

ERC Consolidator Grant 2019 Research proposal [Part B2]

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a State-of-the-art and objectives

a.1 Background

The interaction of light and matter is central in chemistry, physics, and biology, playing a significant role in the proper description of several key physical, chemical and biological processes, e.g., photovoltaic devices [1], the photophysics of vision [2], and photochemistry in general [3–9]. At the very heart of photochemistry lies the subtle role played by the low-lying electronic states and their mutual interactions. In general, the correct description of this phenomenon requires to locate with enough accuracy the first few low-lying excited states of the system and to understand how such states interact not only between themselves (conical intersections, spin-orbit effects, ...) but also with other degrees of freedom (coupling with ro-vibrational modes, environment effects, ...). In the case of the photophysics of vision, precious information can be gained by exploring the excited states of polyenes [10–22] that are closely related to rhodopsin which is involved in visual phototransduction [23–31].

After mainly focussing on the calculation of ground-state energies and properties for half a century, accurate electronic structure theory methods have emerged for the computation of molecular excited states in the last decades. There is no doubt that one of the main driving forces behind this evolution has been the emergence of the time-dependent (TD) version [32] of density-functional theory (DFT) [33] which has practically revolutionized computational quantum chemistry due to its user-friendly, black-box nature compared to more expensive complete active space (CAS) methods where one has to choose an active space based on chemical intuition. Although the adiabatic approximation of TD-DFT [32] yields reliable excitation spectra with great efficiency in many cases, fundamental deficiencies have been reported for the computation of extended conjugated systems [34, 35], charge-transfer states [36–40], Rydberg states [35, 41–44], conical intersections [45, 46], and double

excitations [42, 46, 47]. Although, using range-separated hybrids [48, 49] provides an effective solution to the first three cases, one must go beyond the ubiquitous adiabatic approximation to capture the latter two. One possible solution is provided by spin-flip TD-DFT which describes double excitations as single excitations from the lowest triplet state [27, 50–54]. However, major limitations pertain [27]. In order to go beyond the adiabatic approximation, a dressed TD-DFT approach has been proposed by Maitra and coworkers [14, 15] (see also Refs. [19, 21, 22, 47, 55]). In this approach the exchange-correlation kernel is made frequency dependent [56, 57], which allows to treat doubly-excited states. Albeit far from being a mature black-box approach, DFT for ensembles (eDFT) [58–61] is another viable alternative currently under active development [62–69].

More expensive methods, such as CIS(D) [70, 71], CC2 [72, 73], CC3 [74, 75], ADC(2) [76], ADC(3) [77], EOM-CCSD [78] (and higher orders [79, 80]) have been designed to palliate these shortcomings, but they usually require large one-electron basis sets in order to provide converged results. Explicitly-correlated F12 versions of these methods requiring, by design, much smaller basis sets (but large auxiliary basis sets) are yet to become mainstream [81, 82].

Multiconfigurational methods constitute a more natural class of methods to properly treat excited states. Amongst these approaches, one finds complete active space self-consistent field (CASSCF) [83], its second-order perturbation-corrected variant (CASPT2) [84], as well as the second-order n -electron valence state perturbation theory (NEVPT2) [85–87]. However, the exponential scaling of such methods with the number of active electrons and orbitals also limits their application to small active spaces in their traditional implementation [88].

Alternatively to CC and multiconfigurational methods, one can also compute transition energies for various types of excited states using selected configuration interaction (sCI) methods [89–96] which have recently demonstrated their ability to reach near full CI (FCI) quality energies for small molecules [97–119]. The idea behind such methods is to avoid the exponential increase of the size of the CI expansion by retaining the most energetically relevant determinants only, thanks to the use of a second-order energetic criterion to select perturbatively determinants in the FCI space [100, 102, 104, 106, 109, 110, 112, 120, 121]. However, although the “*exponential wall*” is pushed back, this type of methods is only applicable to molecules with a small number of heavy atoms with relatively compact basis sets.

In summary, each method has its own strengths and weaknesses, and none of them is able to provide accurate and reliable excitation energies in all scenarios. The aim of **PTEROSOR** is to pursue a different avenue to obtain excited states with the purpose of palliating some of the well-known shortcomings of DFT, EOM-CC and GW (in particular). Moreover, **PTEROSOR** is also designed to advance our knowledge on non-Hermitian Hamiltonians and their use in the computation of excited states.

a.2 PTEROSOR’s aims



PTEROSOR proposes a shift in paradigm. Instead of using the aforescribed excited-state methods, we aim at developing **a totally novel approach for obtaining excited-state energies and wave functions by exploiting the properties of non-Hermitian Hamiltonians**. In particular, we propose to investigate \mathcal{PT} -symmetric Hamiltonians which can be seen as complex extensions of conventional Hermitian Hamiltonians while retaining a real energy spectrum [122]. Our key idea is to analytically continue (via the complex plane) conventional electronic structure methods in order to obtain excited states. Indeed, through the complex plane, ground and excited

states are naturally connected and are smooth and continuous analytic continuation of one another. Our plan is to thoroughly study both single-determinant methods (such as HF and DFT) as well as correlated methods like CC and GW. Moreover, we will use these tools to gain new insight into the convergence properties of perturbative methods in which singularities, also known as exceptional points, dictates the radius of convergence of the perturbative series. All the new features developed during the lifetime of **PTEROSOR** will be implemented in **QUANTUM PACKAGE**, an open-source, multi-purpose and robust programming environment for quantum chemistry developed in our group. This task is essential to ensure that the theoretical advances emerging from this proposal are translated into useable software that will benefit the scientific community.

a.3 Quantum chemistry in the complex domain

The notion of quantised energy levels is a central feature of Hermitian quantum mechanics. In quantum chemistry, the ordering of the energy levels represents the different electronic states of a molecule, the lowest being the ground state while the higher ones are the so-called excited states. Within this quantised paradigm, electronic states look completely disconnected from one another. However, one can gain a different perspective on quantisation if one extends quantum chemistry into the complex domain. In a non-Hermitian complex picture, the energy levels are *sheets* of a more complicated topological manifold called *Riemann surface* (see Fig. 1), and they are smooth and continuous *analytic continuation* of one another. In other words, our view of the quantised nature of conventional Hermitian quantum mechanics arises only from our limited perception of the more complex and profound structure of its non-Hermitian variant.

Imagine entering a parking garage. Obviously, one can go from one level to another continuously by going around and around using curved ramps designed for such purposes. The level are not quantised, they are only quantised if one looks at a cut through the parking garage. Thankfully, by considering the entire space, the levels are smooth and continuous, similar to the electronic states in a molecule when one looks at them through the complex domain.

Therefore, by analytically continuing the energy $E(\lambda)$ in the complex domain (where λ is a coupling parameter), one can smoothly connect the ground and excited states of a molecule. This connection is possible because, by extending real numbers to the complex domain, one loses the ordering property of real numbers. Hence, one can interchange electronic states away from the real axis, as the concept of ground and excited states has been lost. However, it is far from obvious to design a practical method for such a purpose. The main objective of **PTEROSOR** is to develop a novel theoretical approach to connect, through the complex plane, electronic states. Amazingly, this smooth and continuous transition from one state to another has been recently realised **experimentally** in physical settings such as electronics, microwaves, mechanics, acoustics, atomic systems and optics [123–139].

a.4 Objectives

Upon completion of **PTEROSOR**, we expect four main outcomes:

