**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 dynamics occurring in excited electronic states and the ability to model them is crucial to the advancement of our knowledge.*

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

***The goal of the proposed research is to fill this gap by building a computationally inexpensive framework within ensemble DFT that will enable the study of excited-state 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 mechanisms and resulting products. To obtain this information, quantum chemistry is needed. While accurate modeling 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 have 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 the B3LYP functional with the 6-31g\* basis set [17]. In a different study, Zhou et al. studied the fragmentation dynamics of the benzene trimer representing a prototype of higher-order aromatic clusters. To model the dynamics of the system, *ab initio* molecular dynamic simulations were performed using DFT with the B3LYP functional and cc-pVDZ basis set, in which 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 the B3LYP functional and 6-31G(d,p) [12].

In a recent experimental and theoretical combined 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 included excited states, they calculated both the singlet and triplet states using DFT (B3LYP/6-311G(d,p)) [20].

In my laboratory, we modelled chemical growth upon the photoionization of different clusters of acetylene, HNC and cyanoacetyle by using DFT with the functional on the ground state of the *cationic system* under the assumption that after 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].

Nonadiabatic relaxation dynamics were incorporated with time-dependent DFT (TDDFT) calculations [26, 27]. In a 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 than those from experiments, demonstrating the deficiencies in TDDFT [28].

The dynamics of highly excited PAHs at the femtosecond and attosecond timescale was studied by Marciniak et al. [29]. They suggested a mechanism in which a XUV photon ionizes a molecule and creates a hole in the valence shell, which can then lead to the excitation of another electron forming an excited “shake-up” state. The excited molecular cationic state relaxes through a nonadiabatic 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 these geometries, wave-packet propagation was employed using the multiconfigurational time-dependent Hartree (MCTDH) method [31] to calculate the nonadiabatic relaxation of the states determined by ADC. Due to the large 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 states, we can use multideterminant wavefunction methods such as second-order, complete, active, space perturbation theory (CASPT2) [33, 34]; second-order, perturbation theory, restricted active space (RASPT2) [35, 36]; or N-electron, valence-state, perturbation theory (NEVPT2) [37, 38], which have been successful in modeling fragmentation pathways – albeit at high computational cost, which limits the system that can be modeled in this way.

The ability to study photochemical reactions requires an efficient way to model excited-state dynamics – for which the toolkit of quantum chemistry is currently 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 for both the description of the ground and excited states, with computational scaling similar to DFT. In addition, it can be used to calculate excited states. ***Thus, this approach has the potential for enlarging the current capabilities of computational quantum chemistry.***

Ensemble DFT in regard to the description of excited states is based on the work of Gross Oliveira and Kohn (GOK), 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, as well as the parallel rapid progress and success of TDDFT. Indeed, TDDFT is currently widely used and has been 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 a multireference character, which is of great relevance to astrochemical problems. Therefore, there has been a steep rise in interest in the **time-independent extension of DFT** for ES descriptions [41-44]. Among them is ensemble DFT, which attracted much attention in the last decade. Despite many difficulties and scarce practical applications, it has enormous potential, and many efforts have been carried out to make it a rigorous, reliable, low-cost, black-box method [45-57].

The promise of the abovementioned methods lies in the fact that the ensemble of states is composed of the ground-state (GS) and excited-state configurations, and is thus 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 exchange term. In ground-state DFT, we have:

and

where 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:

The use of the GS functional is very appealing as it easily allows the use of standard available functionals in the framework of ensemble DFT. However, the use of the 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 attempted 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 an approximated XC built for ensembles; therefore, 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 in which 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 showed that not only should be kept linear with the ensemble weights, but also each of its components should be kept linear.

This realization places an important constraint on the exact ensemble , 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 analogous 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 an 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 restoration of the correct (linear) behavior results in fixing many of the ailments that it has caused (such as the disobedience of the ionization–potential theorem, description of the HOMO–LUMO gap and diffuse states, to name a few) [76-78].

