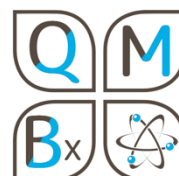




QuantumChemPhys Transborder Lab Meeting

Baiona, 28th-29th November 2024

Sponsored by:



PROGRAM

Thursday November 28th

09h45-10h15: Welcome Coffee at "Hotel Le Bayonne"

Scientific Session 1

[10h15-10h30](#): Opening

[10h30-10h50](#): 1. A. Rivero - Ab Initio Molecular Dynamics calculations on NO oxidation over oxygen functionalized Highly Oriented Pyrolytic Graphite (O-HOPG)

[10h55-11h15](#): 2. R. Bombin - Hydrogen scattering from W(110) surface

[11h20-11h40](#): 3. J. Lew Yee - Arming Natural Orbital Functional Theory to face the current challenges of quantum chemistry

[11h45-12h05](#): 4. M. Ylla - Machine Learning model for Multireference diagnostics based on Kohn-Sham energies

[12h10-12h30](#): 5. J. Grebol - Can Aromaticity be Evaluated Using Atomic Partitions based on the Hilbert-space?

12h30-14h00: Lunch at "Hotel Le Bayonne"

Scientific Session 2

[14h00-14h20](#): 6. R. Martin Barrios - Angular distribution of molecular hydrogen desorption from tungsten surface

[14h25-14h45](#): 7. M. Nguyen - Quasiparticle interference in twisted bilayer graphene

[14h50-15h10](#): 8. M. Hugget - Characterization of hyperfine interactions in high-spin state open-shell nanographenes

[15h15-15h35](#): 9. N. Vaquero - Towards implementation of ADAPT-VQE in real quantum hardware

[15h40-16h00](#): 10. L. Viaud - Dynamics of hydrogen interaction on tungsten surfaces: quantum or classical?

16h00-16h30: Coffee Break

[16h30-16h50](#): 11. A. Dellai - Second Harmonic Responses of Azobenzene-based Self-Assembled Monolayers: Effects of Chemical Functionalization

[16h55-17h15](#): 12. A. Omist - Electronic and magnetic properties of triangulene monomer and its oligomers

[17h20-17h40](#): 13. A. Cebreiro - Efficient state-interaction approach for the g-tensor analysis

[17h45-18h05](#): 14. J. Babu - Enhancing RASCI Excitation Energy Accuracy with Second-Order Perturbation Theory

[18h05-18h30](#): 15. N. Omar - Effect of H₂ Zero-Point Energy on dissociation dynamics on Tungsten Surfaces with Impurities

21h00: Diner at 'Auberge du Cheval Blanc'

Friday November 29th

Scientific Session 3

[9h45-10h05](#): 16. A. Patt - Investigation of the diffusion within clathrate hydrates by coupling DFT and Kinetic Monte Carlo

[10h10-10h30](#): 17. M. Frankerl - Substrate stabilization of Jahn-Teller distortion in a single molecule

[10h35-10h55](#): 18. A. Bejarano - Light emission from current-driven plasmonic nanocavities

[11h00-11h20](#): 19. J. Owona - Computational Insights into Room Temperature Phosphorescence of Carbazole and the Impact of Aggregation

11h20-11h40: Coffee Break

[11h40-12h00](#): 20. I. Merrit -Towards Eco-Friendly Photodetection : Molecular Design of ESIPT Molecules for Novel Capacitance Based Photodetectors

[12h05-12h25](#): 21. A. Rodriguez - Assessing the performance of a Quantum Krylov Subspace Diagonalization method

[12h30-12h50](#): 22. V. Postils - Benchmarking study of the sTD-DFT and XsTD-DFT methods to compute first hyperpolarizabilities

[12h55-13h15](#): 23. R. Boto - Electron–spin relaxation in boron–doped organic molecules

13h15 : Lunch at 'Hotel Le Bayonne' and farewell

Additional information:

- Time slots allocated for the talks are 15 minutes + questions. Please stick to your time.

Ab Initio Molecular Dynamics calculations on NO oxidation over oxygen functionalized Highly Oriented Pyrolytic Graphite (O-HOPG)

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Nitrogen monoxide (NO) belongs to the group of the most polluting gases in the atmosphere. It serves as a critical precursor for the formation of smog and acid rain, which currently pose significant environmental and human health challenges. Understanding the molecular interactions between NO and models of carbonaceous surfaces is essential for developing effective strategies to mitigate its adverse effects on the environment.

We presented here ab initio molecular dynamics (AIMD) calculations on the NO oxidation over oxygen functionalized Highly Oriented Pyrolytic Graphite (O-HOPG) surface [1]. We examined the impact of four different NO incidence energies and two orientations of incidence on the reaction. Our simulation results indicate that the probability of the oxidation reaction ($\text{O-HOPG} + \text{NO(g)} \rightarrow \text{HOPG} + \text{NO}_2\text{(g)}$) varies between 10-30 %, depending on these initial conditions. Notably, the reaction occurs even at the lowest incidence energy studied (0.025 eV) which corresponds approximately to room temperature (300 K). The angular distribution of the products and the energy losses during the reaction were also analyzed. The scattered NO molecules (non-reactive channel), lose 50-60 % of their initial translational energy and are vibrationally cold but rotationally excited. The detected NO₂ molecules share the same angular distribution as the scattered NO molecules, suggesting a swift and direct reaction dynamic for NO oxidation characterized by effective energy transfer. These findings provide important insights into the reaction mechanism of NO oxidation on activated carbonaceous surfaces, contributing to the potential development of applications to mitigate environmental pollution.

