the valence electron density in terms of atom-centered Slater functions. In the second step, a van der Waals potential (for the Pauli, dispersion and induction interactions) is extracted from the partitioning data. The Slater functions and atomic charges are used directly to model the electrostatic interactions, including the penetration effect. Remarkably, the charge-transfer interaction is approximately proportional to the overlap of the same Slater functions, with a proportionality constant that is rather universal, i.e. the same for different types of molecular dimers. In the same vein, the model valence electron density is used to construct dispersion and Pauli repulsion terms. This finally leads to a force field with only 5 universal parameters that still need to be determined once and for all.

The proposed method was tested on the S66x8 database[5] of dimers. SAPT calculations were used to ensure physical parameters that reproduce the different components of the interaction energy correctly. After a final refinement of the parameters with respect to CCSD(T)/CBS reference energies, our force field shows an RMSD of less than 1kcal/mol with respect to these high-quality CCSD(T)/CBS values.

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A theoretical study on charge transport of dithiolene nickel complexes

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Organic semiconducting materials play an important role in the fabrication of high performance organic electronic devices. In the present work, we theoretically designed a series of organic semiconductors based on nickel complexes. Their characteristics of charge transport were investigated using DFT computational approaches. Based on the computed results, all compounds designed are found to be excellent candidates for ambipolar organic semiconductors with low reorganization energies for both holes and electrons. The (I–V) characteristics and transmission spectra of materials show that the replacement of benzene rings by thiophene rings results in an increase of their HOMO and LUMO energy levels. HOMOs of compounds containing thiophene end-groups are likely dominant for their conductance, while LUMOs of compounds containing benzene end-groups mainly affect their conductance. The electron distribution in these frontier MOs is identified as the main reason which makes the conductance the compounds of in the first series higher than those in the later series.

Mixed defect incorporation modes for rare-earth doped SrTiO3

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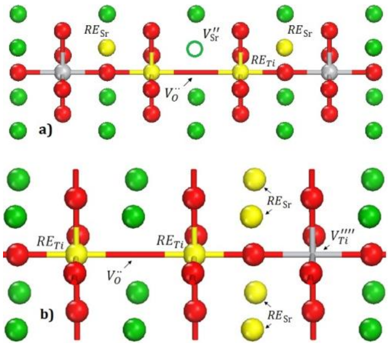
The existence of two novel rare-earth (RE^{3+}) incorporation mechanisms in cubic strontium titanate (SrTiO3) is examined using classical simulations. An overall assessment of rare-earth doping in SrTiO3 is also given. The dependence of solution, binding and final solution energies with respect to dopant ionic radii are discussed.

Similar to previous results, strong binding energies are obtained. The Ti-vac scheme is energetically preferred and it is accentuated for the dopants with large ionic radii. These mechanisms can be used during the fabrication processes of SrTiO3 ceramics to maximise the concentration of oxygen vacancies under non-stoichiometric conditions.

A comparative study of mixed schemes in cubic BaTiO3 and SrTiO3 reveals that mixed schemes could be actived in BaTiO3 rather than SrTiO3.

The figure displays the defect cluster schemes corresponding to the proposed mixed incorporation mechanisms: a) Sr-vac and b) Ti-vac. Green, grey, yellow and red spheres corresponds to Sr^{2+}, Ti^{4+}, RE^{3+} and O^{2-} ions, respectively.



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