In ensemble DFT, to eliminate the ghost interaction, we need to restore the correct linear behavior of the energy components with respect to the ensemble weights. For this task, a lesson can be learned from work on (particle-number) ensemble. Kraisler et al. suggested a scheme to restore the required piecewise linearity in approximate density functionals by transforming to (particle-number) ensemble formalism [79]. Working in an (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 semilocal functionals!

***A key component for the success of ensemble DFT in describing excitation energy is that not only the total ensemble energy 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 a structure is lacking in the GS–KS formalism due to the absence of derivative discontinuity in approximated local and semilocal 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 the 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 advancing our understanding of astrochemical 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 include organic photovoltaic devices [82], photocatalysis [83], photosynthesis [84] and DNA interactions with radiation [85], to name just a few.

**Section b. Methodology**

The primary goal of the proposed research 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 performed using nonadiabatic, *ab initio* molecular dynamic simulations.** In *ab initio* molecular dynamics, the propagation of the system in time is performed via solving Newton's equation of motion numerically, in which the forces acting on the nuclei are calculated "on the fly" as the simulations progress, 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 provides an indication to the dominance of static correlation in these systems. Thus, electronic structure methods cannot accurately model the correlation in large PAHs due to this radicaloid character [86-88]. **A correct modeling of the electronic structure of such systems requires an accurate description of static electron correlation.** In addition, the bond-breaking processes and highly correlated excited states also require multideterminant solutions for their qualitative and quantitate description.

Therefore, I will develop an approach within ensemble DFT that will provide the means to study PAH systems in the ground and excited electronic states inexpensively, in regard to the cost of DFT, and accurately as ensemble DFT can model multideterminant effects. The developed ensemble DFT approach will be incorporated with the molecular dynamic simulations to model the propagation of the system in 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 conducted in Work Package A.

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

To account for nonadiabatic effects in our simulations, I will also use Q-Chem code, which provides a way to incorporate nonadiabatic effects in molecular dynamic simulations by performing trajectory surface hopping (TSH) [89]. Using TSH, we treat the nuclei classically and the electrons quantum mechanically, which makes the calculations computationally feasible. 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 prefer to use Q-Chem software for several reasons. The first one is that I have previously worked with the source code and hence am familiar with it and have experience in contributing codes to it. The second reason is that it already supplies much of the needed infrastructure; it contains codes for performing *ab initio* molecular dynamic simulations, including nonadiabatic 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 existing algorithm for performing nonadiabatic, *ab initio* molecular dynamic (NA-AIMD) simulations.

Once my team and I 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 conducting 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 performed preliminary calculations to demonstrate the importance of nonadiabatic dynamics in fragmentation processes, starting with the basic building blocks of large PAHs: benzene and anthracene. We modeled two fragmentation pathways: one was fragmentation of hydrogen, and the second was fragmentation of acetylene. For each fragmentation pathway, we calculated the ground and excited states along the fragmentation path.

To describe the excitation energies, we initially 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 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 0.1 Å (namely, unrelaxed scan). For the reverse Diels–Alder reaction (resulting in 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 was not at equilibrium within the aromatic rings (i.e., it was not linear), we switched to its linear equilibrium structure at an arbitrarily chosen distance of 1.8 Å between the acetylene and diene.

To perform the CASSCF calculation, the determination of the active space was required. It was only sensible at the very least to include all π electrons within the systems; therefore, we included at least 6 electrons in the benzene and 10 electrons in the naphthalene. As we were breaking bonds, we thought it wise to consider the additional two electrons that we were breaking, making a total of 8 electrons in benzene and 12 electrons in naphthalene. After some trial and error, we concluded that the “square” CASSCF of 8 electrons and 8 orbitals in the benzene, and 12 electrons with 12 orbitals in the naphthalene provided 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, triplet excitations are also close in energy and will be considered when performing nonadiabatic dynamic simulations.