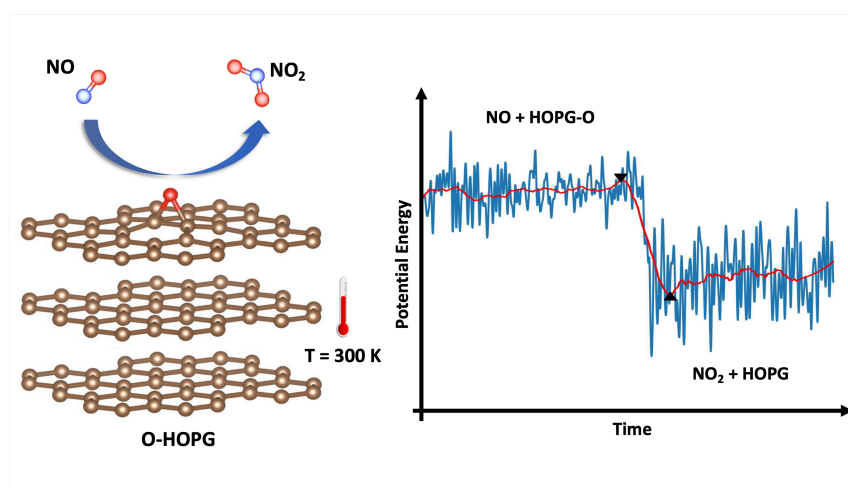


Fig.1 Left Panel: Sketch of the system studied in AIMD simulations (NO molecule impacting the O-HOPG surface). Right Panel: Time evolution of the total potential energy along a representative reactive trajectory.

References

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Hydrogen scattering from W(110) surface

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An understanding of the dynamics of hydrogen atom scattering on metal surfaces is of great importance for a number of applications, including catalysis and material science. Of particular interest is the case of tungsten surfaces, as it will be the material of plasma facing components in future fusion reactors. In this study, we investigate the scattering of hydrogen atoms on the W(110) surface, employing both classical and quantum dynamics approaches to elucidate the importance of quantum effects in this system.

The focus of this study is on several key observables, including the sticking probability and diffraction channels, which are used to characterize the scattering process. Furthermore, the vibrational excitation spectra of H atom adsorbed on the tungsten surface is studied at both the semiclassical and quantum levels. This enables the quantification of quantum effects by direct comparison with classical molecular dynamics results[1,2]

References

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Arming Natural Orbital Functional Theory to face the current challenges of quantum chemistry

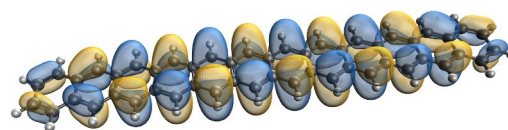
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Natural Orbital Functional Theory (NOFT) offers a framework for the development of energy functionals derived from the first-order reduced density matrix (1RDM) in the diagonal representation, that is, functionals of natural orbitals (NOs, φ_i) and their corresponding occupation numbers (ONs, $0 \leq n_i \leq 1$). In particular, the family of Piris Natural Orbital Functionals (PNOF) leverage the exact and known functional of the second-order reduced density matrix (2RDM) to build NOFs based on an approximate cumulant reconstruction of the 2RDM from the NOs and ONs. Contemporary NOFs exhibit a formal fifth-order arithmetic scaling, which can be effectively reduced to the fourth-order, thereby becoming a promising cost-effective method for challenging problems, such as multireference systems. However, the widespread adoption of NOFT has been hindered by the associated long convergence process. In this work, we present a deep learning-inspired algorithm implemented in the [DoNOF software](#) that enables efficient convergence of NOF calculations, thereby allowing for practical application to complex systems. Furthermore, we present initial findings on the efficacy of the latest NOFs within the DietGMTKN55 benchmark set, providing insights into the capabilities and potential improvements for these functionals. Finally, we conclude with a perspective on the implications of NOFT in the context of the variational quantum eigensolver for quantum computing applications.



References

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Machine Learning model for Multireference diagnostics based on Kohn-Sham energies

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Understanding molecules behavior relies on electronic structure methods, which are grouped by their ability to account for dynamic or nondynamic electron correlation effects. Accurately portraying molecular systems depends on wisely choosing a suitable electronic structure method. Specifically, when dealing with systems with predominant nondynamic correlation (known as multireference or MR), using single-reference methods can lead to major errors in describing the molecule's properties and energies. In an era dominated by the generation of extensive molecular datasets requiring computational treatment, there's a growing demand for affordable methods to identify multireference characteristics. Unfortunately, as far as we know, there are no cost-effective tools available for a quick assessment of a molecule's multireference nature.

Recently, we have conducted a thorough analysis of wavefunction theory based MR diagnostics using extensive datasets [1], identifying a single well-behaved representative metric of electron correlation that could be employed in single-reference wavefunctions. In this work, we present the extension of the multireference diagnostic to be applied in density functional theory. We used a supervised learning model to establish a map between Kohn-Sham orbital energies and the MR character of the molecule, achieving an excellent agreement with the predictions furnished by MP2 and CCSD calculations.

This work thus offers an economical approach requiring a single DFT calculation to assert the MR character of a molecular system, showcasing its potential as a cost-effective, high-accuracy solution for the detection of nondynamic correlation.

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Can Aromaticity be Evaluated Using Atomic Partitions based on the Hilbert-space?

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Aromaticity is a fundamental concept in chemistry that explains the stability and reactivity of many compounds by identifying atoms within a molecule that form an *aromatic ring*. Reliable aromaticity indices focus on electron delocalization and depend on atomic partitions, which give rise to the concept of an *atom-in-the-molecule* (AIM). Real-space atomic partitions present two important drawbacks: a high computational cost and numerical errors, limiting aromaticity measures to medium-sized molecules with rings up to 12 atoms. This restriction hinders the study of large conjugated systems like porphyrins and nanorings.

On the other hand, traditional Hilbert-space schemes are free of the latter limitations but can be unreliable for the large basis sets required in modern computational chemistry. This paper explores AIMs based on three robust Hilbert-space partitions ---meta-Löwdin,^[1] Natural Atomic Orbitals (NAO),^[2] and Intrinsic Atomic Orbitals (IAO)^[3]--- which combine the advantages of real-space partitions without their disadvantages. These partitions can effectively replace real-space AIMs for evaluating the aromatic character.

For the first time, we report multicenter index (MCI) and I_{ring} values for large rings and introduce ESipy, an open-source Python code for aromaticity analysis in large conjugated rings.^[4]

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Angular distribution of molecular hydrogen desorption from tungsten surface

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A comprehensive understanding of the angular distribution of molecular hydrogen desorption from metallic surfaces is a prerequisite for advancing our knowledge of surface reaction dynamics. It plays a pivotal role in optimising the design of catalytic processes and the development of materials for nuclear fusion applications. In this study, the angular distribution of molecular hydrogen desorption from tungsten surfaces is investigated through a theoretical approach based on the principle of detailed balance. This work concentrates on two crystallographic planes, W(100) and W(110), and examines the impact of surface temperature, isotopic variation and diverse potential energy surfaces derived from density functional theory calculations. The results demonstrate that the angular distribution is largely unaffected by variations in surface temperature (which ranged between 300 and 800 K) and isotopic effects. However, the crystallographic orientation of the surface has a significant influence on the desorption profiles, while variations in the exchange correlation functional used in the potential energy surfaces have only a minor impact.