1. The development of a new class of single-determinant methods based on an analytic continuation of the well-known HF and DFT methods. In particular, we are interested in developing \mathcal{PT} -symmetric versions of single-determinant methods and to further understand the mechanisms behind \mathcal{PT} -symmetry-breaking processes.
2. New insight into the convergence properties of perturbation theory. Moreover, we wish to investigate how suitable are non-Hermitian Hamiltonians as starting points for perturbation theory. Are non-Hermitian Hamiltonians yielding better and faster convergence than Hermitian ones? We hope to be able to provide an answer to this question.
3. The development of non-Hermitian post-HF methods taking explicitly into account the correlation between electrons. In particular, we propose to design an analytic continuation of CC methods. Green’s function-based methods (such as GW) will also be investigated.
4. The efficient and parallel implementation of the aforementioned methods in the electronic structure code **QUANTUM PACKAGE**. We believe that this task is essential to ensure that the theoretical advances emerging from **PTEROSOR** are translated into a useable software that will benefit the electronic structure community.

b Methodology

b.1 \mathcal{PT} -symmetric Hamiltonians

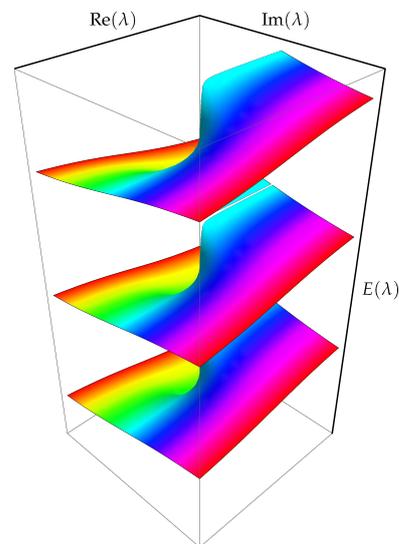


Figure 1: Riemann surface representing the analytic continuation of the energy $E(\lambda)$ in the complex domain.

In order to ensure that a real energy spectrum and probability conservation, it is commonly believed that a physically acceptable Hamiltonian \mathbf{H} must be (Dirac) Hermitian, i.e. $\mathbf{H} = \mathbf{H}^\dagger$, where \dagger stands for complex conjugation and matrix transposition. Although the condition of Hermiticity is sufficient to ensure these properties, it is *not* by any means necessary. In particular, as put into light by Bender and coworkers [122], the family of \mathcal{PT} -symmetric Hamiltonians [122, 141], defined such that $\mathbf{H} = \mathbf{H}^{\mathcal{PT}}$, is a new, more general class of Hamiltonians allowing for the possibility of non-Hermitian and complex Hamiltonians while retaining a physically-sound quantum theory [142]. Here, \mathcal{PT} represents the combined space-time reflexion with

$$\mathcal{P} : \mathbf{p} \rightarrow -\mathbf{p}, \quad \mathbf{r} \rightarrow -\mathbf{r}, \quad (1a)$$

$$\mathcal{T} : \mathbf{p} \rightarrow -\mathbf{p}, \quad \mathbf{r} \rightarrow +\mathbf{r}, \quad i \rightarrow -i, \quad (1b)$$

where \mathbf{p} and \mathbf{r} are the momentum and position vectors of the quantum particle, respectively. Using \mathcal{PT} -symmetric quantum theory, a Hermitian Hamiltonian can be analytically continued into the complex plane, becoming non-Hermitian in the process and exposing the fundamental topology of eigenstates. \mathcal{PT} -symmetric Hamiltonians can be seen as an intermediate class between Hermitian Hamiltonians commonly describing closed systems (i.e. bound states) and non-Hermitian Hamiltonians which are peculiar to resonance phenomena (i.e. open systems) where they naturally appear (see, for example, Ref. [143]). Note that, here, we only consider bound states in closed systems.

The textbook example of \mathcal{PT} -symmetric Hamiltonian is [122]

$$\mathbf{H} = p^2 + ix^3, \quad (2)$$

which has been studied exhaustively by Bender and coworkers [122, 140–142, 144–152]. Although obviously complex, this Hamiltonian has a real, positive spectrum of eigenvalues, none of them being complex!

By generalising the Hamiltonian (2) to the more general parametric family of \mathcal{PT} -symmetric Hamiltonians [122]

$$\mathbf{H} = p^2 + x^2(ix)^\epsilon, \quad \epsilon \in \mathbb{R}, \quad (3)$$

one discovers a more complex structure (see Fig. 2). It has been observed [122] and proved [153] that, for $\epsilon \geq 0$, the Hamiltonian (3) has an entirely positive and real spectrum, while for $\epsilon < 0$, there are some complex eigenvalues which appear as complex conjugate pairs. More specifically, in particular regions of parameter space, some eigenvalues coalesce and disappear by forming a pair of complex conjugate eigenvalues. The region where some of the eigenvalues are complex is called *broken* \mathcal{PT} -symmetric region (i.e. some of the eigenfunctions of \mathbf{H} are not simultaneously eigenfunctions of \mathcal{PT}), while the region where the entire spectrum is real is named *unbroken* \mathcal{PT} -symmetric region. It turns out that the parameter values where the symmetry breaking occurs ($\epsilon = 0$ in Fig. 2) are just those values where *exceptional points* appear.

b.2 Exceptional points

Exceptional points (EPs) [154–157] are non-Hermitian analogs of conical intersections (CIs) [158] where two states become exactly degenerate. CIs are ubiquitous in non-adiabatic processes and play a key role in photochemical mechanisms. In the case of auto-ionizing resonances, EPs have a role in deactivation processes similar to CIs in the decay of bound excited states. Although Hermitian and non-Hermitian Hamiltonians are closely related, the behaviour of their eigenvalues near degeneracies is starkly different (see Fig. 3). In order to highlight these differences, we propose to consider the following 2×2 Hamiltonian commonly used in quantum chemistry

$$\mathbf{H} = \begin{pmatrix} \epsilon_1 & \lambda \\ \lambda & \epsilon_2 \end{pmatrix}, \quad (4)$$

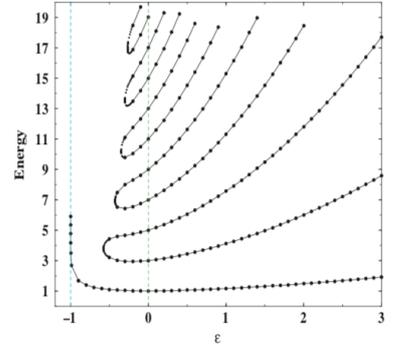


Figure 2: Eigenvalues of the Hamiltonian (3) as a function of ϵ . (Figure taken from Ref. [140].)

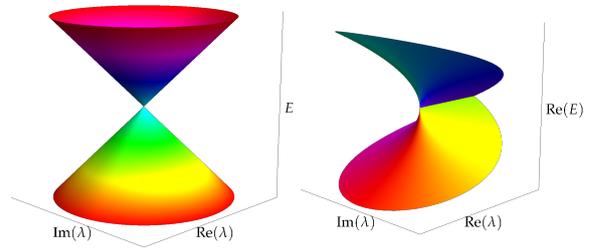


Figure 3: Topological differences between conical intersections (left) and exceptional points (right).

which represents two states of energies ϵ_1 and ϵ_2 coupled with a strength of magnitude λ . This Hamiltonian could represent, for example, a minimal-basis configuration interaction with doubles (CID) for the hydrogen molecule [159].

For real λ , the Hamiltonian (4) is clearly Hermitian, and it becomes non-Hermitian for any complex λ value. Its eigenvalues are

$$E_{\pm} = \frac{\epsilon_1 + \epsilon_2}{2} \pm \frac{1}{2} \sqrt{(\epsilon_1 - \epsilon_2)^2 + 4\lambda^2}, \quad (5)$$

and they are represented as a function of λ in Fig. 4. One notices that the two states become degenerate only for a pair of complex conjugate values of λ

$$\lambda_{\text{EP}} = \pm i \frac{\epsilon_1 - \epsilon_2}{2}, \quad \text{with energy} \quad E_{\text{EP}} = \frac{\epsilon_1 + \epsilon_2}{2}, \quad (6)$$

which correspond to square-root singularities in the complex- λ plane (see Fig. 4). These two λ values, given by Eq. (6), are the so-called EPs and one can clearly see that they connect the ground and excited states. Starting from λ_{EP} , two square-root branch cuts run on the imaginary axis towards $\pm i\infty$. In the real λ axis, the point for which the states are the closest ($\lambda = 0$) is called an avoided crossing and this occurs at $\lambda = \text{Re}(\lambda_{\text{EP}})$. The ‘‘shape’’ of the avoided crossing is linked to the magnitude of $\text{Im}(\lambda_{\text{EP}})$: the smaller $\text{Im}(\lambda_{\text{EP}})$, the sharper the avoided crossing is.

