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**Book of abstracts**

# Bound states of $H_2^+$ using a multicenter approach based on complex Gaussian functions

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The behavior of molecules in a variety of chemical and physical environments is strongly determined by their quantum states. Therefore, an accurate theoretical description is essential for the understanding of a variety of phenomena. Moreover, in diverse fields such as astrophysics, radiobiology, and plasma physics, certain collision processes involve both bound and continuum molecular states.

In this study, we aim to represent the bound and continuum states of the molecular ion  $H_2^+$  using a set of complex Gaussian-Type Orbitals (cGTOs), that is to say GTO characterized by complex exponents. For continuum states, these functions have been employed so far only within a monocentric approach [1, 2]. For  $H_2^+$ , we tackle the theoretical challenge of a multi-center system.

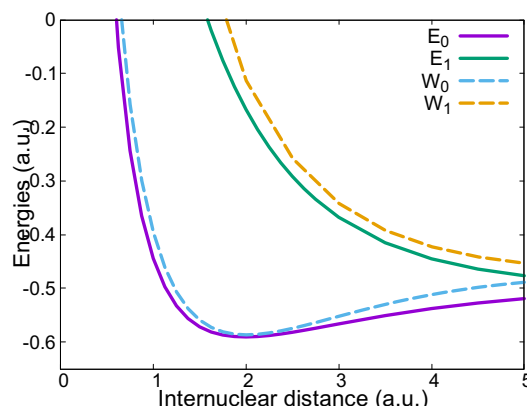
To start with a simple model of a bound state, we express the molecular orbital ( $1\Sigma_g^+$ ) as a linear combination of atomic orbitals (1s) given by a single Slater type function centered on both nuclei. Each Slater function is represented by an expansion of optimized cGTOs. The calculation of the molecular bound state energy, given by the expectation of the system's Hamiltonian, requires the evaluation of several integrals (Coulomb, exchange, kinetic...). With the cGTOs expansion we have been able to perform them analytically thanks to mathematical properties of Gaussian functions [3].

In a second step, we develop a computational code for a variational approach using a fixed cGTOs basis, and where only linear coefficients are optimized. This allows us to recompute the eigen-energies (refer to Figure 1) and generate the wave functions (see Figure 2) of the diatomic  $H_2^+$  system, thus providing a clear improvement in the results.

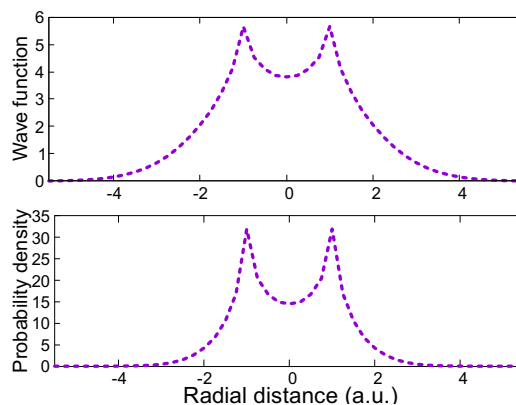
For the future, we plan to apply our cGTOs methodological approach to address the more challenging problem

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of the multicentric continuum.



**Figure 1.** The energy curves of the bound state ( $E_0$ ,  $W_0$ ) and first excited state respectively ( $E_1$ ,  $W_1$ ), as a function of the internuclear distance. The solid lines correspond to the calculation using a fixed cGTO basis within the variational method, while the dashed lines correspond to the use of the initial Slater functions.



**Figure 2.** Representation of the ground state wavefunction as well as the probability density using cGTOs. The equilibrium internuclear distance is 2 a.u.

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# Mixed-Reference Spin-Flip Time-Dependent Density Functional Theory for Accurate core, ionization and neutral excitations

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Conventional adiabatic linear response (LR) spin-flip theories usually employ a single reference to ensure its corresponding density idempotent property, and hence, only singly excited configurations are included. This limited configurational space can have critical problem in the excited states.<sup>1</sup> The mixed-reference spin-flip (MRSF)–time-dependent density functional theory (TDDFT) overcomes this limitation by a spinor-like transformation in the context of spin-flip excitations, which allows to combine the reduced density matrices of the two  $MS = \pm 1$  triplet-ground references within the realm of LR theory.

