**Section a. State-of-the-art and objectives**

Polyaromatic hydrocarbons (PAHs) are omnipresent in the interstellar medium (ISM) and take part in its chemical evolution. Their unique stability enables their survival in the harsh environment of the ISM. Despite their importance, the direct molecular mechanisms responsible for their formation are still not known. Photochemistry is expected to play a major role in the chemistry of the ISM; for example, photodissociation or ionization photodissociation can lead to the fragmentation of smaller PAHs or other important molecular species.[1, 2] *Understanding the dynamic taking place in excited electronic states and the ability to model it is crucial to the advancement of our knowledge.*

The field of astrochemistry is rapidly progressing with new data accepted to arrive from the James Webb Space Telescope launched earlier this year, as well as progress made in astrophysics laboratory experiments. Quantum chemistry has a crucial role in deciphering chemical mechanisms at the molecular level and does work hand in hand with experimentalists. Unfortunately, when it comes to astrochemistry photochemical reactions, the quantum chemistry toolbox is lacking in modelling capabilities of excited-state dynamics - and thus cannot supply the missing pieces of the puzzle.

***The goal of this proposal is to fill this gap by building a computationally inexpensive framework within ensemble DFT that will enable the study of excited states' dynamics of large systems.***

#  **Study of photodissociation processes**

Photodissociation of PAHs has been widely studied experimentally both for neutral and cationic species [3-8]. Photochemical evolution of large PAHs has been demonstrated to form C60 [9], and other studies have demonstrated that a major pathway in the photodissociation of PAHs is the loss of C2H2 units [6, 8, 10]. However, very little is known about the underlying mechanism and resulting products. To obtain this information, the aid of quantum chemistry is needed. While accurate modelling requires taking into account the excited states, for practical reasons and the lack of an efficient way to do so, studies have used density functional theory (DFT) and studied possible reaction mechanisms on the *ground state potential* under the assumption that it is thermally excited[11-16].

For example, Chuvilin et al. studied the formation pathway from graphene to fullerene using B3LYP functional with 6-31g\* basis set [17]. In a different study, Zhou et al. studied the fragmentation dynamics of benzene trimer representing a prototype of higher-order aromatic clusters. To model the dynamics of the system *ab-initio* molecular dynamics simulations were performed using DFT with the B3LYP functional and cc-pVDZ basis set, where the population of the vibrational states was determined by Boltzmann distribution [18]. Zhen et al. demonstrated experimentally that under the influence of a strong laser field small PAH clusters converted into larger PAHs. The dimer cations, for example, will photo-dehydrogenate and photo-isomerize and form fully aromatic cations. Possible formation mechanisms were modelled on the ground-state potential using the dispersion-corrected functional B3LYP-D3 to account for the intermolecular forces in the clusters [19]. The dissociation path of dibenzopyrene was studied experimentally by spectroscopy with VUV photons using synchrotron radiation. To model the main dissociation pathways (2H/H2 loss) DFT was used, and the potential energy surfaces were built using B3LYP functional and 6-31G(d,p) [12].

In a recent combined experimental and theoretical study, Kaiser et al. demonstrated the importance of excited-state dynamics on the reaction products. They studied benzyl self-reaction to form phenanthrene and anthracene, demonstrated isomer-selective excited-state dynamics, and showed the important role of excited states in forming aromatic products. To model the process, which includes excited states, they calculated both the singlet and the triplet states using DFT (B3LYP/6-311G(d,p)) [20].

In my laboratory, we modelled chemical growth upon photoionization of different clusters of acetylene, HNC and cyanoacetyle by using DFT with $wB87-X $functional on the ground state of the *cationic system* under the assumption that after the ionization the cation is in its ground state. Upon ionization, we demonstrated the formation of various molecules, including cyclic and bicyclic molecules and nitrogenated PAHs [21-25].

Non-adiabatic relaxation dynamics were incorporated with Time-Dependent DFT (TDDFT) calculations [26, 27]. In the study of the allyl radical and its 1- and 2‑methylated counterparts, excited state energies were also calculated using EOM-CCSD, which gave more accurate excitation energies when compared to the experiments, demonstrating the deficiencies in TDDFT [28].

The dynamic of highly excited PAHs at the femtosecond and attosecond timescale was studied by Marciniak et al.[29]. They suggest a mechanism in which a XUV photon ionizes a molecule and create a hole in the valence shell, which then can lead to the excitation of another electron forming an excited ‘shake-up’ state. The excited molecular cationic state relaxes through a non-adiabatic mechanism. To theoretically model the process, coupled electronic and nuclear dynamics were carried out. The potential energy surfaces were obtained using the algebraic diagrammatic construction (ADC) scheme [30] of the one-particle many-body Green's function. All-in-all 19 geometries were chosen, and for those geometries wave-packet propagation was employed using the multiconfigurational time-dependent Hartree (MCTDH) method [31] to calculate the non-adiabatic relaxation of the states determined by ADC. Due to the huge computational effort of the computational scheme, studies were limited to naphthalene [29]. In a recently published paper, Recio et al. demonstrated experimentally and computationally the importance of intersystem crossing in the entrance channel of the reaction between atomic oxygen and pyridine [32].

To accurately perform the dynamics of excited state on can use multideterminant wave-function methods such as second-order complete active space perturbation theory (CASPT2) [33, 34], second-order perturbation theory restricted active space (RASPT2) [35, 36], or the N-electron valence state perturbation theory (NEVPT2) [37, 38], which have been successful in modelling fragmentation pathways - albeit at high computational cost which limits the system that can be model this way.