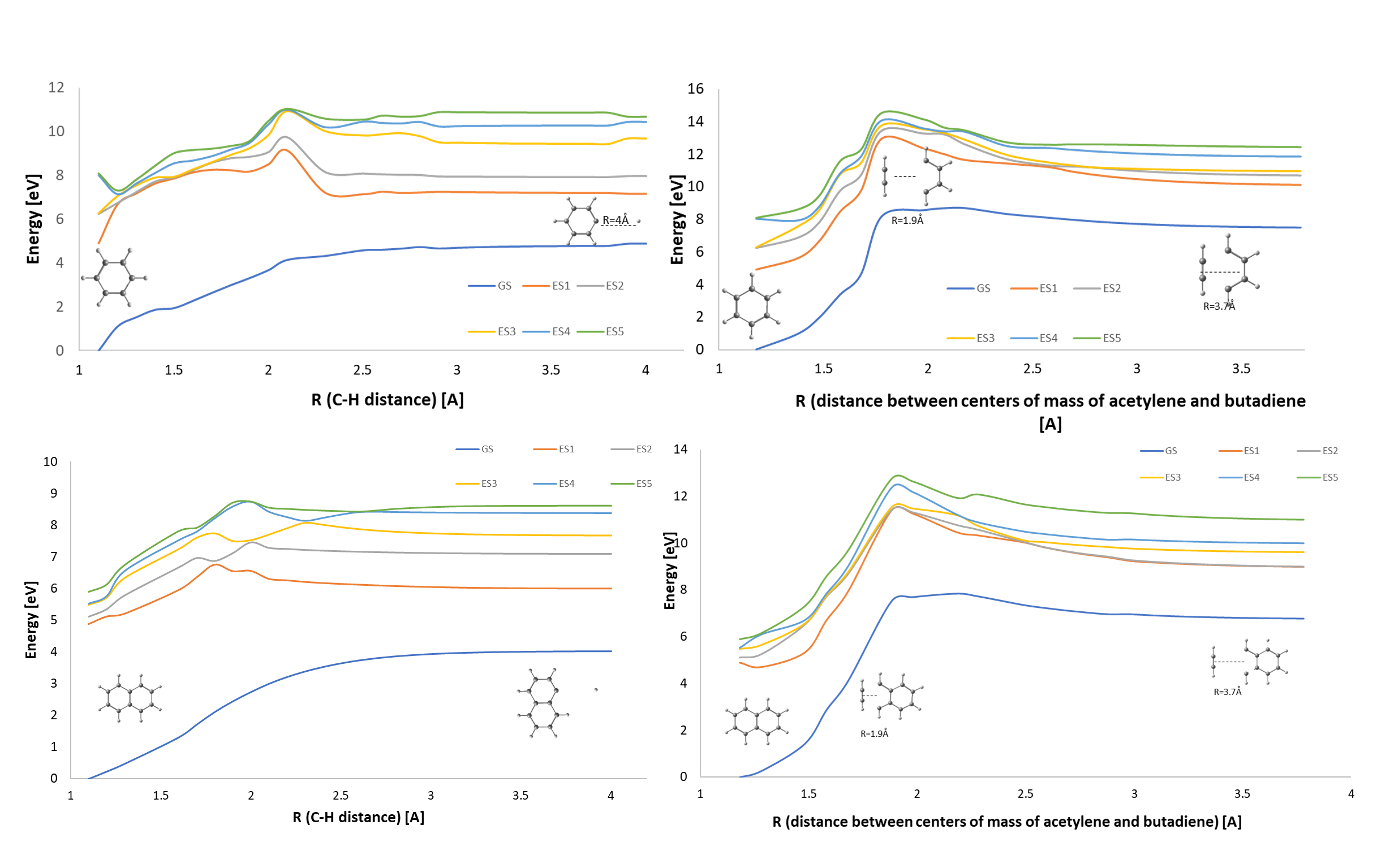
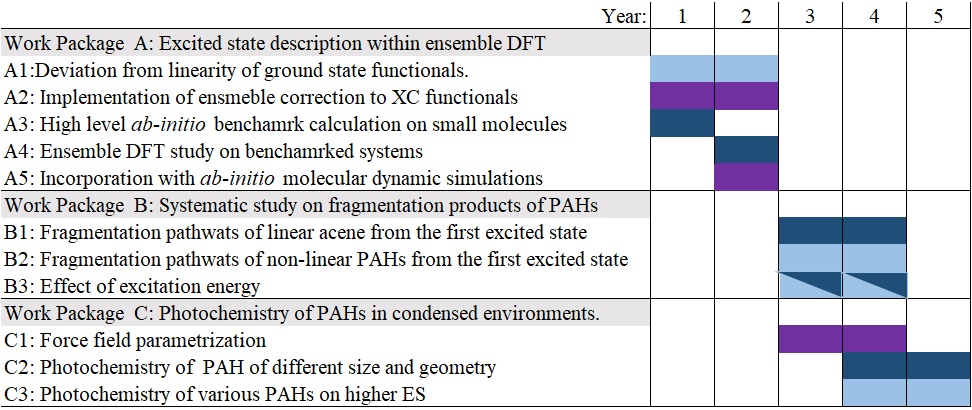