Quasiparticle interference in twisted bilayer graphene

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Transport properties of electrons in materials are usually investigated based on the electronic dispersions and their associated topology. However, there may exist hidden mechanisms determining how electrons scatter, such as the conservation of pseudospin in graphene. Quasiparticle interference imaging is a method that provides information on how electrons scatter and is accessible via scanning tunneling microscopy experiments. Employing the kernel polynomial method, we numerically investigate the quasiparticle interference in twisted bilayer graphene. The interference spectra exhibit four scattering mechanisms with the chiral properties of possible pseudospin conservation.

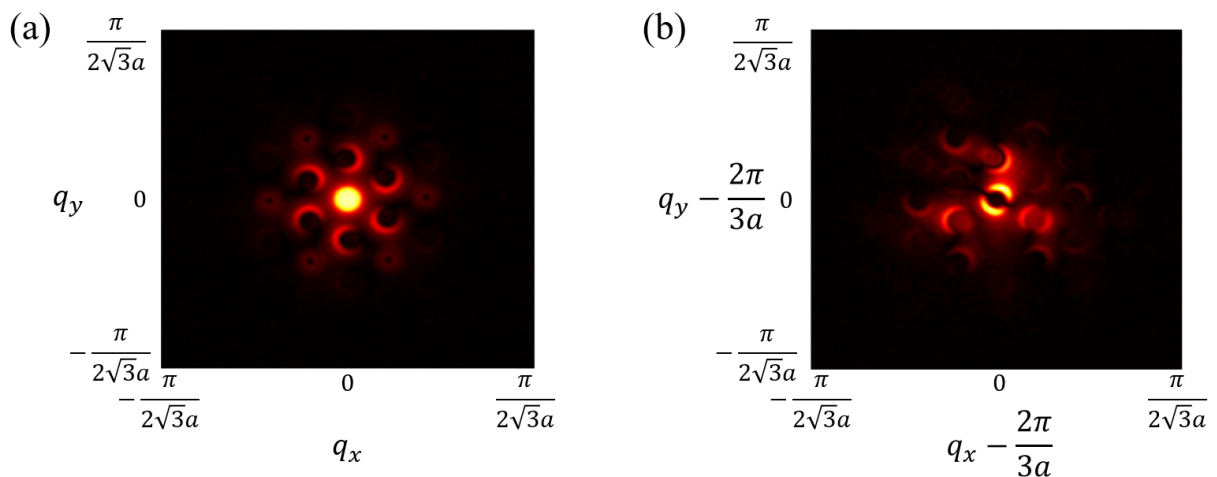


Fig. Quasiparticle interference (QPI) patterns of twisted bilayer graphene. (a) the QPI near $(q_x, q_y) = (0, 0)$, showing the intralayer intravalley and interlayer intravalley scatterings. (b) the QPI near $(q_x, q_y) = (2\pi/3a, 2\pi/3a)$, which is associated with the intralayer intervalley and interlayer intervalley scatterings of electrons. Here, a is the lattice constant of a graphene layer.

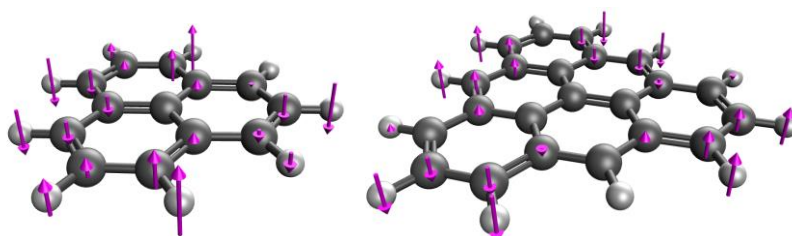
Characterization of hyperfine interactions in high-spin state open-shell nanographenes

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The π active magnetic systems have gained significant attention over recent years, particularly in the fields of spintronics [1] applied to quantum computing. Among zigzag-edged triangular nanographene molecules, phenalenyl and [3]-triangulene radical species with a high ground spin-state exhibit a spin decoherence under the fluctuations of phonon coupled intramolecular magnetic interactions [2]. More specifically the electro-nuclear magnetic moment, namely the hyperfine interaction (HFI), plays an important role in the spin relaxation. To estimate the decoherence time of such systems, a novel computational methodology is introduced to compute the electronic spin dynamics of the nanographenes based on ab-initio calculation and a second-order time-convolutionless quantum master equation [3]. The importance of the spin-vibration couplings is enlightened through the Holstein and Peierls reduced density matrix terms and reveals the key role of each normal vibrational mode symmetry. The main contribution in phenalenyl spin decoherence are the HFIs whereas in [3]-triangulene, zero-field splitting dominates and the direct spin transition is preferred over the Orbach relaxation mechanism. Finally, the dynamics of the diabatic spin states suggest long spin-coherence times in both systems, making them promising candidates for spintronics quantum technologies.



Vibrational modes of phenalenyl (left) and [3]-triangulene (right)

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Towards implementation of ADAPT-VQE in real quantum hardware

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ADAPT-VQE [1] is an algorithm within the VQE family used to calculate the ground state of a given Hamiltonian by optimizing an ansatz. This ansatz is built iteratively by adding at each iteration the excitation operator with the largest energy gradient. We propose two optimizations to enhance the feasibility of implementing this algorithm on real quantum hardware. First, we utilize natural orbitals as the basis for the excitation operators [2] and second, we combine the staircase and inverse staircase approaches to reduce circuit depth.

After applying these optimizations, we use the Qiskit package to transpile and further optimize the resulting circuits, analyzing how these modifications improve circuit quality. Finally, we execute a single-point calculation using one of the optimized circuits on an IBM quantum computer and evaluate its performance. These results provide insight into the challenges of implementing quantum chemistry algorithms on current quantum hardware.

References

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Dynamics of hydrogen interaction on tungsten surfaces: quantum or classical?