The ability to study photochemical reactions requires an efficient way to model the excited-state dynamic - for which currently the toolkit of quantum chemistry is lacking. To **bridge the gap** between the current capabilities of quantum chemistry and the urgent need to model photochemical reactions, **we will develop the computational framework within Ensemble DFT**.

# **Ensemble DFT**

Ensemble DFT is a simple extension to DFT with the potential to solve strong multiconfiguration correlation effects both for the description of the ground and the excited states, with computational scaling similar to DFT. In additionally, it can be used to calculate excited states. ***Thus, this approach bears the potential of enlarging the current capabilities of computational quantum chemistry.***

Ensemble DFT for the description of the excited state is based on Gross Oliveira and Kohn's (GOK) work, which derived the Rayleigh-Ritz variational principle for a general ensemble [39]. The development of ensemble DFT for the description of excited states started in the 1970s, when the methods for excited-state calculations were inaccurate or extremely expensive computationally [40]. However, the development of ensemble DFT was abandoned due to difficulties in the method and the parallel rapid progress and accomplishment of TDDFT. Indeed, today, TDDFT is widely used and successful in many cases. However, there are important phenomena that cannot be treated within TDDFT, among them are the description of double excitations and excited states with multi-reference character, which is of high relevance to astrochemistry problems. Thus, today, there is a steep rise in interest in **time-independent extension of DFT** for ES descriptions [41-44]. Among them is ensemble DFT - which drew much attention in the last decade. Despite many difficulties and scarce practical applications, it has enormous potential, and many efforts have been put forward to make it a rigorous, reliable, low-cost black-box method [45-57].

The promise of the above mentioned methods lies in the fact that the ensemble of states is composed of the ground-state (GS) and excited-states configurations - and thus is multiconfiguration in nature. Working with ensemble densities (as in the ground-state) we rely on a self-consistent one-electron Kohn-Sham (KS) equation: thus the computational cost is similar to the computational cost of ground-state KS. ***The multiconfiguration character is realized in the KS orbitals as fractional occupations.***

One of the challenges in the framework of ensemble DFT is the description of the Hartree and the exchange term. In ground-state DFT, we have:

$$ E\_{H}\left[n\right]≡\frac{1}{2}∬\_{}^{}\frac{n\left(r\right)n\left(r^{'}\right)}{\left|r-r^{'}\right|}drdr'$$

And

$$E\_{X}\left[n\right]≡ -\frac{1}{2}∬\_{}^{}\frac{\left|ρ\_{s}\left(r,r^{'}\right)\right|^{2}}{\left|r-r^{'}\right|} $$

Where $ ρ\_{s}\left(r,r^{'}\right)= \sum\_{i}^{}f\_{i}ϕ\_{i}^{\*}\left(r\right)ϕ\_{i}\left(r^{'}\right)$ is the one-body reduced density matrix. In order to extend the expressions for Hartree and exchange into ensemble DFT formalism, we can use the following natural definitions in the ensembles, where the ensemble density and 1-body RDM are simply plugged into the GS equations:

$$E\_{H}^{Ens}\left[n\right]≔E\_{H}\left[\sum\_{I}^{}w\_{I}n^{I}\left(r\right)\right]$$

$$E\_{x}^{Ens}\left[n\right]≔E\_{x}\left[\sum\_{I}^{}w\_{I}ρ\_{s,I}\left(r,r^{'}\right)\right]$$

The use of the GS functional is very appealing as it allows the use of standard available functionals easily in the framework of Ensemble DFT. However, the use of GS functional in ensemble DFT is unfortunately not straightforward: when using approximate GS functionals in the ensemble formalism they contain the so-called **ghost-interaction**, which has no analogue in GS DFT and results from the spurious interactions between cross-terms in the ensemble components [58-64].

Several correction schemes have been proposed to correct the unphysical ghost interactions [58, 61]; other researchers have tried to develop methods to approximate the ensemble XC functional [65-71].

***One of the reasons for the lack of success of GOK-DFT is the absence of approximated XC build for ensembles, thus efforts have been made to develop ensemble XC functionals [72, 73].***

Progress has been reported in the work of Fromager and coworkers [74]. They presented the generalized adiabatic connection to ensembles where the ensemble density is fixed along the adiabatic connection path, and both interaction strength and ensemble weights are varied. In their work, which set the ground for a rigorous multideterminant treatment at the DFT level, they are showing that not only $E^{W}\left[n\right]$ should be kept linear with the ensemble weights, but also each of its components.

This realization places an important constraint on the exact ensemble $E\_{Hxc}\left[n\right]$,which is crucial when developing ensemble functionals. When using GS Hxc functionals, they present a curvature in the energy versus the ensemble weights due to the unphysical ghost interactions. This is in analogy to the self-interaction errors in GS DFT. The spurious self-interaction results in an unphysical curvature in the energy curve with respect to occupation number when approximate XC functional is used. PPLB showed in their seminal work that this curve should be a series of straight lines with slope discontinuities at integer N [75]. The unphysical curvature is closely related to the self-interaction error, and its elimination and restoring of the correct (linear) behavior results in fixing many of the ailments it caused (such as the disobedience of the ionization-potential theorem, description of homo-lumo gap, diffuse states, to name a few)[76-78].

In ensemble DFT, to eliminate the ghost interaction, one needs to restore the energy components' correct linear behavior with respect to the ensemble weights. For that task, a lesson can be made from work on (particle-number) ensemble. Kraisler et al. have suggested a scheme to restore the required piecewise linearity in approximate density functionals by transforming to (particle-number) ensemble formalism [79]. Working in a (particle-number) ensemble formalism, they were able to restore the piecewise linearity and correct orbital energies and the IP theorem even when using local and semi-local functionals!