It is recently demonstrated that the challenging core-hole particle (CHP) orbital relaxation for core electron spectra can be readily achieved by MRSF-TDDFT thanks to its open shell formalism.<sup>2</sup> The particular  $\Delta$ CHP–MRSF(R) exhibited near perfect predictions with RMSE  $\sim 0.5$  eV. The same protocol with a double hole particle relaxation also produced remarkably accurate K-edge spectra of core to valence hole excitation energies from the first ( $n\pi^*$ ) and second ( $\pi\pi^*$ ) excited states of thymine, confirming the assignment of  $1s \rightarrow n$  excitation for the experimentally observed 526.4 eV peak.

On the other hand, the performance of MRSF-TDDFT is dependent on the choice of exchange-correlation (XC) functionals due to its density functional origin. It is demonstrated that significant accuracy improvements can be achieved by introducing two different XC functionals for the reference Kohn–Sham DFT and the response part of the calculations, respectively. The resulting doubly tuned Coulomb attenuated method (DTCAM)-XI functional achieved remarkably high accuracy in their predictions with errors of less than half eV. The second functional, DTCAM-XIV exhibits consistent overall prediction accuracy  $\sim 0.64$  eV. By preferentially optimizing vertical excitation energies (VEEs) within the same valence attenuation concept, a third functional of DTCAM-VAEE was obtained, which exhibits improved performance as compared to previous DTCAM-VEE and DTCAM-AEE in the prediction of VEE, making it an attractive alternative to BH&HLYP.

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# Plasmon satellites in Cesium

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Photoemission spectroscopy is one of the most direct ways to access the electronic structure of materials. The main peaks usually correspond to the quasiparticle band structure. Replicas of these peaks, called satellites, are entirely due to interactions [1]. Here, we address satellites that can be interpreted in an electron-boson coupling picture, where the bosons are charge excitations such as plasmons and electron-hole pairs that are induced by the removal of an electron from the sample. In the homogeneous electron gas (HEG) at a density corresponding to a simple metal like sodium, plasmons are the prominent collective excitations [2]. At lower densities, instead, the HEG exhibit exotic features: the plasmon dispersion switches sign becoming negative and additional excitonic collective modes have been recently predicted [3,4]. It is, therefore, very natural to ask whether such signatures can be seen in real materials and ponder about their impact on the shape of photoemission satellites. Cesium is a metal with low electron density that shows a negative plasmon dispersion [5]. In this study, we investigate the effect of such dispersive nature on the shape of the satellites in the photoemission spectra of cesium using Time-Dependent Density Functional Theory and Many-Body Perturbation Theory, where we combine the GW approximation for the self-energy with the cumulant expansion for the Green's function [1]. Our calculations provide guidance for ongoing experiments.

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# Excited Many-Electron States Using Coupled-Cluster Theory for Extended Systems

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One major challenge of first principles methods in computational materials science is the accurate prediction of optical properties for real materials. Although there exist a number of widely-used methods, such as time-dependent density functional theory (TD-DFT) or *GW*-BSE to compute, for example, linear optical absorption spectra, these methods lack in general systematic improvability. More accurate and systematically improvable methods, however, would be needed to study systems where TD-DFT and *GW*-BSE fail to achieve the desired level of accuracy. One such approach is the equation-of-motion coupled cluster (EOM-CC) theory based on the exponential coupled cluster ansatz that is already widely used for ground state calculations.

In the field of molecular quantum chemistry a well-established method for the calculation of excited states is the excitation-energy (EE) EOM-CC approach including single and double excitations, denoted EE-EOM-CCSD. Thereby, a linear operator acts on the introduced CC wavefunction leading to an eigenvalue problem to get discretized excitation energies. The EE-EOM-CCSD approach, however, is not the only possibility to compute excitation energies. In this poster we focus on a related approach, namely the time-dependent (TD) EOM-CCSD theory which is based on the time evolution of the electric dipole moment function governed by the time-dependent Schrödinger equation. The high-dimensional eigenvalue problem of the EE-EOM-CCSD theory is reformulated into an initial value problem at the price of losing the discretized excitation energy spectrum and corresponding wave functions. This slightly complicates the interpretation of the spectra but introduces numerical advantages such as a significantly lower memory footprint. The computational bottleneck of the state-of-the-art TD-EOM-CCSD calculations originates from the calculation of the dipole moment at arbitrary time steps using conventional integration techniques.

We seek to overcome this drawback by applying a more efficient integration technique. As a proof of principle, we analyze this impact on the example of the  $\text{H}_2\text{O}$  molecule with the aim of decreasing the computational cost. We further look at the basis set and system size convergences. As a second system, we investigate defects in solids in the example of F-centers in  $\text{CaO}$ .