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Because of its fundamental role in natural and technological processes, surface reactivity has been intensively studied both experimentally and theoretically for decades. Currently, understanding the microscopic mechanisms in the interaction of hydrogen with the surface of tungsten is a major challenge for nuclear fusion technologies. [1]

With this in mind, we study the collision dynamics of hydrogen on tungsten via classical and quantum molecular dynamics approaches, using a multidimensional Potential Energy Surface (PES) interpolated from Density Functional Theory (DFT) energies based on the vdW-DF2 functional. [2] In particular, we focus on the sticking probability, which has been previously measured experimentally. [3] Preliminary results show a considerable improvement concerning the quantitative agreement between theory and experiment with respect to previous work [4] using the PW91 functional, [5] pointing out the decisive role of the density functional on the sticking dynamics.

We also implement quantum corrections based on semi-classical considerations to reach an agreement between quantum and classical calculations. Existing quantum corrections [6,7] have been refined to reach quantum-like accuracy from classical calculations, which lead to a deeper understanding of the physics underlying the reaction.

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Second Harmonic Responses of Azobenzene-based Self-Assembled Monolayers: Effects of Chemical Functionalization

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Light-responsive nonlinear optical (NLO) materials have raised a great interest in the development of optoelectronics. In particular second harmonic generation (SHG) allows the utilization of near-infrared wavelength conferring a non-destructive readout process. The suitability of a material for practical use in a photoresponsive NLO device is mainly conditioned by two requirements. Firstly, the molecular building blocks must show large NLO-activity in one of the form, and large contrast. Molecular photoswitches, such as azobenzene derivatives (AZOs) are promising candidates by virtue of the significant change in the response upon *trans-to-cis* photoisomerization [1]. Secondly, their spatial orientation must avoid centrosymmetric stacking. Surface functionalization with self-assembled monolayers (SAMs) [2] constitutes the most effective strategy for introducing NLO chromophores into a device in a controlled alignment and concentrations, see Figure 1a.

In this context, a mixed quantum/classical computational methodology combining molecular dynamic simulations (MD) and Density Functional theory (DFT) calculations is employed to characterize the NLO responses of SAMs functionalized with AZO derivatives bearing either electron withdrawing (NO_2) or electron donating groups (NH_2), as illustrated in Figure 1b. This computational study follows on from an earlier one [3], which aimed to rationalize the NLO responses of the SAMs characterized experimentally [4], based on non-substituted azobenzenes. Here, we explore the impact of chemical substitution of the azobenzene core on the morphology and NLO properties of the SAM.

The interfacial NLO properties have been computed in first approximation considering isolated fragments extracted from MD simulations, and therefore considering only the effect of structural fluctuations and steric interactions of individual AZO units within the SAMs. In a second step, the electrostatic contribution to the intermolecular interactions has been included in the DFT calculation by the application of a point-charge embedding surrounding the previously characterized AZO units.

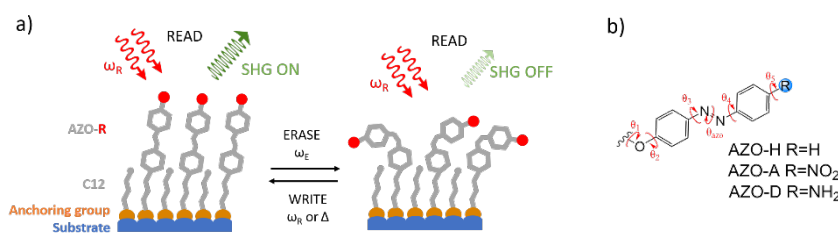


Fig. a) Representation of photoresponsive NLO-based optical memory devices incorporating SAM of AZO. b) Investigated AZO derivatives bearing a pristine azobenzene unit, AZO-H (from Ref. 3), and functionalized with electron donor ($\text{R} = \text{NH}_2$) and electron acceptor ($\text{R} = \text{NO}_2$) group, AZO-D and AZO-A, respectively.

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Electronic and magnetic properties of triangulene monomer and its oligomers

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Triangular zig-zag nanographenes, including metal-free magnetic systems such as triangulene,[1] have acquired considerable scientific attention since their theoretical conception. These compounds, possessing an inherent spin polarization,[2] emerge as promising systems holding substantial importance for innovative magnetic and electronic devices. Here, we investigate the electronic and magnetic properties of several structures including the triangulene monomer and its oligomers combining density functional theory (DFT) and wavefunction correlated methods. We evaluate magnetic couplings, spin-polarization energies and spin Hamiltonian parameters and discuss the of the suitability and limitations of the different methods employed. Moreover, the computed properties are rationalized through the analysis of molecular orbital diagrams, fractional occupation densities and natural transition orbitals between ground and excited states. We further describe these systems by means of spin localized states by diabating spin-adapted eigenstates of the molecular electronic Hamiltonian using the spin permutation operator. This decomposition enables the evaluation of spin exchange couplings. By combining this new spin diabatisation scheme with a variety of electronic structure calculations, we provide a clear framework that improves the understanding of spin interactions in triangulene compounds.

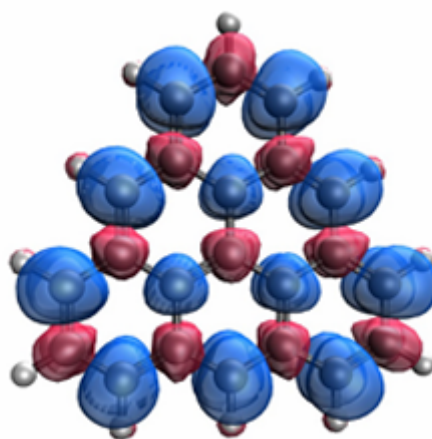


Figure 1. Spin density of a triangulene.

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Efficient state-interaction approach for the g-tensor analysis

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The g-tensor (also expressed as g-shift Δg) is a magnitude that parameterizes the Zeeman effect, involving the interaction of the spin magnetic moment with a magnetic field. It provides significant information about the environment of unpaired electrons.

In this talk, I will present an efficient state-interaction approach for evaluating g-tensor [1, 2]. Using a spin-orbit-coupled effective Hamiltonian with a restricted active space configuration interaction (RASCI) wavefunction [3], this method captures key excited-state contributions to g-tensor (Figure 1) without requiring large orbital spaces while maintaining computational efficiency. Additionally, we introduce a property-driven algorithm to automatically optimize the active space.