***A key component for the success of ensemble DFT in describing excitation energy is that not only the total ensemble energy*** $E\_{w}$ ***should be kept linear with respect to the weighting factor, but also its component should be kept linear in the ensemble weighting factors.***

The description of the systems in an ensemble formalism also leads to a correct step structure description of the XC potential which is crucial for describing dissociation processes. The XC potential should exhibit a step structure as observed for the exact potential, such structure is lacking in the GS-KS formalism due to the absence of derivative discontinuity in approximated local and semi-local functionals[80, 81].

I am planning to extend the abovementioned correction to state-ensemble DFT: a good starting point is the already available functionals for ground-state, and testing their performance when obeying the exact condition of linearity and *naturally* eliminating ghost interactions: this step is expected to yield significantly improved excitation spectra at DFT computational scaling. The identification of the importance of this constraint on the XC functional can pave the way for developing new functionals obeying this essential condition.

# **Impact:**

Theoretical progress and the ability to model highly electronic excited states will enable the leap needed for progressing our understanding of astrochemistry processes. The ability to model excited states will significantly advance our understanding of interstellar chemical processes. Specifically, they will enable us to study not only chemistry starting from the basic building blocks, but also fragmentation processes of large molecules that may be responsible for many of the observed species in molecular clouds.

The theoretical progress we will make is expected to lead to progress in many other fields as photoinduced processes are central in a variety of scientific and technological arenas and will likely affect scientific areas such as physics, chemistry, and biology. Examples are organic photovoltaic devices [82], photocatalysis [83], photosynthesis [84], and DNA interaction with radiation [85], to name just a few.

**Section b. Methodology**

The primary goal of this proposal is to study the excited state reactivity of PAHs. Highly excited PAHs play a major role in the chemistry of the ISM. To this end, I will model photochemical reactions, and the propagation of systems in time after being excited by a UV photon. **This will be done using non-adiabatic *ab-initio* molecular dynamics simulations.** In *ab-initio* molecular dynamics the propagation of the system in time is done via solving Newton's equation of motion numerically, where the forces acting on the nuclei are calculated "on the fly" as the simulations progressed, using electronic structure calculations.

Large PAH molecules are characterized by a small gap between the highest occupied molecular orbital and the lowest unoccupied molecular orbital (HOMO-LUMO gap), which give an indication to the dominance of static correlation in those systems. Thus, electronic structure methods cannot accurately model the correlation in large PAHs due to this radicaloid character [86-88]. **A correct modelling of the electronic structure of such systems requires an accurate description of static electron correlation.** Additionally, the bond breaking processes, and highly correlated excited states also require multi-determinant solutions for their qualitative and quantitate description.

For this aim, I will develop an approach within ensemble DFT that will provide the means to study PAH systems in the ground and in excited electronic states cheaply at the cost of DFT, and accurately as ensemble DFT can model multideterminant effects. The developed ensemble DFT approach will be incorporated with the molecular dynamics simulations to model the propagation of the system with time. **The newly developed computational tools** will be incorporated into Q-Chem quantum chemistry code, and will be available for the community to use. This will be done in work package A.

When performing dynamic simulations of the PAH systems, and modelling an electronic excitation, one needs to consider the coupling between electronic and vibrational degrees of freedom. This requires to go beyond the Born-Oppenheimer approximation to account for the non-adiabatic coupling between states leading to splitting of population among several states which results in intricate dynamic processes upon excitation. Specifically, with increasing size, PAHs’ optical gap is lowered, making the coupling between the ground state and the first excited state more pronounced - and non-adiabatic effects play a significant role in the chemistry taking place! Moreover, the singlet-triplet gap of PAH systems is small - and is getting smaller with its length, which can lead to intersystem crossing.

To account for non-adiabatic effects in our simulations, I will also use the Q-Chem code, which provides a way to incorporate non-adiabatic effects in the molecular dynamic simulations by performing trajectory surface hopping (TSH) [89]. Using the TSH, we treat the nuclei classically and the electrons quantum mechanically - which makes the calculations feasible computationally. The nuclear dynamic is then propagated on an electronic potential energy surface (PES), and at each time step the probability to transition to a different electronic state is calculated. A stochastic algorithm is used to decide on which transition the trajectory will continue on the next time step.

I have chosen to use the Q-Chem software for several reasons: the first one is that I have previously worked with the source code and hence I am familiar with it and have experience in contributing codes to it. The second reason is that it already supplies much of the needed infrastructures: it contains codes for performing *ab-initio* molecular dynamic simulations, including non-adiabatic effects and trajectory surface hopping algorithms. Moreover, it contains all the newest functional and DFT infrastructure. We will contribute and code ensemble DFT formalism into Q-Chem code, and then combine it with the existent algorithm for performing non-adiabatic *ab-initio* molecular dynamics (NA-AIMD) simulations.

Once me and my team have set the stage for the performance of NA-AIMD, we can move forward and study photochemical reactions relevant to astrochemistry. We will start by a systematic study of fragmentation pathways of PAHs (WP B), and continue to study photochemical reactions in condensed environments (WP C).

### **Preliminary results**My team has performed preliminary calculations to demonstrate the importance of non-adiabatic dynamics in fragmentation processes, starting with the basic building blocks of large PAHs, benzene and anthracene. We have modeled two fragmentation pathways: one is fragmentation of hydrogen, and the second is fragmentation of acetylene. For each fragmentation pathway, we calculated the ground and excited states along the fragmentation path.