Around $\lambda = \lambda_{\text{EP}}$, Eq. (5) behaves as [143]

$$E_{\pm} = E_{\text{EP}} \pm \sqrt{2\lambda_{\text{EP}} \sqrt{\lambda - \lambda_{\text{EP}}}}, \quad (7)$$

and following a complex contour around the EP, i.e. $\lambda = \lambda_{\text{EP}} + R \exp(i\theta)$, yields

$$E_{\pm}(\theta) = E_{\text{EP}} \pm \sqrt{2\lambda_{\text{EP}} R} \exp(i\theta/2), \quad (8)$$

and we have

$$E_{\pm}(2\pi) = E_{\mp}(0), \quad E_{\pm}(4\pi) = E_{\pm}(0). \quad (9)$$

This evidences that encircling non-Hermitian degeneracies at EPs leads to an interconversion of states, and two loops around the EP are necessary to recover the initial energy. Additionally, the wave function picks up a geometric phase (also known as Berry phase [160]) and four loops are required to recover the starting wave function. In contrast, encircling Hermitian degeneracies at CIs introduces only a geometric phase while leaving the states unchanged. More dramatically, whilst eigenvectors remain orthogonal at CIs, at non-Hermitian EPs the eigenvectors themselves become equivalent, resulting in a *self-orthogonal* state [143]. **Exceptional points are going to be our gateway to excited states.** Moreover, as we shall discuss later, although EPs usually lie off the real axis, these singular points are intimately related to the convergence properties of perturbative methods and avoided crossing on the real axis are indicative of singularities in the complex plane.

b.3 Complex adiabatic connection

In one of our recent paper [161], using holomorphic Hartree-Fock (h-HF) [162–164] as an analytic continuation of conventional HF theory, we have demonstrated, on a very simple model, that one can interconvert states of different symmetries and natures by following well-defined contours in the complex λ -plane, where λ is the strength of the electron-electron (e-e) interaction. In particular, by slowly varying λ in a similar (yet different) manner to an adiabatic connection in DFT (we do not enforce a density-fixed path), one can ‘‘morph’’

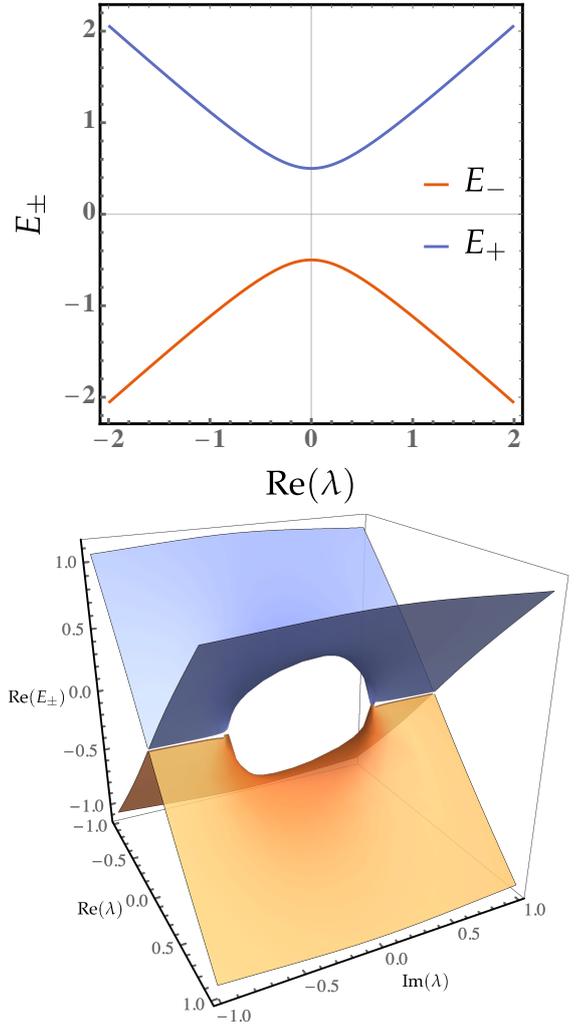
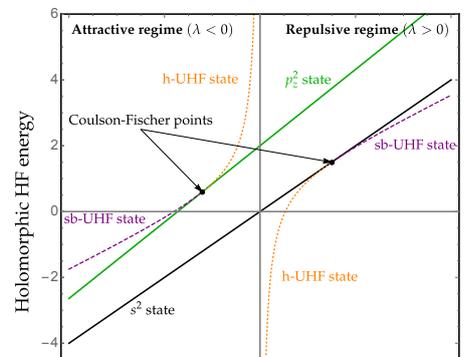


Figure 4: Energies, as given by Eq. (5), of the Hamiltonian (4) as a function of λ with $\epsilon_1 = -1/2$ and $\epsilon_2 = +1/2$.



a ground-state wave function into an excited-state wave function via a stationary path of HF solutions [165]. In such a way, we could obtain a doubly-excited state wave function starting from the ground state wave function. One of the fundamental discovery we made was that Coulson-Fisher points (where multiple symmetry-broken solutions coalesce) play a central role and can be classified as *quasi* exceptional points, as the wave functions do not become self-orthogonal. The findings reported in Ref. [161] represent the very first study of non-Hermitian quantum mechanics for the exploration of multiple solutions at the HF level. It perfectly illustrates the deeper topology of electronic states revealed using a complex-scaled e-e interaction. Through the introduction of non-Hermiticity, we have provided a more general framework in which the complex and diverse characteristics of multiple solutions can be explored and understood. **This proof of concept study will serve as a kick-starter for the PTEROSOR project.** Below, we provide further details on how it can be done.

A proof of concept using a simple model. Let us consider a very simple model system consisting of two opposite-spin electrons interacting through the long-range Coulomb potential but confined to the surface of a sphere of radius R (which will be set to unity for convenience). Moreover, let us consider only two basis functions: a s -type orbital “ s ” and a p -type orbital “ p_z ”. We have $\lambda = 0$ for the non-interacting system and $\lambda = 1$ for the physical (i.e. interacting) system. The “two-electrons-on-a-sphere” paradigm (see Ref. [166] for more details) possesses a number of interesting features [166–169], and it can be seen as a unique theoretical laboratory to test various theoretical methods [169].