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# Improved Design of Semi-Empirical Density Functional Approximations

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## ABSTRACT

While density functional theory is the most widely used method to calculate molecular properties of medium and large sized molecules, vast majority of modern density functional approximations (DFAs) are unreliable for the calculation of vibrational properties. [1] This can lead to errors in frequencies, intensities and nuclear relaxation contributions to electric response properties of up to thousands of percent in systems with low-frequency modes. We have since found that the problem of the same origin appears in the calculation of purely electronic properties. We show that the fundamental origin of this problem lies in the unphysical oscillations of the real-space exchange-correlation energy density derivatives with respect to external perturbations. By directly connecting the magnitude of these oscillations to specific behaviors of the DFAs at different reduced density gradients, we developed a strategy to design functionals that are robust for calculating molecular properties. Using this strategy, we designed DFAs which are loosely based on the mathematical structure of the  $\omega$ B97 family of functionals, yet are robust for calculating molecular properties while achieving similar accuracy as the base functionals. Finally, by adding purely density and density-gradient based range-separation of the correlation energy, we construct a DFA that is not only robust for the calculation of molecular properties, but also has a competitive edge in the general performance compared to state of the art density functional approximations.

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## **SHEDDING LIGHT ON NONLINEAR OPTICAL PROPERTIES: A COMPARATIVE COMPUTATIONAL ANALYSIS**

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Great attention has been paid to materials characterized by a large nonlinear optical (NLO) response due to their applications in electrooptics, as optical switches or three-dimension fluorescence microscopy, among others. One example of an NLO process is the second harmonic generation, a physical process where photons with frequency  $\omega$  interact with a non-centrosymmetric material, causing the combination of two photons and resulting in the refraction of a photon with double frequency. Despite the interest arisen by nonlinear optical properties (NLOPs), most of the quantum chemistry methods were designed to calculate thermodynamic reactions and barrier energies, whereas only few methods are designed to compute molecular properties.

In the presence of the so-called nondynamic correlation, only a few methods can be applied, the most popular of them is the complete active space self-consistent field (CASSCF) method.

This project focuses on the computational analysis of different lengths polyacetylene (PAs) chains using HF, MP2, CASSCF and CCSD methods with different basis (aug-cc-pVTZ, aug-cc-pVDZ, cc-pCTZ, cc-pVDZ and Sadlej's POL). Our goal is to compare the methods and their reliability to compute NLOPs. The Partitioning of NLOPs into Orbital Contributions (PNOC) tool was used to analyse the results<sup>[3]</sup>. This is a new tool to measure the contribution of the different molecular orbitals to the (hyper)polarizabilities.

The results obtained show that, for polyacetylene (PAs) chains, MP2 can predict accurately the total values of the NLOPs and their orbital contributions. Nonetheless, we found that CASSCF significantly underestimates the NLOPs, giving larger errors with respect to CCSD than HF. The latter finding suggests caution using CASSCF to compute NLOPs, and opens the question of which method should be used to compute NLOPs for multireference systems.

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**Poster Title:** A Multiscale, Non-Standard Approach for the Electronic Excitations in Molecule/Nanoparticle Systems

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**Abstract:**

Hybrid nanosystems (NH) composed of semiconductor nanoparticles (NP) and small organic molecules (M) have the potential to significantly enhance their electronic and optical properties by integrating the distinct advantages of each individual component. These systems have applications in lighting, display technology, sunlight harvesting, drug delivery, catalysis, biosensors, and photodynamic therapy [1].

Simulating the electronic excitations of NHs, which typically consist of around  $10^9$  atoms, using first-principles methods for each fragment, is computationally unfeasible. Traditional approaches often treat each part with distinct accuracy levels but tend to neglect electron correlation within and between fragments. Additionally, size-tuning simulations for NHs are impractical due to the computational cost dependency on the NP size [2].

We present here the Hybrid Configuration Interaction (HyCI) method [2], a non-standard approach that consistently computes excitation energies, optical properties, and excitonic transfer rates for NHs with appropriate accuracy. HyCI combines first-principles simulations for the M, such as Configuration Interaction (CI) or Time-Dependent Density Functional Theory (TD-DFT), with CI under the Effective Mass and Envelope Function Approximations (EM-EFA) for the NP. The interaction Hamiltonian is then diagonalized in the tensor product basis of the non-coupled excited states of the fragments. The spherical symmetry and angular momentum selection rules of the NP allow for the inclusion of all multipole moments and make calculations computationally feasible.