To describe the excitation energies, initially, we calculated the equilibrium structure of both benzene and naphthalene using the *ωB97X-V* functional with the aug-cc-PVTZ basis set. Starting from the equilibrium structures, we have separated the leaving groups (hydrogen and acetylene), and gradually increased the distance. At each distance, we calculated excitation energies by performing a single point calculation using CASSCF with the aug-cc-PVTZ basis set. For the removal of the hydrogen atom, we artificially separated the hydrogen atom from the equilibrium structure and performed the CASSCF calculations gradually increasing the separation distance between the units by 0.1Å (namely unrelaxed scan). For the reverse Diels-Alder reaction (resulting with the acetylene) we first marked the center of mass of the acetylene, and the center between the exterior carbons of the diene. By doing so, we could artificially separate the acetylene from the diene while keeping the molecules parallel. As the acetylene is not at equilibrium within the aromatic rings (i.e it is not linear), we switched to its linear equilibrium structure at an arbitrary chosen distance of 1.8Å between the acetylene and diene.

To perform CASSCF calculation, the determination of the active space is required. It is only sensible at the very least to include all the π electrons within the systems, therefore at least 6 electrons for the benzene, and 10 electrons for the naphthalene. As we break bonds, it would be wise to take into account the additional two electrons which we break, to a total of 8 electrons for benzene, and 12 electrons for naphthalene. After some trial and error, we concluded the “square” CASSCF, of 8 electrons and 8 orbitals for the benzene, and 12 electrons with 12 orbitals for the naphthalene, gives acceptable results in comparison to the equilibrium excitation energies. It should be noted, that for demonstration purposes, we only described the singlet excitation states, however, triplets exictations are also close in energy and will be take into account when performing non-adiabatic dynamic simulations.



Figure 1:PES of ground and excited stated along the ffragmentation path of hydrogen and acetylene from benzene (Top panel) and naphthalene (bottom panel)

The results are presented in Figure 1: at the top panel, fragmentation paths of benzene are shown; left graph shows the ground state and first five exited states along the hydrogen fragmentation coordinate. The top right panel shows ground state and first five excited state along the acetylene fragmentation coordinate. Bottom panel of Figure 1 shows fragmentation paths of naphthalene; the results of hydrogen (left) and acetylene (right) fragmentations path starting from equilibrium structure. One can see from the figure that the excited states are close to one another and crosses one another, and thus it is crucial to include curve crossing when performing dynamic simulations. Moreover, it is well established that the HOMO-LUMO gap of acene is getting smaller with the increasing size[90], thus crossing between ground and excited state is also likely emphasizing the need to perform non-adiabatic simulations.

### **Work and Time Schedule**





**Work Package A: Ensemble DFT framework**

The aim of this project is to lay the theoretical grounds to enable accurate description of systems that contain static correlation in the ground and in the excited states. The theoretical framework developed here will be used throughout the next work packages.

In ensemble DFT, the term $E\_{Hxc}^{W}\left[n\right]$ should be kept linear with respect to $W$,the weights of the ensemble. This is not obeyed when using functionals developed for ground state DFT which makes their use in ensemble DFT not valid as it leads to ghost interactions. In this work package (WP) we will first incorporate ensemble DFT into Q-Chem code, and then we will assess the deviation from linearity of different functionals and study the connection between their deviation to their performance in describing bond-braking processes and double excitations (WP A1). We will then implement the ensemble correction terms to improve the linear behaviour and reassess their performance (WP A2). In parallel, we will perform benchmark calculations using wave-function methods on small molecular systems, and the resulting ground and excited potential energy surface along bond-breaking coordinates (WP A3).

The aims of the benchmark study are two folded: first, it will allow us to demonstrate the connection between functionals’ performance and the deviation from linearity of the different functionals prior to the correction. At a second stage, we would be able to assess the performance of different corrected functionals with respect to the benchmark systems and choose the corrected functional best fit to our purposes (WP A4).

After establishing a framework that enable the accurate description of ground and excited states, we will continue and combine the code with the code performing NA-AIMD simulations (WP A5), which will allow us to progress and study evolution of astrochemical relevant systems with time.

This WP involves method development and programming, for which I intend to recruit a postdoctoral fellow with expertise in ensemble DFT. I anticipate that this unit will result in several contributions and benchmark for the computational chemistry and DFT community, with the ability to accurately describe processes involving dominant contribution of static electron correlation to be the most important one.

**A1: Deviation from linearity of ground state functionals.**

In this WP we will assess the deviation of different XC functionals from linearity with respect to the weights when they are plugged in to the ensemble DFT scheme. We will compare functionals from different Rung in Perdew’s ‘Jacob ladder’, and test their deviation from linearity. The deviation from linearity will then serve as a predictor of the performance of different functionals when used in ensemble formalism. This will be tested by comparing results of ground and excited electronic states of stretched bonds of various multiatomic molecules, for which exact results will be available from a benchmark study we will perform. We will test the performance and check the interrelationship between performance and deviation from linearity.