Here, we wish to illustrate how one can obtain the restricted HF (RHF) doubly-excited state p_z^2 (at $\lambda = 1$) starting from the RHF ground state configuration s^2 (also at $\lambda = 1$). Similar to the H_2 molecule, we define a unrestricted HF (UHF) wave function

$$\Psi_{\text{UHF}}(\theta_1, \theta_2) = \varphi(\theta_1)\varphi(\pi - \theta_2), \quad (10)$$

and its associated energy as

$$E_{\text{UHF}}(\chi, \lambda) = (1 - \cos 2\chi) + (\lambda/75)(67 - 6 \cos 2\chi + 14 \cos 4\chi), \quad (11)$$

where the spatial orbital is

$$\varphi = s \cos \chi + p_z \sin \chi, \quad (12)$$

χ is the mixing angle between the two basis functions, θ_i is the polar angle of the i th electron. For $\chi = 0$ and $\pi/2$, we recover the RHF s^2 ground state and the p_z^2 doubly-excited state with respective energies $E_{\text{RHF}}^{s^2}(\lambda) = \lambda$ and $E_{\text{RHF}}^{p_z^2}(\lambda) = 2 + 29\lambda/25$. They are represented, as a function of λ , by the black and green solid lines in Fig. 5. By ensuring the stationarity of the UHF energy, i.e., $\partial E_{\text{UHF}}/\partial \chi = 0$, one gets

$$E_{\text{UHF}}(\lambda) = -75/(112\lambda) + 25/28 + 59\lambda/84. \quad (13)$$

For $\lambda > 3/2$, the UHF wave function is a real-valued “symmetry-broken” UHF (sb-UHF) solution of the ground-state RHF wave function, while it is a real-valued sb-UHF solution of the excited RHF wave function for $\lambda < -75/62$ (purple dashed lines in Fig. 5). For $-75/62 < \lambda < 3/2$, the UHF solution is a holomorphic UHF (h-UHF) solution with pure imaginary coefficients (orange dotted lines in Fig. 5). Its energy, though, still given by Eq. (13), stays real. These energies are represented in Fig. 5 as functions of λ where one can observe two different regimes: the repulsive regime ($\lambda > 0$) and the attractive regime ($\lambda < 0$). The Coulson-Fischer points corresponding to the λ values where the RHF and sb-UHF solutions coalesce are located at the “kissing” points of Eq. (13) with the ground and excited RHF states (black dots in Fig. 5). Note that the h-UHF energy is singular at $\lambda = 0$ due to the self-orthogonality phenomenon (see Chapter 9 of Ref. [143] for a detailed discussion).

The key observation is that the h-UHF solution is a ground state wave function in the repulsive regime but becomes, after going through $\lambda = 0$, an excited state wave function, as shown in Fig. 5. This can be evidenced looking at the number of nodes of the wave function. **Therefore, similar to the adiabatic**

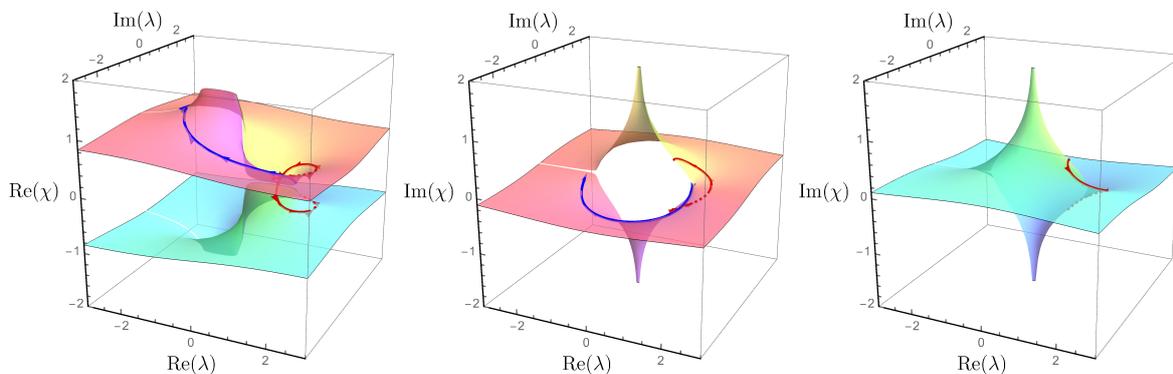


Figure 6: Real (left) and imaginary (center and right) components of the mixing angle χ for the two degenerate sb-UHF solutions as a function of the real and imaginary parts of λ . The colouring indicates the phase of χ . Following a path once around the branch point at $\lambda = 3/2$ interconverts the two sb-UHF solutions (solid red), whilst completing a second rotation returns the solutions to their original states (dashed red). The adiabatic contour enabling a smooth transition from the ground state to the excited state is represented by the solid blue curve.

connection in DFT, by constructing a complex adiabatic path from the repulsive to the attractive regime (i.e. slowly varying the e-e strength from one point to the other), one can “morph” a ground state wave function into an excited state wave function. However, because of the singularity of the holomorphic energy at $\lambda = 0$, one cannot stay on the real axis to connect the repulsive and attractive states, i.e. it does not provide a smooth transition of the wave function coefficients. Luckily, we know, thanks to complex analysis, that an alternative way of getting from positive to negative real numbers is to follow a contour around the logarithmic branch cut running from the repulsive Coulson-Fischer point (see Fig. 6). In such a way, one can ensure a smooth transition of the wave function coefficients from the repulsive to the attractive states.

The complex adiabatic path followed to obtain the physical transition $s^2 \rightarrow p_z^2$ (at $\lambda = 1$) is shown in Fig. 7. Starting on the RHF ground state wave function at $\lambda = 1$, one increases λ in order to reach the repulsive Coulson-Fischer (branch) point at $\lambda = 3/2$. From this point, one follows the complex contour represented in the right panel of Fig. 7 in order to avoid the branch cut running along the real axis. Doing so, one ends up on the excited sb-UHF state where one can then increase λ up to the attractive Coulson-Fischer point at $\lambda = -75/62$. From here, one can adiabatically follow the p_z^2 RHF state up to $\lambda = 1$, completing the complex adiabatic connection path.

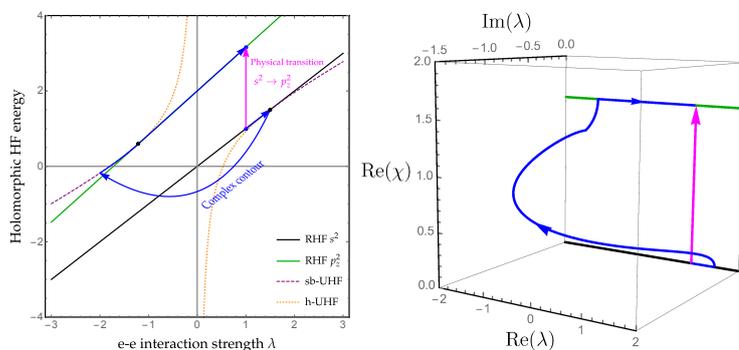


Figure 7: Complex adiabatic connection path followed to obtain the physical transition $s^2 \rightarrow p_z^2$ (at $\lambda = 1$).

b.4 Work plan

PTEROSOR is organised in 4 work packages (WPs), each of them being divided in well-defined tasks. These work packages are largely independent although WP2 and WP3 will benefit from the theoretical advances accomplished during WP1. The PTEROSOR team will carry out all the tasks under my supervision. The aforementioned analytic continuation of quantum chemistry methods puts forward novel strategies to study excited states requiring the design of novel computational tools and methods. This will be addressed in the first three work packages. WP4 deals with their implementation in the electronic structure code [QUANTUM PACKAGE](#) which is currently being developed in our team.

b.4.1 WP1: Single-determinant methods

The first work package proposes to study the so-called single-determinant methods such as HF and DFT. We believe that it is paramount to thoroughly “dissect” these two methods as HF theory performs a pivotal role in quantum chemistry providing a mean-field platform upon which electron correlation can be computed, and DFT is indisputably the most widely-used method in electronic structure calculations.