We apply the HyCI methodology to the trans-cis isomerization reaction of azobenzene (AB), a photoswitch molecule functionalized with a nanoparticle (NP). We present partial results on comparing the energies, oscillator strengths, and absorption spectra for the AB+NP system with those of AB alone, over different values of the reaction coordinate. We highlight the capabilities of the HyCI strategy and demonstrate its flexibility by using varied sizes and materials for the NP. Further results will be presented elsewhere.

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# Optimized effective potential forces with the plane-wave and pseudopotential method

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Several approaches for studying properties of the electronic ground-state exist. One of them is the Random Phase Approximation (RPA) [1], an approach that is compatible with both the Kohn-Sham Density Functional Theory (KS-DFT) and the GW approximation within Many-Body Perturbation Theory (MBPT) [2]. The RPA functional has within KS-DFT an explicit dependence on Kohn-Sham orbitals instead of the electronic density, thus allowing for a better description of exchange and correlation effects. Self-consistency requires solving the Optimized Effective Potential (OEP) equation to obtain the exchange-correlation potential [3].

In this work, the calculation of analytical ionic forces within OEP is presented using plane-waves, basis set functions that offer high numerical accuracy [4]. It is found that an extra force term needs to be added to the traditional Hellmann-Feynman expression of forces whenever nonlocal pseudopotentials are used to approximate the influence of core electrons. The extra force term deriving from the evaluation of the OEP exchange has been implemented within the QUANTUM ESPRESSO distribution [4,5]. Ionic forces for the OEP variant functionals of Hartree-Fock and the PBE0 hybrid DFT have been computed. The calculated forces show high numerical accuracy both on molecular and solid systems. The forces have also been used to perform geometry relaxations and predict vibration frequencies, yielding results in very good agreement with the approximation method each OEP variant is adapted from.

These different results confirm that functionals relying on the OEP approximation can be used to calculate force properties [6]. This work represents a first step for a generalization to more advanced functionals based on the OEP such as the Random Phase Approximation.

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# Modeling quantum emitters beyond the point-dipole approximation and assessing its validity in proximity of nanoscale structures

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Modeling the spontaneous emission rate of a quantum emitter can usually be carried out via a semi-classical development that remains limited to the dipolar term, where in addition, the emitter is generally approximated as a point-dipole. However, particular nanoscale structures support strongly confined fields where the point-dipole approximation (PDA) fails and can even be surpassed by higher-order transitions [1].

Recently, a first-principle framework [2] that considers both the full extension of the wavefunction, and therefore including all multipolar terms, and their interferences, was developed and applied to the case of Hydrogen. This framework is based on an eigenpermittivity mode expansion. Here, for the first time, we combine this framework with quantum chemistry to assess the validity of the point-dipole approximation for large molecular emitters.

To achieve the above-mentioned work, we use a quantum chemistry package (Gaussian in our case) to calculate the emitter's transition density matrix with Time-Dependent Density Functional Theory (TD-DFT). This can be fully incorporated within the framework and expanded over the natural transition orbitals for cost-effectiveness. This allows us to model the molecular emitter beyond the point-dipole approximation.

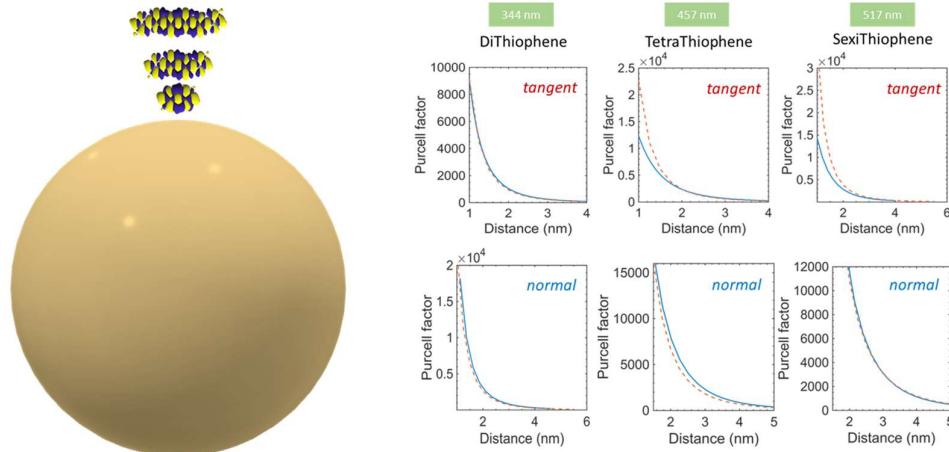


Figure 1 : (left) Representation of oligothiophene emitters placed in the vicinity of a gold nanosphere – molecule sizes are in scale with respect to the nanosphere (right) Distance dependence of the Purcell factors computed using point-dipole approximation (dashed line) and full emitter expansion (solid line), for two different molecule orientations, with their emission wavelength written on top.