**A2: Implementation of ensemble correction to XC functionals**

Next, we aim to correct the behavior of the ground state functionals so that the property of linearity of Hartree Exchange-correlation functionals will be obtain. The ensemble properties of the Coulomb energy of the KS system, associated with the operator $\hat{W}=\frac{1}{2}\sum\_{i}^{}\sum\_{i}^{}\left|\vec{r\_{i}}-\vec{r\_{j}}\right|^{-1}$ have been demonstrated for ensemble of different number of electrons.[79] Following the same arguments, we can write:

$$W\_{H}=\left(1-w\right)E\_{H}\left[ρ\_{0}^{(w)} \right]+wE\_{H}\left[ρ\_{1}^{(w)} \right]$$

$$W\_{X}=\left(1-w\right)E\_{X}\left[ρ\_{0}^{(w)} \right]+wE\_{X}\left[ρ\_{1}^{(w)} \right]$$

Where:

$$E\_{H}\left[n\right]=\frac{1}{2}∬\_{}^{}d^{3}rd^{3}r'\frac{n(\vec{r})n(\vec{r}')}{\left|\vec{r}-\vec{r}'\right|}$$

$$E\_{X}\left[n\right]=-\frac{1}{2}\sum\_{i,j}^{\infty }g\_{i}g\_{j}∬\_{}^{}d^{3}rd^{3}r'\frac{φ\_{i}^{\*}\left(\vec{r}'\right)φ\_{j}^{\*}\left(\vec{r}\right)φ\_{i}\left(\vec{r}\right)φ\_{j}\left(\vec{r}'\right)}{\left|\vec{r}-\vec{r}'\right|}$$

As $E\_{H}\left[n\right]$ and $E\_{X}\left[n\right]$ are not linear $n$, the required $W$ cannot be obtained by simply inserting fractional-electron density - and the Hartree and exchange terms do not retain they usual form for ensemble state.

Instead we have $W\_{H}=E\_{H}\left[n\right]+ΔE\_{eH}\left[φ\_{j}^{w};w\right]$ and $W\_{X}=E\_{H}\left[n\right]-ΔE\_{eH}\left[φ\_{j}^{w};w\right]$ were the ensemble correction is:

$$ΔE\_{eH}=\frac{1}{2}w\left(1-w\right)∬\_{}^{}d^{3}rd^{3}r'\frac{\left|φ\_{j}^{w}\left(\vec{r}\right)\right|^{2}\left|φ\_{j}^{w}\left(\vec{r}'\right)\right|^{2}}{\left|\vec{r}-\vec{r}'\right|}$$

As expected for $w=0$ or $w=1 $,$W\_{X} $and $W\_{H}$ reduce to their usual form.

Explicit linear form of the exchange-correlation can be obtained in the same spirit:

$$E\_{XC}\left[n\right]=\left(1-w\right)E\_{XC}\left[ρ\_{0}^{(w)} \right]+wE\_{XC}\left[ρ\_{1}^{(w)} \right]$$

The excited state energy can then be simply obtained from the ensemble expression using the corrected functional form via

$$E\_{K}=E^{W}+\sum\_{I>0}^{}\left(δ\_{IK}-w\_{I}\right)\frac{∂E^{W}}{∂w\_{I}}$$

The ensemble correction will be implemented in the Q-Chem software. Ensemble formalism with the corrected functionals will be thus available to the whole quantum chemistry community to use and benefit from.

While we can write $E\_{XC}[n]$ explicitly linear, some implicit non-linear dependencies from the function $ρ^{w}$ will arise, we thus test again the deviation from linearity with respect to the weights of the ground-state corrected functionals. The success of the correction scheme is crucial for the success of the whole project, as this key step will enable the study of large systems relevant to astrochemistry. We thus suggest two remedies for the case that this will not provide satisfactory in ‘feasibility and risk assessment ‘section.

**A3: High level *ab-initio* benchmark calculation on small molecules**

We will perform a benchmark study on *small* cyclic and non-cyclic carbonaceous systems containing $π$ electrons and model the energy of the ground and excited states of the systems along different bond-breaking coordinates for both the neutral and charged species. The choice of the systems stems for the astrochemical scenarios we will need to model. For the benchmark calculations, will use the extended multi-state (XMS)-CASPT2 method to build the PES of the different fragmentation paths under study, as they produce improved potential on the near crossing regions.

Having benchmark results will serve two purposes:

* The energy of the available functionals deviates from linearity with respect to the ensemble weights. Prior to any correction we will systematically compare the deviation of different functionals and the interrelation with their ability to reproduce the benchmarked results.
* Having a set of benchmark PES will allow us to test the performance of the corrected functionals and their ability to reproduce accurate wave-function results.

**A4: Ensemble DFT study on benchmarked systems**

We will systematically test the correction scheme and the performance of corrected functionals of different Rungs on “Jacob’s Ladder”, including LDA, GGA and hybrid functionals to test which corrected functionals gives the best results and are best suited for our purposes. For each functional, we will repeat calculation of fragmentation path performed in WP A3 and obtain a benchmark of the performance of the corrected functionals in the ensemble formalism. This will enable us to choose the functional best suited for our purposes, and provide a valuable information on the performance of the functionals in the ensemble formalism.

It is crucial to test the performance of the corrected functionals in the ensemble formalism on larger systems as well, as static correlation effects might be more prominent in larger aromatic systems. As a direct comparison between ensemble DFT and wave-function methods cannot be achieved for large systems, we will work in close collaboration with the experimental group of Dr. Musa Ahmed at Lawrence Berkley National Laboratory. Dr. Ahmed is currently building capabilities in its laboratory that will allow for excited state dynamics experiments and thus will allow a direct comparison to the calculated PES of fragmentation pathways in the ground and excited states.

 **A5: Incorporation with *ab-initio* molecular dynamic simulation**

Once the ensemble DFT formalism together with the corrected ground-state functionals is incorporated into the Q-Chem code, we can combine it with the code performing the *ab-initio* molecular dynamic simulations. The *ab-initio* part will be calculated via the ensemble formalism and will require the calculation of the forces. For many of the ground-state functionals the forces are already implemented in Q-Chem, and we will extend them for use in the ensemble formalism with the corrected functionals.