Task 1.1— Further understanding of the HF energy landscape. Our primary task is to further understand the plethora of h-HF solutions forming this intricate energy landscape. To do so, we propose to use the same system as in Ref. [161] (which consists of two electrons restricted to remain on the surface of a sphere [166, 170]) and to push further its analysis. This simple system, also known as spherium, provides a unique paradigm to study electronic correlation effects from the weakly correlated regime to the strongly correlated regime, since the mathematics are simple while the physics is rich [166–169, 171–182]. In particular, the study of Ref. [161] only considers a minimal basis and a certain type of symmetry-broken solutions. We are eager to consider a larger number of basis functions and more complex symmetry-breaking processes. Moreover, we are contemplating studying other systems like the Hubbard model as well as small diatomic molecules to see how transferable are the results obtained during this task. Using a (hyper)spherical parametrisation of the occupied orbital [see Eq. (12)], we should be able to investigate, in details, the different h-HF solutions in the attractive and repulsive regimes for larger numbers of basis functions. For example, in the three-basis function case (adding a d_{z^2} basis function), this parametrisation reads

$$\varphi = s \cos \phi \sin \theta + p_z \sin \phi \sin \theta + d_{z^2} \cos \theta. \quad (14)$$

This procedure can be easily generalised to larger numbers of basis functions. Moreover, we would like to consider symmetry-broken RHF solutions, which have the form

$$\Psi_{\text{RHF}}(\theta_1, \theta_2) = \varphi(\theta_1)\varphi(\theta_2). \quad (15)$$

They might evidence some new hidden connections between states of different natures. For example, it might be possible to link RHF and UHF solutions by following new complex contours. Of particular interest is a deeper understanding of the quasi-EPs in λ -space where symmetry-broken solutions coalesce. Some solutions may not actually exhibit EPs and some of them may be off the real axis. Moreover, it might be possible to have solutions which are never real and stay complex for any value of λ . Their physical significance will be investigated. At this stage, we claim that different flavours of quasi-EPs points may exist depending on the nature of the energy function before and after the EP. For example, some solutions might be real in the sb-UHF region and become complex when they enter the holomorphic region. We believe that, in that case, the topology of the EP might differ from what we have already observed. Finally, it is crucial to understand the interconnection between excited states. Are they forming a well-organised structure like in Fig. 1 or a more complex structure with more subtle connections between excited states? In Ref. [171], we have observed that the excited states of Wigner crystals are interconnected within the HF manifold, forming a “fountain” of saddle points.

Risk level: LOW. The risks for this task are low as it is guaranteed that we are going to discover some interesting new features. However, we might face technical difficulties due to the exponential increase of the number of HF solutions with respect to the number of basis functions.

Task 1.2— Towards a \mathcal{PT} -symmetric theory for single-determinant methods. Holomorphic HF is a very useful tool which provides an analytic continuation of conventional HF theory. However, it is not *per se* a \mathcal{PT} -symmetric theory. The first part of *Task 1.2* will be to study in which conditions h-HF is a \mathcal{PT} -symmetric theory. The important factor for consideration is the symmetry of the one-electron effective Hamiltonian, the Fock operator. The challenge is therefore to identify the conditions for a \mathcal{PT} -symmetric Fock operator. Moreover, because the HF wave function is built as a Slater determinant of the eigenfunctions of the Fock operator, the link between the symmetry of the Fock operator and the overall HF wave function is not trivial. Another possibility would be to directly study the symmetry of the one-electron density which completely determines the symmetry of the Fock operator. To do so, we may have to work in a spinor basis as the \mathcal{PT} operator also reverses orbitals and spin angular momentum in the case of fermions. Another related question would be to know whether \mathcal{PT} can be defined as a genuine symmetry, similar to spatial and spin symmetries. In most practical applications, the HF wave function is required to display at least some of the symmetries of

the exact wave function. For example, RHF is chosen to be an eigenfunction of the spin operators \mathcal{S}^2 and \mathcal{S}_z . In UHF, the wave function is allowed to break symmetry under \mathcal{S}^2 but not \mathcal{S}_z . Yet another HF flavour, generalised HF (GHF), imposes none of the correct symmetries [183]. During this task we would like to answer the following question: can \mathcal{PT} symmetry be considered as a new type of symmetry one can break similar to the symmetries associated with \mathcal{S}^2 and \mathcal{S}_z ? Related to this point, we note that symmetry-breaking and restoration techniques are promising methods to catch strong correlation at polynomial cost and are actively developed [184–187]. The main goal of *Task 1.2* is to design a proper \mathcal{PT} -symmetric version of quantum chemistry single-determinant methods. To do so, we believe that the crux lies in the definition of the inner product [142]. Indeed, in the case of \mathcal{PT} -symmetric Hamiltonians, in order to obtain a well-defined quantum theory, one has to be extra careful in the definition of the metric to ensure positive probabilities. To obtain a proper quantum theory, Bender et al. [145] have shown that one needs to introduce a new operator called \mathcal{C} which is defined, a posteriori, by the eigenfunctions φ_i of the problem, i.e. $\mathcal{C} = \sum_i |\varphi_i\rangle\langle\varphi_i|$. This operator defines the inner product and one has $\langle a|b\rangle_{\mathcal{CPT}} = \langle \mathcal{CPT}a|b\rangle$. For example, in h-HF theory [162–164], the complex conjugation of orbital coefficients is simply removed from the HF equations, resulting in a non-Hermitian Hamiltonian and an energy function that is complex analytic with respect to the orbital coefficients. This strategy is not always suitable to ensure \mathcal{PT} -symmetric requirements. The very exciting feature here is that we may have to use a different inner product depending on the type of symmetry-broken solutions!

Risk level: HIGH. The risks associated with this task are high as it is very exploratory and we may struggle to design a \mathcal{PT} -symmetric version of HF and DFT. Nonetheless, in the worst-case scenario, it will provide new insight into symmetry-breaking processes and their multiple solutions. The reward will be very high in case of success as it will deliver a new type of single-determinant method with very peculiar and mathematically-sound properties.

Task 1.3— A time-independent DFT formalism for excited states. Within Kohn-Sham (KS) DFT, the standard paradigm to obtain excited states is TD-DFT [32], and, in its adiabatic approximation, it yields reliable excitation spectra with great efficiency in many cases. Nevertheless, fundamental deficiencies have been reported in various cases [34–39, 41–47]. More importantly here, TD-DFT is well known to be unable to describe certain types of excited states such as charge-transfer [36–40], Rydberg [35, 41–44] and doubly-excited [42, 46, 47, 121] states. Some of these failures can be tracked down to the inadequacy of the ground state KS orbitals to describe these excited states [188–190]. Similarly to HF, KS-DFT exhibits many broken-symmetry solutions that one can follow to walk through the complex plane via a complex adiabatic connection. Therefore, by extending our work of Ref. [161] and detailed above, we propose to take advantage of the holomorphic and/or \mathcal{PT} -symmetric version (see *Task 1.2*) of KS-DFT to obtain excited states of different natures. Using this time-independent formalism, we are curious to know if the interconnection between ground and excited states is topologically different depending on the nature of the excited states. Obviously, this kind of formalism will not be adequate for all types of excited states. Indeed, open-shell singlet states are, by nature, badly described by single-determinant methods. To palliate this, we propose to investigate whether or not a complex adiabatic connection formalism could be applied to DFT for ensembles [62–69] for which a generalised adiabatic connection has been developed [191]. Also, we believe that it would be particularly interesting to study the influence of the quality of the exchange-correlation (xc) functional on the location of the Coulson-Fisher points. Indeed, the universal, exact xc functional should *never* break any symmetry, implying the total absence of these EPs. Consequently, the location of the EPs could be a way of probing the accuracy of the xc functionals: these points should move towards $\pm\infty$ when the xc functional becomes more accurate.

Risk level: MEDIUM. The risks for this task are mild but the reward is very high as it could deliver a new way of computing excitation energies at a low computational cost using the DFT machinery.

Task 1.4— Following stationary states in the complex plane. From a strict computational point of view, converging single-determinant calculations on excited states is not a straightforward task as the variational principle will always lean towards the lowest-energy solution. Following excited-state solutions when one varies λ (or other parameters such as the bond length) is even harder. Therefore, peculiar strategies must be designed in order to stay on the desired solution. Moreover, in the complex plane, due to the lack of ordering, one has to employ a complex extension of the variational principle [143]. Therefore, *Task 4.1* deals with the development of a pragmatic yet efficient method to following stationary states in the complex plane. More explicitly, in the spirit of the maximum overlap method [189, 190, 192], we propose to follow a given solution

by populating the orbitals resembling the most to the previous iteration. This can be done by computing the overlap between the previous and current set of molecular orbitals. This procedure has been shown to be fairly robust and does not involve any additional computational cost. However, such method must be adapted to the complex domain. We also plan on adapting a recent algorithm to locate EPs for our purposes [193, 194]. Indeed, locating EPs is going to be crucial in the present context as they are going to be points where one can link ground and excited states.