We apply our new method to the system shown in Figure 1. The system consists of oligothiophene chains sitting in the proximity of a nanosphere scatterer (with a radius of 5nm). A comparison is laid down with the case of a point-dipole using the COMSOL software. The goal is to assess the validity of the PDA and to study the recovery distance at which it is valid. The thiophene chains were translated along the radial axis for two orientations. A tangent setup (as shown in Fig.1 (left)) and a normal setup where the chain becomes oriented along the radial axis. The Thiophenes showed an interesting orientation-dependent behavior. The PDA breakdown was seen in the tangent setup at 1.8 nm and 2.1 nm, for the Tetrathiophene and Sexithiophene respectively. This value correlates with their extended length approximately (2 nm and 2.4 nm, respectively). However, the same chains were described accurately by the PDA in the normal setup. To interpret these findings, a rule of thumb can be suggested: The PDA is valid when the molecule-scatterer separation is larger than the size of the molecule.

### **Acknowledgments**

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## A novel 'moment'-based GW algorithm for molecules and solids

A novel GW approach is examined for molecular and periodic systems using Gaussian basis functions and  $k$ -point sampling for periodic systems. The approach is independent of any numerical frequency or time grids, based instead around exact conservation of an increasing number of moments of the self-energy spectrum (Scott et al., 2023). This recursive moment framework allows us to avoid the frequency integration or diagonal quasi-particle approximations associated with many practical GW implementations, enabling a full-frequency construction of the final quasi-particle spectrum while retaining competitive computational costs compared to other approaches.

Within this procedure, both random phase (RPA) and Tamm-Dancoff (TDA) approximations are investigated for the screening of the Coulomb repulsion (Langreth & Perdew, 1977). While both screening methods have the same scaling, there is a significant reduction in the prefactor of the computational cost for TDA. We observe rapid convergence in both approaches with respect to the moment order for molecular and solid systems with accurate spectra and when compared to established benchmarks.

We have explored further improvements to the system scaling through the implementation of tensor hypercontraction (THC) for electron repulsion integrals (ERIs) (Parrish et al., 2012), and finite-size corrections to the long-range divergence of the Coulomb potential in periodic systems (Gajdoš et al., 2006).

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# Preconditioning the Self-Consistent Field for Inhomogeneous Semiconductors in Kohn-Sham DFT

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The Kohn-Sham equations are typically solved using self-consistent iterations and the convergence of these iterations strongly depends on the mixing and preconditioning scheme used. The widely used Kerker[Ker81] and Resta [Res77] preconditioners allow for an efficient compensation of the Coulomb divergence in metals and semiconductors, respectively. However, these preconditioners are not suitable for inhomogeneous systems, due to their expression in plane waves. An inhomogeneous adaptation of the Kerker preconditioner has been developed in [HL20] and in this poster, we present the ongoing development of an inhomogeneous adaptation of the Resta preconditioner.

Our preconditioner is derived from Resta by introducing local polarizability, which allows us to treat different types of material in a unit cell. The results obtained with this preconditioner in one-dimensional systems are very promising.

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# Multi-channel Dyson equation: application to neutral excitations

S. Paggi, A. Berger, P. Romaniello

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## Abstract

In this poster I will discuss a new method to calculate neutral excitation energies, which is based on the use of the four-body Green's function instead of the two-body one employed in standard approaches. More specifically, I will use a multi-channel Dyson equation [1], which couples the two-body and four-body Green's functions through a multi-channel self-energy that has the advantage of being static and containing only the bare Coulomb interaction. I will illustrate our approach by applying it to a two-level model which has single and double excitations [2]. Our method can correctly describe both kind of excitations, unlike standard approaches (e.g. Bethe-Salpeter with a static kernel), in good agreement with the exact results.