Application to high-spin molecules demonstrates accuracy comparable to advanced methods, providing detailed insight into the origins of g-tensor. This methodology offers a flexible, efficient tool for exploring magnetic properties in complex molecules.

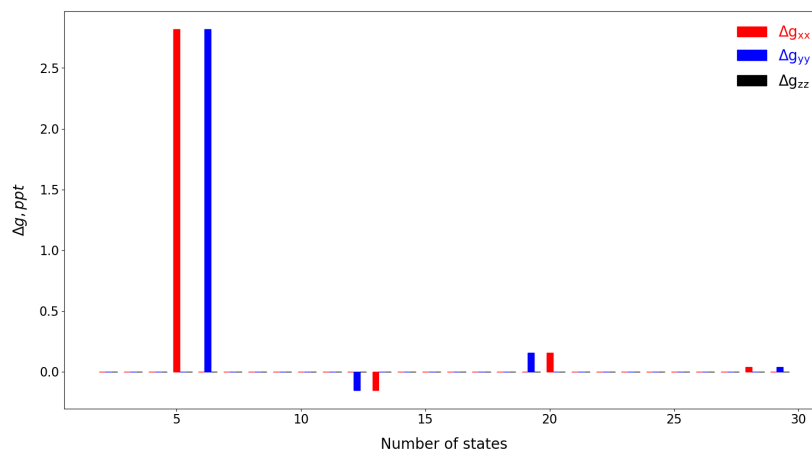


Fig. 1. Δg between the ground state (state 1) and the corresponding excited states for O₂ molecule

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Enhancing RASCI Excitation Energy Accuracy with Second-Order Perturbation Theory

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Multiconfigurational (MC) wave function methods effectively describe large regions of the molecular potential surface, especially in degenerate systems[1]. Unfortunately, in most cases, relative energies obtained at this level of theory are not sufficiently accurate due to the lack of dynamic correlation. To address this, dynamic correlation is typically added perturbatively. The application of perturbative approaches to MC methods is often limited by the intrinsic computational cost derived from the optimization of the reference orbitals[2]. Alternatively, restricted active space configuration interaction (RASCI(h,p)) method, which doesn't include orbital optimization, significantly lowers computational costs. RASCI(h,p) divides orbital space into three subsets: RAS1 (doubly occupied), RAS2 (electrons distributed in occupied/unoccupied), and RAS3 (unoccupied) [Fig.1]. This approach introduces most of the static correlation of the molecular system, but it does not properly account for dynamic correlation[3].

To overcome this limitation, we introduce the second order MC perturbation theory scheme (RASCI(2)), which improves the performance of RASCI(h,p) in the evaluation of vertical transition energies by adding contributions from higher-order hole/particle excitations[3]. In some cases, this approach might be affected by the presence of intruder states, causing energy singularities that reduce performance. To address this, level shifts are applied in the second-order energy correction. Applying RASCI(2) to medium-sized organic molecules, we find that it produces excitation energies comparable to CASPT2 and NEVPT2. Thus, we conclude that RASCI(2) is a promising method for strong-correlation effects in complex molecular systems.

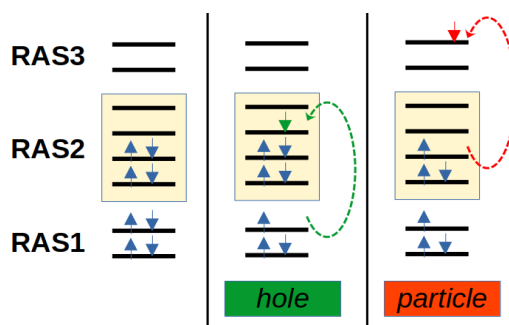


Fig.1 Schematic representation of the RASCI orbital partitioning into RAS1, RAS2, and RAS3 subspaces.

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Effect of H₂ Zero-Point Energy on dissociation dynamics on Tungsten Surfaces with Impurities

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Tungsten (W), chosen for its advantageous properties, is used as a plasma-facing material in devices like the tokamak divertor, including the ITER (International Thermonuclear Experimental Reactor) project. The primary role of the divertor is to remove impurities and heat from the plasma, thereby assuring a complete fuel recycling. Fuel recycling is the ratio between the flux of particles reaching the divertor surface and those returning back to the plasma. It is essential for understanding plasma behavior, though it does not always reach 100 %. The strong coupling between plasma and tungsten surfaces leads to reciprocal reactions that can significantly disrupt ideal plasma behavior. Controlling these interactions is a key challenge in the development of magnetic fusion reactors, requiring a profound understanding of the fundamental mechanisms of tungsten's interaction with hydrogen on a microscopic scale. The W surface in ITER can be pristine or covered with intrinsic impurities such as oxygen (O) or extrinsic impurities like nitrogen (N). The interaction of hydrogen molecules (H₂) shows a different behavior on a clean W surface compared to those covered with impurities. The type and amount of impurities play a crucial role in influencing the processes involved.

In a previous study, our research team carried out a theoretical analysis of H₂ dynamics on the clean W(110) surface [1] and on O-covered one [2]. The approach revealed a substantial decrease of the sticking coefficient with increasing coverage, in agreement with experimental findings. The present investigation focuses on the impact of nitrogen covering the W(110) surface on H₂ dissociation dynamics. The Pfnür team investigated the chemisorption of N₂ on the W(110) surface, noting surface reconstruction [3]. We aim here to examine the influence of this reconstruction on the H₂ dissociation process by studying it on two distinct tungsten surfaces covered with nitrogen, using ab-initio molecular dynamics (AIMD) both with and without considering the zero-point energy of the H₂ molecule. The first one involves N adsorption on the W(110) surface, while the second involves N inside W(110) surface, as observed experimentally by the Pfnür research group. This reconstruction results in a significant increase in H₂ dissociation compared with other W(110) surfaces clean and covered with either oxygen or nitrogen adsorbed on the surface. Consequently, the sticking coefficient of H₂ is considerably increased, even at low collision energies, exerting an attractive effect towards H₂ dissociation, as experimentally [4] suggested in polycrystalline tungsten, where the formation of deuterated ammonia, ND₃, was detected. However, when nitrogen is present on the surface, it tends to inhibit the H₂ dissociation.