Risk level: LOW. The principal risks are of technical order here. Self-orthogonal states might bring some complications while following states or locating EPs.

b.4.2 WP2: Perturbation theory

The main goals of PTEROSOR’s second work package is to gain further insight into the convergence properties of perturbation theory and to investigate how suitable are non-Hermitian Hamiltonians as starting points.

Task 2.1— Towards a better understanding of perturbation theory. Within perturbation theory, the Schrödinger equation is usually rewritten as

$$\mathbf{H}\Psi(\lambda) = (\mathbf{H}^{(0)} + \lambda\mathbf{H}^{(1)})\Psi(\lambda) = E(\lambda)\Psi(\lambda), \quad \text{with} \quad E(\lambda) = \sum_{k=0}^{\infty} \lambda^k E^{(k)}. \quad (16)$$

However, it is not unusual that the series $E(\lambda)$ has a radius of convergence $|\lambda_0| < 1$. This means that the series is divergent in the domain $|\lambda| < |\lambda_0|$, hence for the physical system at $\lambda = 1$. As eluded above, $|\lambda_0|$ is determined by the location of the singularity of $E(\lambda)$ closest to the origin. These singularities are nothing but EPs at λ_0 and λ_0^* . In the first task of WP2, we propose to thoroughly investigate the connection between Coulson-Fisher quasi-EPs and the radius of convergence of Møller-Plesset perturbation theory (MPPT). MPPT has the particularity of relying on a HF wave function as a zeroth-order wave function. However, the flavour of HF one can select (restricted, unrestricted, generalised, holomorphic, ...) is up for grabs, and the convergence properties of the MPPT series will drastically change depending on this choice. For example, MPPT calculations based on UHF wave functions have shown to be slowly convergent due to spin contamination while RHF-based MPPT calculations can be divergent [195, 196]. Although MPPT is widespread in the community, its convergence properties have not, to the very best of our knowledge, attracted much attention [197–199]. We believe that they deserve greater understanding, particularly in a non-Hermitian setting. Following Olsen’s footsteps [198], we will use a simple 2×2 model to start with, and slowly build up on these results. Moreover, we are interested in testing some of the summation techniques for divergent series, such as Padé approximant, Shanks transformation and Richardson extrapolation [200].

Risk level: MEDIUM. The risks associated with this task are mild, and in any scenario, this will provide a greater understanding of perturbation theory in general.

Task 2.2— Hermitian vs \mathcal{PT} -symmetric Møller-Plesset perturbation theory. Mostafazadeh has shown that, for any \mathcal{PT} -symmetric Hamiltonian \mathbf{H} , there exists an antisymmetric Hermitian operator \mathbf{Q} such as the operator

$$\mathbf{h} = e^{-\mathbf{Q}/2} \mathbf{H} e^{\mathbf{Q}/2} \quad (17)$$

is Hermitian [201–204]. In plain words, a non-Hermitian Hamiltonian that has an unbroken \mathcal{PT} -symmetry can be converted by means of a similarity transformation to a physically equivalent Hermitian Hamiltonian. Unfortunately, it has been observed that the Hermitian operator \mathbf{h} is sometimes much more complicated than its \mathcal{PT} -symmetric version \mathbf{H} . For instance, a local \mathcal{PT} -symmetric Hamiltonian can be converted to a highly non-local Hamiltonian via such similarity transform [148, 204, 205]. This hints that the \mathcal{PT} -symmetric Hamiltonian might be a more convenient object to work with than its Hermitian counterpart. In the context of MPPT, we propose to answer the following question: is the non-Hermitian Hamiltonian more suitable as reference Hamiltonian $\mathbf{H}^{(0)}$ than the Hermitian one? Indeed, as mentioned in *Task 2.1*, the radius of convergence is intimately connected to the location of singularities in the complex plane; these singularities are, themselves, linked to the choice of $\mathbf{H}^{(0)}$. Really, it depends on our ability of selecting a zeroth-order Hamiltonian such as \mathbf{H} does not have any EP inside the unit λ circle. A different choice — Hermitian or not — would then move these singularities to a different location with a direct consequence on the radius of convergence. Two questions have to be addressed regarding the choice of a non-Hermitian zeroth-order Hamiltonian: i) are the terms $E^{(k)}$

of the perturbative series easier/cheaper to compute? ii) is the radius of convergence consistently larger? As in *Task 2.1*, we will consider a 2×2 model as a first, simple example and slowly increase the complexity of our problem. The effect and nature of the similarity transform will be thoroughly investigated as it is intimately connected to the \mathcal{C} operator defined above ensuring a physically-sound inner product for \mathcal{PT} -symmetric Hamiltonians.

Risk level: MEDIUM. Similar to the previous task, the risk level here is mild and the reward is high. Finding a new starting point for perturbation theory with a larger radius of convergence could potentially be highly beneficial to the electronic structure community. Moreover, similarity transform-based methods are steadily appearing in quantum chemistry and the present results might drive further the development of such methods.

b.4.3 WP3: Correlated methods

The third work package deals with the so-called correlated or post-HF methods which takes explicitly into account the correlation between electrons.

Task 3.1— Analytic continuation of coupled cluster methods. The CC family of methods offers a powerful wave function approach for the description of most chemical systems and is well regarded as the gold standard of quantum chemistry. Similar to HF, CC methods, because of their non linearity, exhibit a large manifold of genuine real and complex solutions exhibiting unbroken or broken symmetry [206]. In the first task of WP3, we propose to apply a similar complex adiabatic connection as the one described in *Task 1.1* (see also Ref. [161]) to CC methods. This would allow us to access, through the complex plane, excited states at the CC level without the need of a time-dependent formalism such as EOM-CC. In particular, we are eager to know if the obtention of CC excited states via the complex plane could potentially cure some of the drawbacks of EOM-CC. For example, it is possible to rely on high-level truncation of EOM-CC in order to capture double excitations as shown in recent studies [111, 121, 207]. However, in order to provide a satisfactory level of correlation for such states, one must, at least, introduce contributions from the triple excitations. In practice, this is often difficult as the scalings of CC3, EOM-CCSDT, and EOM-CCSDTQ are N^7 , N^8 and N^{10} , respectively (where N is proportional to the size of the system), obviously limiting the applicability of this strategy to small molecules. In order to walk serenely on complex adiabatic paths, we must create an effective analytic continuation of CC methods. We believe that three main strategies could be potentially followed to achieve such task. First, one could perform an analytic continuation of the HF orbitals and energies (as described above) and perform a conventional CC calculation on top of it. The second option would be to analytically continue the CC amplitudes (instead of the orbital coefficients), while retaining a conventional set of HF orbitals and energies. Third, one could combine the first two options and analytically continue both the HF orbitals and the CC amplitudes. We will obviously investigate all these options. Moreover, similar to *Task 1.2*, we will analyse if a \mathcal{PT} -symmetric version of CC can be designed. At this stage, we think that a way of designing a \mathcal{PT} -symmetric CC method is to make the coupling between states pure imaginary. Our preliminary analysis based on a model system has shown that it is possible to link ground and excited states in such a way. The points where the electronic states become degenerate correspond to \mathcal{PT} phase transitions.

Risk level: HIGH. This particular task is one of the most risky task of the PTEROSOR project. However, it is also one of the most rewarding. Moreover, our very preliminary investigation is very encouraging and we are eager to push further this analysis if the present proposal is funded.