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# Frequency Dependent Charge Dipole Model for Calculating Polarizability

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Systems with low energy gap possessing both macroscopic and nanoscopic dimensions, exhibit unconventional van der Waals power laws characterized by slow decay[1]. This peculiarity stems from a distinct charge fluctuation behavior, prevalent in fullerene and carbon nanotube families, known as charge-flow. Despite its significance, conventional force field models often overlook this behavior. In 2007, Mayer et al. reported a charge-dipole (CD) model[2], which focuses on the static polarizability of individual molecules, incorporating the charge-flow and induced dipole to describe polarization response. To get the dynamic polarizability, we develop a model termed ‘frequency-dependent charge-dipole’ ( $\omega$ CD). The suitability of the model has been tested for various model systems. Hence, we can hope the  $\omega$ CD model will provide an efficient way to calculate dynamic response with reduced computation cost. This will be useful for modeling a polarizable force field for a solute in the solvent environment.

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## Spin Waves with Source-Free Time-Dependent Spin-DFT

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Time-dependent spin density functional theory (TD-SDFT) allows the theoretical description of spin and magnetization dynamics in electronic systems from first quantum mechanical principles. TD-SDFT accounts for electronic interaction effects via so-called exchange-correlation fields, which have to be suitably approximated in practice. We consider here an approach that was recently proposed by S. Sharma et al. [1], which enforces the so-called “source-free” condition [2] by eliminating monopole contributions to the exchange-correlation field. This approximation was shown to give good results for the structure of magnetic materials. We test the source-free expression in the linear-response regime for spin waves in a paramagnetic electron gas and find a violation of Larmor’s Theorem and wrong small- $q$  magnon dispersions.

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# Evaluating Aromaticity in Large Conjugated Systems with Hilbert-Space-Based Atomic Partitions

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Aromaticity is a fundamental concept in chemistry, employed to explain the stability and reactivity of numerous chemical compounds.<sup>[1]</sup> A key aspect of most aromaticity measures involves, in one way or another, identifying atoms within the molecule, as these atoms form the *aromatic ring*. Aromaticity indices that focus on electron delocalization are among the most reliable and depend on how we define an atomic partition, *i.e.*, on how we define an *atom-in-the-molecule* (AIM). Although real-space atomic partitions are often preferred for their accuracy, they come with significant drawbacks: high computational costs<sup>[2]</sup> and an increase in numerical errors as the size of the ring grows<sup>[3]</sup>. Consequently, the most dependable real-space measures for assessing electron-delocalization-based aromaticity are restricted to medium-sized molecules and relatively small rings (up to approximately 12 atoms). This limitation significantly impedes the study of aromaticity in large conjugated systems, such as porphyrins and nanorings.

In this project, we explore the use of AIMs based on Hilbert-space partitions. Traditional Hilbert-space schemes often yield unreliable results when applied to the large basis sets typically required for contemporary computational chemistry. We introduce three robust Hilbert-space partitions—meta-Löwdin,<sup>[4]</sup> Natural Atomic Orbitals (NAO),<sup>[5]</sup> and Intrinsic Atomic Orbitals (IAO)<sup>[6]</sup>—that combine the reliability of real-space partitions without their associated disadvantages. These partitions are devoid of numerical errors and are capable of effectively replacing the quantum theory of atoms in molecules (QTAIM)<sup>[7]</sup> partition to evaluate the aromatic character of molecules. For the first time, we report multicenter index (MCI) and  $I_{\text{ring}}$  values for large rings and offer an open-source Python computational code, ESIPy, designed for aromaticity analysis in large conjugated rings.

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# Arbitrariness of the degree of complexity of superoperators in the EOM formulation of TD-DFT objects

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When describing the reorganization of electronic structure induced by the interaction between light and matter, two objects are particularly crucial: the one-body difference density matrix and the one-body transition density matrix. The primary motivation that led us to focus on these two matrices is as follows: the first one allows us to calculate the difference in expectation value of one-body operators between two electronic states without needing these two states explicitly. The second one provides us expectation values associated with transition properties.

If we had access to the exact eigenstates of the stationary Hamiltonian, we could write an exact transition operator. In the equation-of-motion formalism (EOM), it is possible to prove that an arbitrary number of nested commutators, called superoperators, involving this exact operator and second quantization operators allows us to write the exact expression of our two density matrices of interest.