Calculation of the non-adiabatic coupling is crucial for the ability to perform non-adiabatic *ab-initio* molecular dynamics. In order to compute transition probabilities between electronic states we need to calculate the first order derivative coupling $d^{IJ}=\left⟨Ψ\_{J}\right⟩ $and the non-adiabatic coupling vector $h^{IJ}=\left⟨Ψ\_{J}\right⟩$.This terms are also coded in Q-Chem code for the different functionals and we will extend them for the use in ensemble formalism.

**Work Package B: Systematic study on fragmentation products of PAHs**

After establishing the accurate performance of ensemble DFT, we will move forward to the study of PAHs and their fragmentation products. In this project the aim is to reveal possible fragmentation pathways of PAHs upon interaction with UV radiation that excite the molecule to the first excited electronic state, and to answer the following questions:

* What is the distribution of the possible fragmentation products?
* How does the size of the PAH influences the distribution of the fragmentation products?
* How does the geometry of the PAH influences the distribution of the fragmentation products?
* How does the energy of the excited photon influence the distribution of the fragmentation products?
* What is the role of the triplet state in the formation of different products?

At the first stage of the study, I will focus on linear PAHs: benzene, naphthalene, anthracene, tetracene, pentacene, hexacene, heptacene. By comparing different sizes of linear acenes we will understand the effect of size on the fragmentation (WP B1). Additionally, I plan to study the effect of the PAH’s structure on the fragmentation pathway. To do so, we will study acene with the same number of rings as before, but fuzed not linearly. Specifically we will study: biphenyl, fluorene (containing two aromatic rings), phenantrene,[benzo[c]fluorene](https://en.wikipedia.org/wiki/Benzo%28c%29fluorene) and phenalene, (containing three aromatic rings), chrysene, triphenylene, and [pyrene](https://en.wikipedia.org/wiki/Pyrene) (containing four rings), perylene, benzo[a]pyrene, corannulene, (containing five aromatic rings) benzo[ghi]perylene (six aromtic ring), and in addition to coronene and ovalene (WP B2).To study how the UV radiation effects fragmentation pathways, we will start the dynamic simulations from higher excited states, this will be examined in WP B3.

*I anticipate that outcomes of this WP will be of high interest to the astrochemical community, as PAHs fragmentation products are key astrochemical reactions.*

**B1: Ensemble DFT study on the fragmentation pathways of linear acene from the first excited state**

The goal of this work package is to model PAHs’ fragmentation that occur as a result of interaction with UV radiation. I will perform a systematic study of the fragmentation pathways of excited linear PAHs. For this purpose, we will need to perform NA-AIMD simulations starting from an excited electronic state. We will need to calculate large number of trajectories to obtain converged statistics. The starting point will be optimization of the structures under study, namely benzene, naphthalene, anthracene, tetracene, pentacene, hexacene and heptacene shown in scheme 1. Optimization will be done using $ωB97X-V$ with cc-pVTZ basis set as this is expected to yield accurate geometries. For each structure we will perform the dynamics simulations where the *ab-initio* part is the ensemble DFT developed in WP A.



Scheme 1

The molecular dynamic simulations will run in the microcanonical (NVE) in which the energy is conserved. For each structure we will ran at least 50 trajectories, and then verify convergence of the results. If the statistics depend on the number of run trajectories, we will increase the number of the trajectories until convergence. We will sample different initial conditions via the starting velocities, we will randomly sample the nuclear velocities according to Maxwell-Boltzmann distribution. Additionally, we will sample by choosing velocities in order to put zero-point vibrational energy into each normal mode with random signs. While this option requires frequency calculations to run beforehand, this is not an issue as our *ab-initio* method is economic enough. Moreover, we want to eliminate any dependence on the choice of the initial conditions.

The results of this WP will supply us with product distribution as a function of the number of fuzzed benzene rings.

**B2: Ensemble DFT studies on the fragmentation pathways of non-linear PAHs from the first excited state**

After gaining insights into fragmentation pathways of the linear PAHs, we will continue and test the effect of the PAH geometry on the fragmentation products and their relative distribution by starting the excited state dynamics simulations. We will repeat the excited state molecular dynamics simulations as done in WP B1, where our starting structures will be biphenyl, fluorene, phenantrene,[benzo[c]fluorene](https://en.wikipedia.org/wiki/Benzo%28c%29fluorene) and phenalene, chrysene, triphenylene, [pyrene](https://en.wikipedia.org/wiki/Pyrene) perylene, benzo[a]pyrene, corannulene, benzo[ghi]perylene, coronene and ovalene shown in scheme 2. The procedure for the performance of the NA-AIMD will be similar to those we have employed in WP B1. Direct comparison of the results of WP B1 and WP B2 are expected to increase our understanding of the role played by the geometry in fragmentation processes.



Scheme 2

**B3: Effect of excitation energy**

To quantify the effect of the photon’s energy, we will repeat the NA-AIMD simulation performed in projects B1 and B2 - but now we will start from the second and third excited electronic states. The product distribution is expected to differ from what was previously obtained due to the large changes in the energy distribution along the molecular degrees of freedom and possible different relaxation paths. This WP will emphasize the effect of energy distribution and the importance of the starting state on the chemical processes taking place.