Task 3.2— Fixing up GW. The idea behind Green’s function methods, and more particularly its so-called GW approximation, is to transform an unsolvable many-electron problem into a set of non-linear one-electron equations. GW allows an explicit incorporation of electron correlation via a sequence of self-consistent steps [208], known as Hedin’s equations (see Fig. 8). Important experimental properties such as ionisation potentials, electron affinities as well as spectral functions, which are related to direct and inverse photo-emission, can be obtained directly from the Green’s function [209, 210]. Historically, GW methods have been mostly applied to solids [209]. However, studies on atoms and molecules have been flourishing in the past ten years [211, 212]. Nowadays, efficient implementations of GW

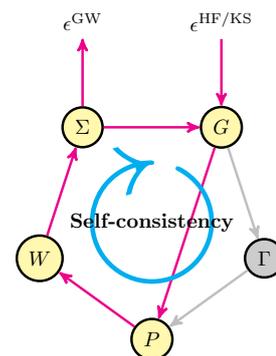


Figure 8: Hedin’s pentagon [208]: the red path shows the self-

methods for localised basis sets are available in several softwares [212–214], and we have recently implemented GW in [QUANTUM PACKAGE](#) in order to perform such types of calculations [111, 215]. There exists many flavours of GW. The simplest and most popular variant is G_0W_0 [216], which has been widely used in the literature [211]. Although G_0W_0 provides accurate results, due to its perturbative nature, it is strongly starting-point dependent. In the present context, we will focus our interest on “*quasiparticle self-consistent*” GW (qsGW) [217–219], where one updates both the quasiparticle energies and the corresponding “Dyson” orbitals. One of the undesirable feature of qsGW is the brutal “*Hermitisation*” (via symmetrisation) of the naturally non-Hermitian self-energy: $\tilde{\Sigma} = (\Sigma + \Sigma^\dagger)/2$. In *Task 3.2*, we are interested to know what are the consequences of this brute force symmetrisation. Our plan is to treat the non-Hermitian part of the self-energy $\Sigma - \tilde{\Sigma}$ as a perturbation of its Hermitian part $\tilde{\Sigma}$. Using this straightforward decomposition, one can show, using perturbation theory, that the first non-vanishing correction is obtained at second order in perturbation at *no extra cost* as all the required quantities have been already calculated during the diagonalisation of $\tilde{\Sigma}$. More precisely, one can show that all odd order contributions are zero, and only even orders contribute. Resummations via Padé approximant techniques will also be investigated [220].

Risk level: MEDIUM. We believe that the risks associated with this task are mild. One potential issue would be to face a divergent perturbative series. However, as mentioned above, tools do exist in order to sum divergent series. GW methods are slowly becoming mainstream in chemistry and it is important to pursue their development and better understand their underlying approximations.

b.4.4 WP4: Implementation

A large amount of time and effort will be dedicated to the efficient and parallel implementation of the ideas developed in WP1, WP2 and WP3. This last work package is fairly independent of the first three and will run continuously throughout the five years of the project. During the last few years, we have developed in our team an open-source, multi-purpose and robust programming environment for quantum chemistry named [QUANTUM PACKAGE](#). Its current capabilities range from high-level *ab initio* methods (such as selected CI [103, 111, 112, 121]) to range-separated DFT methods [221], as well as multi-reference methods [222–224]. [QUANTUM PACKAGE](#) strives to allow easy implementation, collaborative work and experimentation of new methods, while making parallel computation as simple and efficient as possible on modern supercomputer architectures. The second version of [QUANTUM PACKAGE](#) has just been released and the associated article detailing its various features is currently under preparation. **All the new features developed during the lifetime of PTEROSOR will be implemented in [QUANTUM PACKAGE](#).** This task is essential to ensure that the theoretical advances emerging from this proposal are translated into useable software that will benefit the electronic structure community.



b.5 Feasibility and risk assessment

PTEROSOR is a risky project which, I believe, lies perfectly in a “*high risk/high gain*” philosophy. The use of non-Hermitian Hamiltonians in the computation of excited states is in its infancy, and many exciting properties remain to be found and understood. In the worst-case scenario, PTEROSOR will significantly advance our knowledge in this pristine research field. In the best-case scenario, it will deliver to the entire scientific community a completely novel computational tool to study excited states. Here, we propose to embrace a global and detailed study of non-Hermitian quantum mechanics for, in particular, the determination of excited-state properties.

c Resources

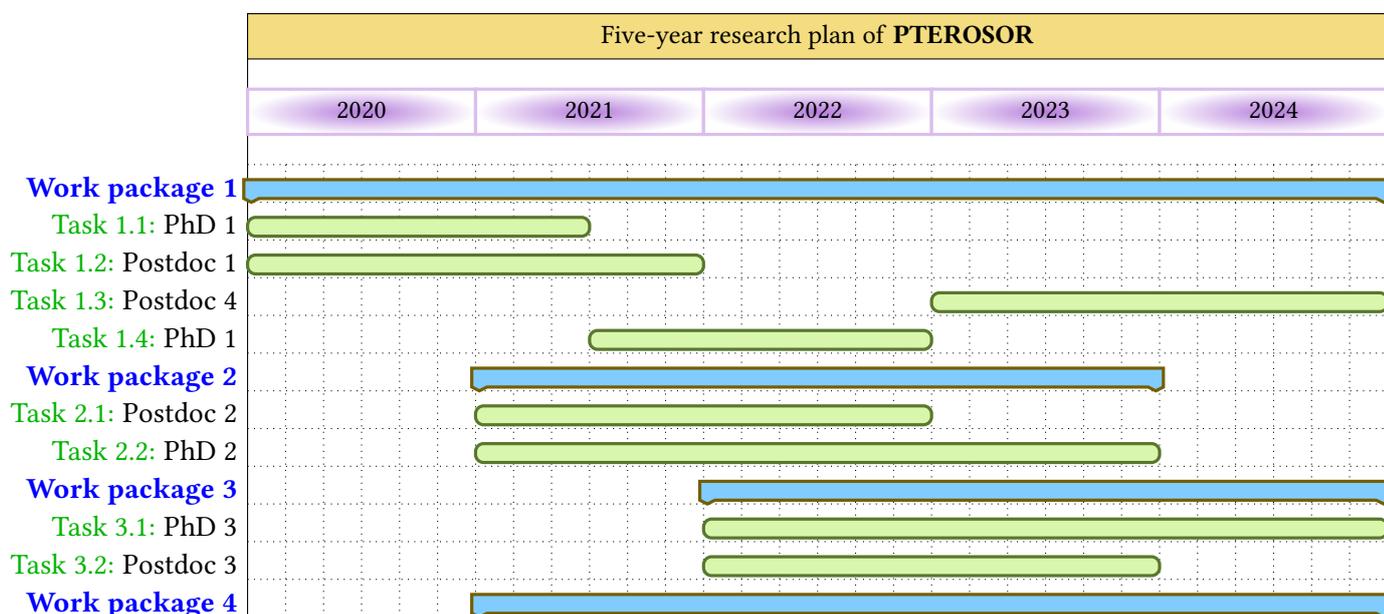
c.1 PTEROSOR’s team

The research team will be composed by the PI, 3 PhD students, 4 postdocs and two CNRS researchers (Anthony Scemama and Michel Caffarel) who will devote 15% and 10% of their time to the PTEROSOR project. PhDs and postdocs will be committed to the project for three and two years (respectively). Each group member will

be briefed about the progress of the project in a monthly meeting. I will assign to each PhD student a postdoc as a mentor who will help them with their day-to-day issues. I will also have weekly research meetings with each of them to follow the progress of their tasks. The **PTEROSOR** team will also include two complementary CNRS researchers from the *Laboratoire de Chimie et Physique Quantiques* (LCPQ). The three of us are actively collaborating on various subjects [103, 109–112, 121].