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Investigation of the diffusion within clathrate hydrates by coupling DFT and Kinetic Monte Carlo

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Gas hydrates, also known as clathrate hydrates, are inclusion compounds where water molecules form a crystalline network of cavities that stabilize by trapping gas molecules or atoms [1].

Those solid forms of water represent promising materials for applications related to current energy and climate challenges, particularly carbon dioxide sequestration. Indeed, gas hydrates offer several advantages: a low environmental impact, relatively "mild" thermodynamic formation and stability conditions, and an interesting trapping capacity [2].

However, industrial applications of gas hydrates face significant hurdles. Typically, formation kinetics are slow, and while the use of promoters is effective in softening formation conditions, it may reduce the overall storage capacity of hydrates. These limitations are also linked to fundamental questions about the diffusive properties of the trapped molecules and the water molecules forming the structure.

To address these issues, we investigate the diffusion of guest molecules within hydrate structures. Our approach aims at determining diffusion coefficients by combining several computational techniques. Using DFT, especially with NEB and AIMD methods, we derive rate constants for inter-cage transitions, the primary diffusion mechanism at the molecular level. These rate constants are then used to feed a Kinetic Monte Carlo model, enabling us to estimate macroscopic properties such as diffusion coefficients with greater computational efficiency.

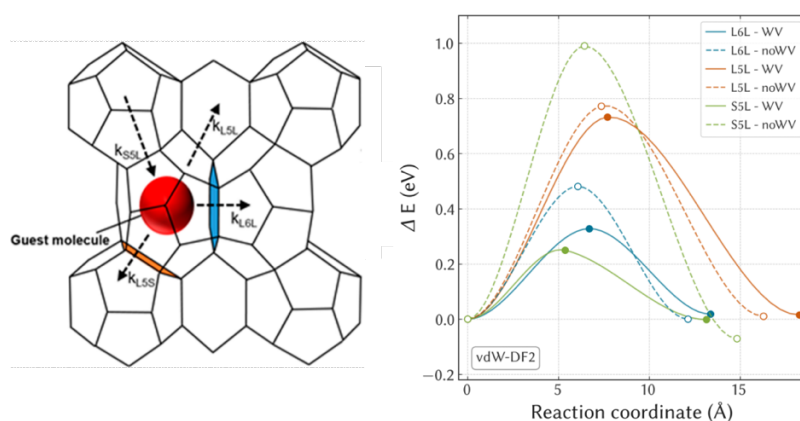


Fig. Schematic representation of the inter-cage transitions (left) and associated energy barriers calculated with DFT-NEB method (right)

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Substrate stabilization of Jahn-Teller distortion in a single molecule

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The utilization of non-conductive NaCl films allows the stabilization of multiple charge states on a single molecule [1]. Consequently, these films enable the observation of electronic transitions between distinct charge states by single-electron alternate-charging scanning tunneling microscopy (AC-STM) [2]. Specifically, when charging a copper-phthalocyanine (CuPc) molecule, the Jahn-Teller (JT) distortion induces a splitting of the degeneracy between the lowest unoccupied molecular orbitals (LUMOs). The AC-STM measurements reveal a double occupation of the same LUMO upon charging CuPc a second time. We show by DFT calculations complemented by a grouptheoretical analysis how the molecular electron-phonon coupling in gas phase is insufficient to explain this behavior. To address this, we propose a coupling between vibronic modes within the NaCl substrate and charges residing on the molecule. This proposition highlights the significant influence of the NaCl substrate on the electronic configuration of charged molecules, extending beyond charge stabilization [3].

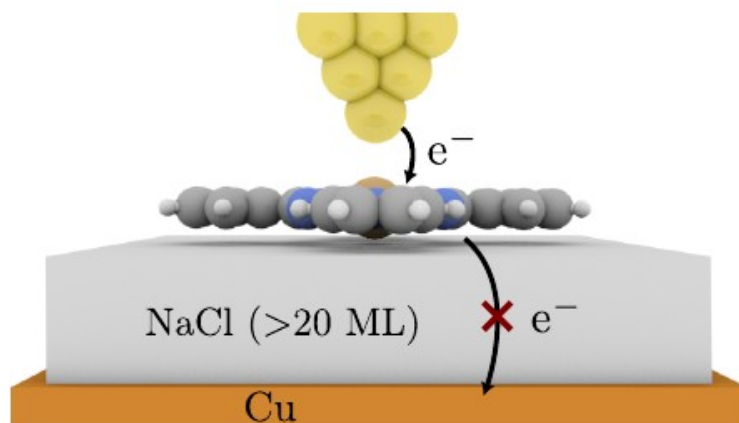


Fig. 1: Schematic depiction of the AC-STM setup. The thick salt layer suppresses tunneling from the molecule to the substrate thus enabling the stabilization of different charge states on the molecule.

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Light emission from current-driven plasmonic nanocavities

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In recent years, the scientific community has shown growing interest in the study of light emission in molecules. The Scanning Tunneling Microscope (STM), in particular, stands out for its remarkable ability to inject electrons with atomic precision (See Fig. 1). This precision enables the probing of various internal molecular transitions, shedding light on the intricate mechanisms behind molecular light emission.

In fact, it has been reported that when the STM tip is positioned close to the molecule, a distinct sharp resonance appears in the emission spectrum. This phenomenon, known as the Purcell effect, arises from the weak interaction between the confined electric field and the molecule, enhancing the emission efficiency [1, 2, 3]. Additionally, several research groups have investigated the statistical behavior of the emitted photons and observed antibunching. This phenomenon indicates that it is unlikely to detect two photons in close temporal proximity, providing further insights into the quantum nature of the light emission process [4, 5, 6, 7].

We propose a microscopic model based on the quantum master equation to accurately describe the emission spectrum and photon statistics, covering a broad range from weak to strong coupling in the plasmon-molecule interaction. This approach not only provides valuable insights into the fundamental mechanisms of light emission for current weak-coupling experiments but also offers a framework to analyze future scenarios in the strong-coupling regime.

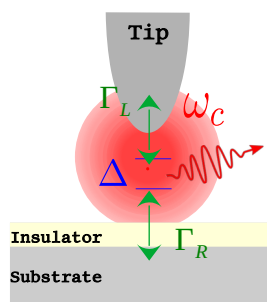


Fig. 1 Scanning tunneling microscope setup: electrons are injected from the tip to a two-level molecule (Δ) with rate Γ_L , which is dipole-coupled to a cavity mode (ω_c). The molecule lies on an insulating layer, isolating it from the substrate where electrons can escape with rate Γ_R .