As time-dependent density-functional theory method (TD-DFT) cannot give access to the exact transition operator, writing an approximate expression for these matrices involves the use of a substitution operator. This operator is inspired by the operator that generates the central equation of the Random Phase Approximation method. The use of superoperators in TD-DFT is enabled by the structure of its fundamental equation and its physical interpretation. Interestingly, there exists a structural and interpretational identity between the fundamental equations of TD-DFT and Bethe-Salpeter equation (BSE) methods. The development carried out with the substitution operator in TD-DFT is also applicable to BSE.

We intend to demonstrate and justify that, in this specific context, the choice of the complexity degree of the superoperators might not be arbitrary — unlike with an exact transition operator — and require a minimum degree of complexity for superoperators, in order to express the two density matrices.

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# Precise optical absorption spectra of Ag clusters and nanoparticles from efficient RT-TDDFT+U calculation

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The modeling of the Localized Surface-Plasmon Resonance (LSPR) in silver clusters and nanoparticles depends on exchange-correlation functionals (xc-functionals) within Density Functional Theory (DFT) and Time-Dependent DFT (TDDFT). While optical absorption spectra calculated using hybrid and range-separated hybrid functionals are known to have excellent agreement with experiments [1,2] their computational cost restricts their use to smaller clusters. Simple functionals such as LDA or GGA fail to describe the 4d electrons accurately, generally placing them too close to the Fermi energy. Consequently, the inter-band transitions start at lower energies than expected, leading to too low LSPR energies and over-broadening of the LSPR peak. RT-TDDFT+U emerges as a promising alternative [3,4], which improves the description of the 4d electrons by adding an empirical Hubbard-like effective U correction to the Kohn-Sham Hamiltonian. In our present work, we carried out RT-TDDFT+U calculations using the same value of the effective U parameter that has been found to provide good results in bulk silver [5]. Both the electron-hole-type discrete spectra of the smallest clusters and the broad plasmon resonances of the larger sizes ( $\approx 1000$  atoms) are precisely obtained. The excellent agreement with experiment for all sizes indicates that the U parameter is surprisingly transferable.

Our calculations successfully capture the oscillations in the LSPR position caused by the shell-closing effect for intermediate-sized clusters. However, calculations performed using highly symmetric icosahedral clusters, spherical fcc-based clusters, and geometrically optimized lowest-energy clusters of similar sizes reveal that the geometry and the overall shape of the particle are important for the energetic position of the LSPR. Furthermore, we qualitatively and quantitatively confirm the increased localization of the 4d electrons when the U correction is applied. The average occupation of the 4d orbitals reveals a stronger Coulombic screening effect in larger particles compared to smaller ones, as well as reduced screening on the surface compared to inside the particle.

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# Make it simple: benchmarking the performances of XsTD-DFT to compute one- and two-photon absorption

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Multiscale methods allow the computation of one- and two-photon absorption (1PA and 2PA) of large systems by partitioning them into layers. They rely on the assumption that the optical response mostly originates from a small portion of the system, that is treated at a quantum mechanical (QM) level. Despite their computational efficiency, multiscale methods do not fully capture the response of the surroundings. This motivates a full-QM treatment of the entire system for realistic comparisons with experiments. A full-QM treatment is nevertheless out of the reach of current ab initio methods. Grimme and co-workers<sup>1</sup> proposed the simplified TD-DFT (sTD-DFT) method<sup>2</sup> as an alternative scheme to compute excited states. This was extended to nonlinear optical (NLO) properties by de Wergifosse. It was the opportunity to compute, with this “all-atom QM” scheme, NLO properties of systems as large as fluorescent proteins or nanoparticles. These works showed the importance to explicitly account for the impact of surroundings. Recently, de Wergifosse<sup>3</sup> introduced the eXact integral sTD-DFT (XsTD-DFT) scheme which removes the semi-empiricism of the sTD-DFT scheme.