**Work Package C: Photochemistry of PAHs in condensed environments**.

In this work package, I would like to study the photochemical reactivity of PAHs taking place in condensed environments. PAHs fragmentation products, as well as PAHs themselves, are likely to be seeded in astronomical ice in the cold areas of molecular clouds. The ices provide a unique environment in which several molecules are in a close proximity to one another, and the result of the photochemical reactions can be various substituted PAHs. The goal of this WP is to study the chemical reactivity taking place in those condensed environments. To achieve this goal, I will need to model the seeded PAH in an ice composed of CO, CO2, CH3OH, CH4 and NH3 in different compositions (which are a typical components of astronomical ices)[91]. For this aim I will use a hybrid approach, namely quantum mechanics/molecular mechanics (QM/MM)[92, 93]. In QM/MM part of the system (the reactive part) is treated with quantum mechanics - and the rest of the system (the environment) is treated with force field-based molecular mechanics [92, 94]. Dividing the system into QM part and MM part is usually not straight forward. In the systems under study the division is relatively simple, as it does not include any breaking of chemical bonds. As a reactive part, I will choose the PAH together with first solvation shells sounding it in the ice. This choice will allow the study of the photochemical reaction between PAH and the molecules in close proximity to it. The rest of the ice will be considered as the environment.

For this purpose I will also use the Q-Chem program [95] as it has the infrastructure for QM/MM calculations, which can be easily combined with my new implemented code. For realization of these calculations, force fields which are suitable for describing the ice environments will need to be developed to use in the MM part – this is the aim of WP C1. Once we have available force fields to describe the ice environments, we can perform simulations using QM/MM where the description of the quantum part is by ensemble DFT developed in WP A. The simulations will be perform starting from an excited electronic state as in the simulations performed in WP B. This work package will allow us to answer the following questions:

* What are the possible products upon irradiation of different ices seeded with aromatic molecules?
* What are the exact underlying molecular mechanism responsible for the formation of each product?
* What is the relative distribution of the different products?
* How are the size and geometry of the PAHs affecting the identity of the products and their relative distribution?
* How does the composition of the ice affect the resulting products and their relative distribution?
* How does the energy of the excited photon influence the product distribution?
* What is the role of the triplet states in the formation of different products?

We will follow the systematic study performed in WP B and start with study of linear PAHs, and continue with the non-linear structures (WP C2). In WP B, we studied the fragmentation path of PAHs, and we will also seed the ices with important fragmented PAHs identified in WP B.

This project will benefit from close collaboration with the experimental group of Prof. Micha Asscher at the Hebrew University. Asschers’ research group perform experiments on ices of different compositions and has the ability to seed different organic molecules and study the photochemical products. Close collaboration with an experimental group will allow us to calibrate and further validate the developed force-field models. Once the models are calibrated, performing the experiment parallel to the calculations we enable us to further ratify our model and produce a thorough study to the photoreactions.

This WP involves force field parametrization, for which I intend to recruit a postdoctoral fellow with expertise in the field. The force field parameters will be published and will serve the astrochemical community for the study of chemical reactions in ice.

**C1: Force field parametrization**

In order to correctly describe the ices, we need an accurate parametrization for the force fields; we will build several force fields corresponding to different ice compositions. The force field is an empirical model, for which we use a simple mathematical form to model interatomic forces by fitting the force field results to quantum mechanical results. An accurate parametrization is crucial for a reliable description of the effect of the environment. This can be obtained by fitting the parameters so that they will reconstruct results of accurate *ab-initio* calculations modelling the ice environment. To model the bulk systems for parametrization purposes, plane-wave DFT which utilizes plane-wave basis sets will be used. Plane-wave basis allows for the use of fast Fourier transform algorithms by taking advantage of the periodic structure of the bulk system. We will perform these calculations using the VASP code [96] with (projector augmented wave method) PAW [97] pseudopotentials, in which the valence electron wavefunctions are smoothed near the atomic core, reducing significantly computational time.

In order to build the bulk ices, we will take the atomic positions from the literature where available. Otherwise, we will search for the minimum energy in a bulk supercell using DFT calculations together with any applicable ice geometry rules.[98, 99] We will model the ice surface by fixing a bottom ice layer with the relaxed bulk atomic positions; on this several layers of ice with a vacuum above them will be placed and allowed to relax. The organic molecule will then be placed in several different orientations and positions, and the energy minima will be found. As the system involves an ice environment and organic molecules, dispersion forces are crucial, and therefore all our calculations will be carried out with dispersion forces included via the dDsC correction method[100, 101]. In this method, the dispersion coefficients and damping functions are charge-density dependent, and therefore are able to take into account variations in the van der Waals contributions of atoms due to their local chemical environment.

Calculations will be performed using the PBE exchange-correlation functional[102] which is reliable for the accurate prediction of molecular structures. Once the data is obtained, we will create and use the data to optimize the different force fields using the free software ForceBalance, which enables an automatic and systematic determination of force fields using gradient and stochastic minimization[103]. Further verification of the performance of the force fields will be done in collaboration with the experimental group of Prof. Micha Asscher.

Having the force fields to accurately model the ice environment, we can perform QM/MM molecular dynamic (MD) simulations. For this part, we will also use the Q-Chem software package as it allows stand-alone QM/MM calculations with user-defined force fields.

*The force fields that will be developed in this work package will be published and will serve the astrochemistry community for various of different studies on chemical reactions taking place in ice.*

**C2: Photochemistry of PAHs of different sizes and geometry**

In this work package, we will perform simulations of photochemical reactions of PAHs in an ice environment. We will seed the ices with PAHs of different sizes and geometry (using the structures used in WP B). Additionally, we will use PAHs fragmentation products identified in WP B according to their abundance. The more abundant structures are likely more important and more frequently formed and thus will also be considered.