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Computational Insights into Room Temperature Phosphorescence of Carbazole and the Impact of Aggregation

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Persistent room temperature phosphorescence (RTP) is a particular type of photoluminescence linked to the production of long-lived triplet excited states. The phosphorescence of heavy-metal complexes has been intensively studied, relying on an efficient intersystem crossing (ISC) mechanism induced by large spin-orbit couplings (SOC) of the metal ions. In contrast to that, their purely organic counterparts have only recently attracted significant interest for their many advantages (lower toxicity, higher biocompatibility, lower cost, more tunable photophysical properties) and potential applications such as optoelectronics (OLED technology), bioimaging or photocatalysis. However, apart from rare examples, organic materials generally fail in achieving efficient phosphorescence at room temperature which usually suffer from a loss of triplet excitons via non-radiative decay processes.

To enhance the production of RTP in organic materials, several strategies have been proposed. [1] Among those, improving the ISC efficiency, either by increasing SOCs using halogen atoms or by introducing heterocycles/carbonyl groups to increase the low-lying transitions following El-Sayed's selection rule, is crucial. Another key aspect lies in enhancing the phosphorescence decay. Additionally, structural factors such as the molecular packing and the intermolecular interactions are important parameters that affect the RTP emission process. But less is known about the impact of the intermolecular interactions on the triplet exciton stabilization and migration and in this context, computational investigations are a useful tool to provide mechanistic insights into the underlying photophysical process of organic, metal-free RTP materials. [2, 3]

In this work, we report a computational study that explores how aggregation affects several key parameters to consider for enhanced RTP in organic materials, using carbazole as a workhorse. Carbazole units have been extensively used for designing RTP materials taking advantage of their ability to form intermolecular aggregates and to ease efficient ISC through the nitrogen atom. [4] Considering carbazole model dimers that were systematically distorted along x and y directions (translations) and around the x, y, and z-axis (rotations), we evaluate the relative energies of singlet and triplet excited states, SOCs, as well as emission and ISC rates to assess how they may be affected by the relative disposition of the constituting monomers. We aim to identify favorable molecular arrangements and ultimately establish structure-property relationships for providing possible new guidelines for the development of organic RTP materials.

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Towards Eco-Friendly Photodetection : Molecular Design of ESIPT Molecules for Novel Capacitance Based Photodetectors

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Photodetectors are essential for applications across many fields, e.g., telecommunications and health. Most are based on inorganic semiconductors, often relying on toxic or limited-availability elements, and they also contribute to the problem of e-waste generation. Organic based photodetectors have in recent years reached comparable performance to such silicon-based devices, while offering flexibility and lower manufacturing energy costs.[1] Unfortunately, high-tech instrumentation is required for low-light detection, and use of PET or PEN also leads to undesirable plastic waste. Within the context of this project, we propose to develop simpler near-zero waste OPDs using bio-sourced and biodegradable materials, through the conception of a novel architecture (Figure 1) based on photo-capacitance detection. By dispersing small photoactive molecules within an inert substrate layer, an optical signal can be converted to an electronic one through the transient generation of polarized species, which increase the substrate permittivity and lead to a detectable capacitance change. The properties of such OPDs could be tailored by the selection of the photoactive molecules.

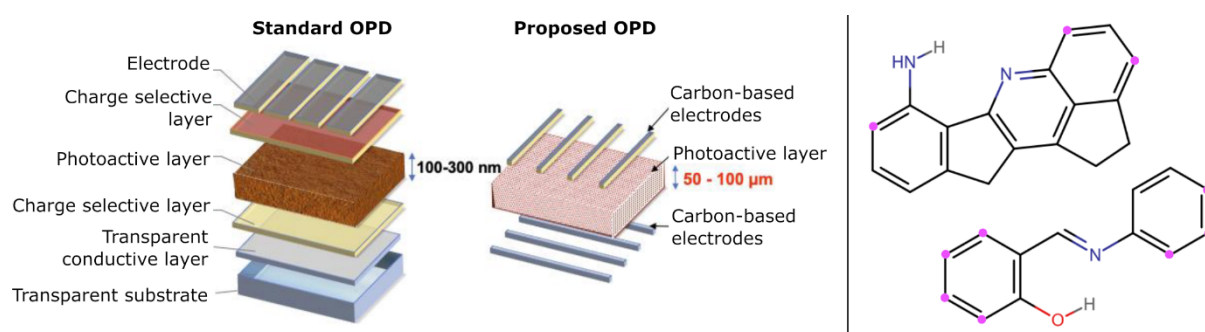


Figure 1: *Left* – Standard OPD architecture vs the proposed capacitance-based detection OPD, *Right* – proposed photochromic cores undergoing ESIPT with labelled substitution positions (pink)

Within this work we aim to design, through the use of quantum chemistry calculations in collaboration with experiment, small photochromic molecules with the ideal properties for such novel capacitance-based OPDs. To this end, we have identified the key target properties : a rapid and efficient photoconversion mechanism, a large difference in polarity between the initial and photogenerated forms, a lifetime of the photogenerated form on the order of ms-μs (balancing sensitivity and response time), and absorption in the visible range. Molecules undergoing the excited state intramolecular proton transfer (ESIPT) reaction[2] are ideal candidates, as these reactions can extremely rapidly (fs-ps) lead to highly polarizable metastable zwitterionic photoproducts.[3] Through a semi-automated approach, we have investigated the impact of substitutions on such molecules. We have tested substitution type and position in order to generate a dataset of singly and doubly substituted molecules, allowing us to identify and predict the best candidates for our novel OPD devices, as well as identify trends in the impacts of substitutions.

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Assessing the performance of a Quantum Krylov Subspace Diagonalization method.