- **Anthony Scemama** (research engineer) is an expert in information technology in general, and in HPC in particular. Dr Scemama’s involvement is essential to ensure that the theoretical advances emerging from **PTEROSOR** are translated into useable, highly efficient and sustainable softwares that will benefit the local and global scientific community.
- **Michel Caffarel** is an expert in correlated methods where he has made several seminal contributions in the last 25 years. His mentoring and experience will be extremely valuable to ensure a successful outcome for this ambitious research project.

c.2 Task distribution



WP1: We will devote one PhD student (PhD 1) and two postdocs (Postdoc 1 & 4) to the first work package. *Task 1.1* and *Task 1.2* require a good background in mathematics. The PhD student and the postdoc will learn how to use the program **MATHEMATICA** which will be used to solve difficult integrals, manipulate large mathematical expressions and simplify them. The second half of PhD 1 will be devoted to a more technical part (*Task 1.4*) which will require good skills in computer science and knowledge in programming languages such as Fortran or C++. Postdoc 4 will be entirely dedicated to *Task 1.3* which deals with the development of a time-independent non-Hermitian DFT method. This will require a fair amount of theoretical work as well as implementation.

WP2: One PhD student (PhD 2) and one postdoc (Postdoc 2) will be devoted to WP2. *Task 2.1*, which requires stronger mathematical skills and experience in perturbative methods will be carried out by Postdoc 2, while *Task 2.2* which will require more time and testing, will be handled by PhD 2. Again, the **MATHEMATICA** software will be used during preliminary studies on the simple 2×2 model. For larger systems, we will develop a specific module in **QUANTUM PACKAGE** for implementing our non-Hermitian perturbative methods.

WP3: For the third work package, we will also dedicate one PhD student (PhD 3) and one postdoc (Postdoc 3). In particular, *Task 3.1* will require a good knowledge in correlated electronic structure theory and we will seek a strong PhD candidate for this task. *Task 3.2* will be carried out by Postdoc 3 with a good knowledge of condensed matter methods as requirement. A general CC module will be developed in **QUANTUM PACKAGE** specifically for *Task 3.1*, while we will rely on the current GW module for *Task 3.2*. The new CC module will include conventional CC methods as well as the new non-Hermitian variants developed in **PTEROSOR**.

WP4: The fourth work package will run through the entire lifetime of the project. I would like that each PhD student and postdoc contributes to the implementation of the methods developed in **PTEROSOR**. Obviously, this might be weighted accordingly to the personal coding skills of each group member. As mentioned earlier, Anthony Scemama will be actively involved in WP4 as he is an expert in HPC and information technology in general.

My tasks involve supervision of the whole project, training of the PhD students and the postdocs, and reorientation of different parts of the project if necessary. The whole **PTEROSOR** team will meet once a week to review the relevant aspects of the project, and I will meet with each member individually once or twice a week (depending on the personal advances) to discuss the latest developments. Twice a month, we will organise Literature Clubs, where we will review the most important papers in the literature that have been published recently. Every second month, we will also organise a series of lectures to cover certain research topics. Some people from other groups will also join these discussions. The size of the team is adequate to carry out the project and it has been designed in such a way that my whole group (including the current members) never has more than six people. Because the postdocs will help with the day-to-day tasks of the PhD students, I am positive I can manage a group of this size. During the third year of the project I will organise a mid-term workshop. This workshop will be open to a maximum of 50 people (including the **PTEROSOR** team) where I will invite several renowned experts in the field to exchange our most recent outcomes and encourage collaboration with our group. During the last year of **PTEROSOR**, I will also organise the final conference dedicated to new methodologies for excited states.

PTEROSOR is expected to produce about 25 peer-review papers related with the objectives planned in the proposal, all of which will be published in an open-access format in the leading journals of the field (PRL, JCTC, PRA, JPCL, PCCP, PRB, JCP, etc.). I will participate in most of the main international conferences of my field (WATOC, ICQC, ACS meetings, etc) and I will encourage the team members to take part too. I have allocated part of the budget to cover one conference per PhD every year, plus their attendance at a Summer School on electronic structure methods (the one organised in Sicily is currently the most adequate one) and the national meeting of French computational chemists (once every two years). For the postdocs, I encourage two conferences per year and, if they need further training also their participation at a Summer School. In addition, the PhD and postdocs will participate in the institute (IRSAMC) joint seminar program and deliver talks in front of a more general audience. The whole team will participate in numerous outreach activities organised by IRSAMC and the LCPQ, which is highly committed to communication and dissemination events among the general public. We will participate in “*Pint of Science*” that organises talks for the general public in local pubs of Toulouse several times a year, as well as other dissemination activities.

c.3 Budget

- Personnel costs: the largest share of resources will be dedicated to salaries.
 - **PI**: the PI is a CNRS researcher and the requested amount corresponds to 75% of his time over five years.
 - **Senior staff**: as stated above, two CNRS employees (Anthony Scemama and Michel Caffarel) will partially work on the project. They will be actively involved in the co-supervision of students and postdocs. Anthony Scemama and Michel Caffarel have agreed to dedicate 15% and 10% of their time to this ERC project.
 - **Post-docs**: 4 postdocs will be recruited in Toulouse, 8 years in total, with a one-year overlap between each contract.
 - **Students**: 3 PhDs will be recruited at the LCPQ. A PhD lasts 3 years in France.
- Other direct costs:
 - **Travels**: the PI and his team will have available budget to attend and travel to international conferences and workshops: €6 000/year for PI (€30 000), €5000 for the senior staff (€50 000); €4 000/year for postdocs (€32 000); €3 000/year for PhDs (€27 000). Overall, this will €95 000 for travel and €37 000 of fees and (i.e. other costs). This will cover flights, accommodation and registration fees for international conferences, and will allow the PI and his team to travel to major international conferences such as WATOC (which will be located in Vancouver in 2020).
 - **Equipment**: We do not require any equipment. All the calculations required to successfully complete this research project will be obtained via CPU allocations from **GENCI**, **CALMIP** and **CINES**. Indeed, we have access to millions of CPU hours thanks to our successful grants from CALMIP (allocations 2019-18005) and from GENCI-TGCC (Grant A0040801738). For the latter attribution, we have obtained 3

000 000 CPU hours on the new GENCI machine, Irene. CALMIP's allocation is also 1 500 000 CPU hours.

- **Other:** these are constituted of two separate costs: i) organisation of the mid-term workshop: €40 000 (we want to maintain the cost as low as possible for the attendees so not to screen participations on the basis of the wealth of their group in such transfer-of-knowledge event); and ii) the final conference dedicated to new methodologies for excited states that will be organised: €55 000 (€30 000 for travels and lodging of keynote speakers; €25 000 for organisation).
- **Publications:** The high-impact journals in chemistry and physics (*Nat. Comm.*, *J. Phys. Chem. Lett.*, *Phys. Rev. Lett.*, *J. Chem. Theory Comput.*, etc) are mainly edited by publishers requiring high fees for open access. Therefore, we decided to dedicate a substantial amount to publication costs (€50 000). These costs could also be used to support cover charges.

Cost Category		Total in Euro	
Direct Costs	Personnel	PI	320 820
		Senior Staff	132 755
		Postdocs	434 304
		Students	351 630
		Other	0
	<i>i. Total Direct Costs for Personnel (in Euro)</i>		1 239 509
	Travel		95 000
	Equipment		0
	Other goods and services	Consumables	0
		Publications (including Open Access fees), etc.	50 000
Other (see below)		132 000	
<i>ii. Total Other Direct Costs (in Euro)</i>		277 000	
1 - Total Direct Costs (i + ii) (in Euro)		1 516 509	
2 - Indirect Costs (overheads) 25% of Direct Costs (in Euro)		379 127	
3a) - Subcontracting Costs (no overheads) (in Euro)		0	
3b) - Other Direct Costs with no overheads (in Euro)		0	
Total Estimated Eligible Costs (1 + 2 + 3) (in Euro)		1 895 636	
Total Requested EU Contribution (in Euro)		1 895 636	

Please indicate the duration of project in months:	60
Please indicate the % of working time the PI dedicates to the project over the period of the grant:	75%

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