As the ice environment is likely to change the geometry of the structures, we will re-optimize the structures in ices of different compositions. Optimization will be performed using QM/MM where for the QM we will use $ωB97X-V$ with aug-cc-pVTZ basis set as this is expected to yield accurate geometries, and for the MM part, we will use the force fields parametrize in WP C1. This study will give insight into the effect of ice composition on PAH geometry and we anticipate will interest the community and will result in a publication.

The next stage is to perform NA-AIMD simulations in the ice environment. As in WP B, we will sample the initial conditions and verify the convergence of the statics. The simulation will be performed on the different structures, and will then be repeated by changing the ice environment. At the end of this WP, we are accepted to achieve the following goals:

* Identify possible products and intermediates. Once we identified the products forming during the simulations, we will proceed and calculates accurate PES for their formation by optimizing the structures along the path (optimization can be done on the ground electronic state and on the excited electronic state).
* Understand the effect of ice composition on the different products.

The outcome of this project will be interesting as it is expected to reveal new organic products and their specific formation mechanism thus providing potential for high-impact publications. This project will benefit from close collaboration with the experimental group of Prof. Micha Asscher at the Hebrew University. Asschers’ research group, which has the ability to radiate different ices at different wave-length and will allow for a direct comparison between experiments and theory.

**C3: Photochemistry of various PAHs on higher ES**

In this WP, we aim to quantify the effect of the radiation energy. Higher energy can alter either distribute along the vibrational degree of freedom (on the excited electronic state) or can result in an excitation to a higher excited state. We will repeat the simulation performed in WP C2, but now start them from the second excited electronic state. Even if the result is a quick decay to lower level, changes in the dynamic are expected. We expect the following changes:

* The change in energy can alter the products distribution.
* The change in energy can lead to product formation via different underlying molecular mechanism.

Performing the simulations will allow us to quantify the effects described above. From the NA-AIMD simulations we will identify products and intermediates and will optimize them (in the ice environment via QM/MM) to produce the relevant PESs, which include ground and higher electronic states.

### **Feasibility and risk assessment**

This project aims at modelling the excited state dynamics of large PAH systems. This is not a simple task and several obstacles may arise along the way as summarised at the table below:

|  |  |
| --- | --- |
| Risks | Remedies |
| The success of the suggested project relies on the ability to accurately describe excited states containing static correlation using ensemble DFT with using functionals inherited from ground-state KS formalism. The risks are: 1. The correction scheme suggested by us will not lead to satisfactory results. 2. While we can write $E\_{XC}[n]$ explicitly linear, some implicit non-linear dependencies from the function $ρ^{w}$ will arise. | We propose two possible remedies for these issues:1. There are suggested techniques in the literature to achieve linear behavior of the functional (some of them by me). In the case that our correction will not lead to satisfactory results, we will try other possibilities to achieve linearity with respect to the ensemble weights.2. We will adopt a different approach - we will directly develop XC functional for a correct description of static correlation by taking the existent functional forms and refit the parameter to describe the problem at hand.  |
| One of the main challenges when performing non-adiabatic molecular dynamic simulations is the including of decoherence effects, which are not properly described via the surface hopping method and can lead to the different populations at the different states and thus provide spurious results in long time dynamic. | Artificial decoherence can be added to the calculation using augmented fewest switch surface hopping, already available in Q-Chem code. The algorithm allows the wave-packet on different surfaces to separate, and be subjected to different forces.[104]  |

**Team description**To accomplish the proposed research, two PhD and two postdoctoral fellows (sequential) will be hired from the requested budget. As a PI, I will dedicate 60% of my time to the realization of this project. I will closely supervise the two PhD students and teach them computational quantum chemistry, and work closely with them in executing the needed calculations. I will guide then until they gradually become independent. Moreover, I will work closely with the postdocs; at the first two years I will work closely with the first hired postdoc to implement the ensemble DFT formalism and the suggested correction (WP A2). I will try to involve the PhD students in the development part as well as it is important for their education. The PhD students will perform the needed calculations on functionals in ensemble formalism (WP A1), and benchmark calculations (WPs A4 and A5). While each member of the group has its own independent project to carry out, they are all in the same fields working to achieve the same goal which will enable mutual exchange of knowledge. At the 3rd and 4th years of the project the PhD students will start performing massive amounts of NA-AIMD simulations (WP B). At this stage a second postdoc will join the group with whom I will work closely on parametrize force-fields. The availability of the force fields will allow performing the study in an ice environment which will be performed by the two PhD students in the fifth year of the project. (WP C2 and C4).

**Estimated budget**The suggested project involves both method development and massive computational effort as we plan to perform a large amount on NA-AIMD simulations. To achieve the goals of this proposal and perform the aforementioned calculations, substantial computational capabilities are needed. We thus request a computer cluster containing 35 nodes with high RAM memory which will be used to perform the NA-AIMD simulations. Additionally, in order to carry out the calculations, two PhD students and two postdocs are necessary.

### **Summary and Outlook**

The proposed research will provide a leap in our ability to model and understand photochemical reactions in conditions crucial for the field of astrochemistry. We will be able to predict the formation of different fragmentation products together with the underlying molecular mechanisms responsible for their formation, including the unique role of excited electronic states. The computational method which we will implement in the realization of this proposed research will enable the study of systems whose size and the computational cost of the available quantum chemistry methods prevented from being studied. The fact that we enlarge the scope of capabilities of quantum chemistry makes it useful in the multidisciplinary study of molecules in the ISM. The ability to accurately model excited states of large systems is of great importance to quantum chemistry, as it will allow its use in many fields from biology to material science.

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