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Solving the Schrödinger equation for quantum many-body systems is central to many computational algorithms in condensed matter physics, quantum chemistry, and high-energy physics. Current approaches to leveraging quantum computers for eigenstate estimation include Quantum Phase Estimation (QPE) [1] and the Variational Quantum Eigensolver (VQE) [2]. While QPE offers theoretical precision guarantees, quantum error correction is necessary to reach the circuit depths needed to achieve this precision. On the other hand, VQE faces challenges due to the bottleneck of parametric optimization, limiting its scalability for studying large systems. Quantum subspace algorithms provide a cost-effective alternative [3], particularly Krylov subspace methods, which enable efficient computation based on two steps as illustrated in Fig.1. In this work, we explore the performance of a quantum Krylov subspace diagonalization (QKSD) algorithm [4] based on a generalized Krylov scheme where the Krylov subspace is constructed through a parametrized real-time evolution. In particular, we discuss significant sources of error encountered in both, simulations and practical applications of the QKSD method. As a first step, we evaluate its performance in ground state simple systems such as the Heisenberg linear spin model and the electronic Hamiltonian of the H₂ molecule.

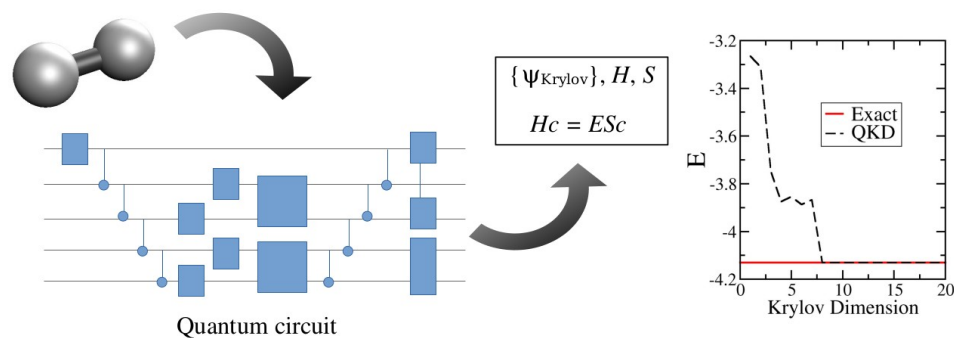


Fig 1. The QKSD method involves two main steps. First, the problem is translated into a quantum circuit, where a quantum subroutine constructs the H and S matrices, representing the projection of the Hamiltonian and the overlap into a subspace. Second, the time-independent Schrödinger equation, projected into this subspace, is solved classically.

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Benchmarking study of the sTD-DFT and XsTD-DFT methods to compute first hyperpolarizabilities

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Simplified time-dependent density functional theory (sTD-DFT) and its eXact integral variant (XsTD-DFT) are computational methods designed to efficiently calculate electronic spectra and linear and quadratic responses of systems as large as the ones for which the DFT ground state can be calculated. These methods achieve their efficiency by applying simplifications to Casida's TD-DFT equations.^{[1][2][3]} An emerging application of the sTD-DFT family of methods is the evaluation of first hyperpolarizabilities (β) in biological structures, which has the potential to drive the development of advanced second-harmonic imaging microscopy (SHIM) biotags.^[4] However, a thorough benchmarking study assessing their performance in computing β has been lacking. This work presents the first comprehensive evaluation of these methods of computing β .

We evaluated the performance of the (X)sTD-DFT methods in calculating β using a molecular set comprising more than 50 medium-sized push-pull π -conjugated systems and seven different hybrid functionals. First, we assessed the capability of the (X)sTD-DFT methods to reproduce standard TD-DFT results, enabling us to identify the error sources of the results related to the underlying quantum-physical approximations and highlight potential areas for improvement. Second, we also compared CCSD(T) reference data with both TD-DFT and (X)sTD-DFT results to evaluate the absolute accuracy of this new family of methods.

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Electron-spin relaxation in boron-doped organic molecules

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The synthesis of organic materials with stable and localized magnetic states has opened new avenues for the development of carbon-based platforms for data processing [1]. These materials are deemed to show extended electron-spin relaxation times due to weak spin-orbit and hyperfine couplings. Thus, carbon nanostructures have been put forward for developing materials able to host stable qubits based on the electronic spin [2].

In this work, we address electron-spin relaxation for some selected magnetic boron-doped organic molecules in solution (Fig. 1a). We use Redfield theory to compute the rate equations for the lowest-energy triplet states of the selected molecules (Fig. 1b). We apply this approach to study the impact of the distance between the boron dopants and of the amplitude of the external magnetic field on the relaxation process. We find that the electronic spin relaxes as a result of rapid fluctuations of spin-orbit and hyperfine couplings induced by thermal (random) motions of the molecule (Fig. 1c). We demonstrate that magnetic boron-doped organic molecules exhibit prolonged coherence times (Fig. 1d), making them potential candidates for developing materials for data storage [3].

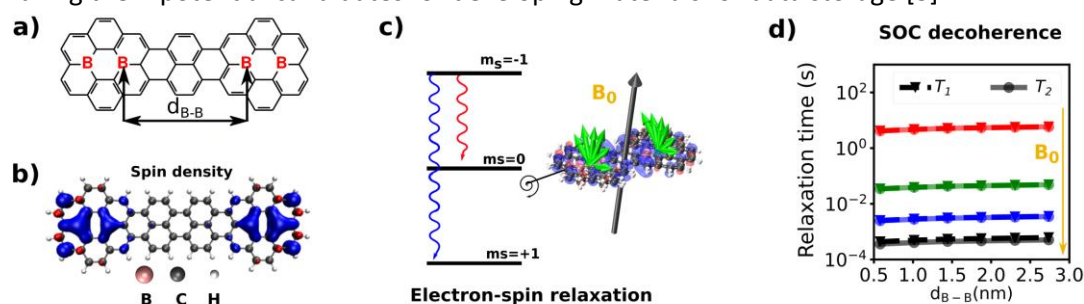


Fig.1. **Electron-spin relaxation for boron-doped coronene dimers.** (a) Schematic representation of the chemical structure of a representative boron-doped coronene dimer. (b) 0.02 bohr^{-3} value isosurface of the spin density for a selected boron-doped molecule. (c) Scheme of the electron-spin process triggered by molecular thermal motions for a triplet state. (d) Relaxation times T_1 (dashed lines) and T_2 (solid lines) induced by spin-orbit coupling decoherence as a function of the boron-boron distance (d_{B-B} ; definition in panel a). Magnetic fields of amplitude 30 mT (red lines), 330 mT (green lines), 1250 mT (blue line) and 3500 mT (black line) are applied for computing the relaxation times shown in panel d.

References

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26	MARTIN BARRIOS Raidel
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