The present work evaluates the performances of the XsTD-DFT method to compute 1PA and 2PA, with respect to reference RI-CC2/aug-cc-pVDZ calculations. We selected three different molecular sets: the first one (from QUEST database) is composed of 29 small molecules with excited states of valence, charge transfer (CT) and Rydberg character, for which theoretical best estimates are available. The second set includes 48  $\pi$ -conjugated medium size molecules exhibiting CT excited states with large 2PA strengths. We also included an ensemble of micro-hydrated molecules to study how local environmental effects are treated by the XsTD-DFT scheme. We first assessed the performance of the XsTD-DFT method for different global and range-separated hybrid exchange-correlation (XC) functionals (TPSSH, B3LYP, PEB0, M06, BHandHLYP, M06-2X, CAM-B3LYP,  $\omega$ B97X-D3,  $\omega$ B97M-V), comparing trends to full TD-DFT and RI-CC2. Second, we studied basis set effects, testing different double- $\zeta$  basis sets (3-21G, 6-31G\*, cc-pVDZ, 6-31+G\*, def2-SVP, aug-cc-pVDZ). We observed that the XsTD-DFT scheme closely reproduces trends in excitation energies, oscillator strengths, and 2PA strengths ( $\delta_{2PA}$ ) with respect to the full scheme. For excitation energies, of 1PA and 2PA active states, we report MADs of 0.10 eV (TD-DFT), 0.63 eV (sTD-DFT), and 0.14 eV (XsTD-DFT) at M06-2X/aug-cc-pVDZ level. For oscillator strengths larger than 0.1, we observed mean absolute deviations (MADs) from RI-CC2 of 0.08 (TD-DFT), 0.23 (sTD-DFT), and 0.10 (XsTD-DFT) at the same level of theory. Hybrid XC functionals with low amount of exact exchange better reproduce magnitudes of  $\delta_{2PA}$ : at PBE0/aug-cc-pVDZ level, MADs of  $\log(\delta_{2PA})$  (within a range of  $10^3$  and  $10^6$  a.u. strengths) are 0.17 (TD-DFT), 0.16 (sTD-DFT), and 0.15 (XsTD-DFT), while MADs of excitation energies (of these 2PA active states) are 0.46 eV (TD-DFT), 0.73 eV (sTD-DFT), and 0.38 eV (XsTD-DFT). The advantage of simplified QC methods is their general computational speed up: XsTD-DFT (sTD-DFT) overall runs 69 (135) times faster than TD-DFT on the same 16 Intel Xeon E5-2650 v2 CPUs (2.60 GHz).

In conclusion, we showed that XsTD-DFT is a computationally efficient and robust alternative to TD-DFT to compute 1PA and 2PA trends. The parameter free XsTD-DFT improves results with respect to sTD-DFT scheme, making it a flexible and general method for excited states calculations. As emerging applications, XsTD-DFT can be used to simulate realistic systems accounting for dynamic structural effects and impact of the surroundings, going beyond the single molecule approach.

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# Structural, electronic and optical properties of $\text{Li}_x\text{Na}_{1-x}\text{H}$ for hydrogen storage

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This study investigates the structural, electronic, and optical properties of LiH and NaH compounds, as well as their ternary mixed crystals  $\text{Li}_x\text{Na}_{1-x}\text{H}$ , adopting a face-centered cubic structure with space group Fm-3m (number 225).

The structural and electronic characteristics are examined using density functional theory (DFT), while empirical methods, specifically the modified Moss relation, are employed for analyzing optical properties.

The exchange-correlation potential is determined through the generalized gradient approximation (PBEsol-GGA) within the density functional theory (DFT) framework, utilizing the projected augmented wave pseudopotentials (PAW) approach. The Quantum Espresso code is employed for conducting these calculations.

The calculated lattice parameters at equilibrium volume and the bulk modulus for  $x=0$  and  $x=1$  exhibit good agreement with existing literature data. Additionally, the  $\text{Li}_x\text{Na}_{1-x}\text{H}$  alloys are identified as having a direct band gap.

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# Exploring the chemical reactivity through a combined Conceptual DFT and Electron Localization Function approach

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## Resume:

Most of the studies performed in the context of the electron density analysis remain semi-quantitative and focus more on the interpretative aspects. This project aims to develop an innovative method to predict the energetic profile of chemical reactivity, from separated reactants to transition states, for complex molecular reactions at a low computational cost, by using the condensed Dual Descriptor (DD) of the Conceptual DFT and the Electron Localization Function (ELF) topology. The DD has been chosen for its ability to evaluate the regioselectivity of neutral and soft species and to potentially mimic the interaction energy derived from the mutual interactions between nucleophilic and electrophilic regions of the building blocks under perturbative theory. This model permits to target on the interactions at the beginning of the mechanism, focusing only on Coulombic interactions of the reactants, taken as monomers, and the difference of energy between the HOMO and the LUMO.

**Keywords:** Density Functional Theory (DFT), Conceptual DFT, Electron Localization Function (ELF), Chemical reactivity, Reactivity descriptor

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