Figure 1: PES of ground and excited states along the fragmentation path of hydrogen and acetylene from benzene (top panel) and naphthalene (bottom panel).

The results are presented in Figure 1. In the top panel, fragmentation paths of benzene are shown. The left graph shows the ground state and first five excited states along the hydrogen fragmentation coordinate. The top right panel shows the ground state and first five excited states along the acetylene fragmentation coordinate. The bottom panel in Figure 1 shows fragmentation paths of naphthalene: the results of hydrogen (left) and acetylene (right) fragmentation paths starting from an equilibrium structure. The figure shows that the excited states are close to one another and cross one another; thus, it is crucial to include curve crossing when performing dynamic simulations. Moreover, it is well established that the HOMO–LUMO gap of acene becomes smaller with increasing size [90]; therefore, crossing between the ground and excited states is also likely, emphasizing the need to perform nonadiabatic simulations.

### **Work and Time Schedule**





**Work Package A: Ensemble DFT framework**

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

In ensemble DFT, the term should be kept linear with respect to ,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-breaking processes and double excitations (WP A1). We will then implement the ensemble correction terms to improve the linear behavior and reassess their performance (WP A2). In parallel, we will perform benchmark calculations using wavefunction methods on small molecular systems and investigate the resulting ground and excited potential energy surfaces along bond-breaking coordinates (WP A3).

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

After establishing a framework that enables 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 the 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 will be a benchmark for the computational chemistry and DFT community, with the ability to accurately describe processes involving the dominant contribution of static electron correlation to be the most important contribution.

**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 into the ensemble DFT scheme. We will compare functionals from different rungs in Perdew’s “Jacob’s 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 that 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 obtained. The ensemble properties of the Coulomb energy of the KS system, associated with the operator , have been demonstrated for an ensemble with a different number of electrons [79]. Following the same arguments, we can write:

Where:

As and are not linear , the required cannot be obtained by simply inserting fractional-electron density, and the Hartree and exchange terms do not retain their usual form for the ensemble state.

Instead, we have and in which the ensemble correction is:

As expected for or ,and reduce to their usual forms.

An explicit linear form of the exchange–correlation can be obtained in the same spirit:

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

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

While we can write to be explicitly linear, some implicit nonlinear dependencies from the function will arise. We will 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. I thus suggest two remedies in the “feasibility and risk assessment” section in case the correction scheme is not satisfactorily successful.

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

We will perform a benchmark study on *small* cyclic and noncyclic carbonaceous systems containing 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 from the astrochemical scenarios we will need to model. For the benchmark calculations, we will use the extended multistate (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 interrelationships with their ability to reproduce the benchmarked results.
* Having a set of benchmark PESs will allow us to test the performance of the corrected functionals and their ability to reproduce accurate wavefunction results.

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

We will systematically test the correction scheme and the performance of corrected functionals on different rungs of “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 the calculation of the 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 will provide 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 wavefunction 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 the laboratory that will allow for excited-state dynamic experiments and thus will allow a direct comparison of 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 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 have already been implemented in Q-Chem, and we will extend them for use in the ensemble formalism with the corrected functionals.

Calculation of the nonadiabatic coupling is crucial for the ability to perform nonadiabatic, *ab initio* molecular dynamics. In order to compute transition probabilities between electronic states, we need to calculate the first order derivative coupling and the nonadiabatic coupling vector .These 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 part of the 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:

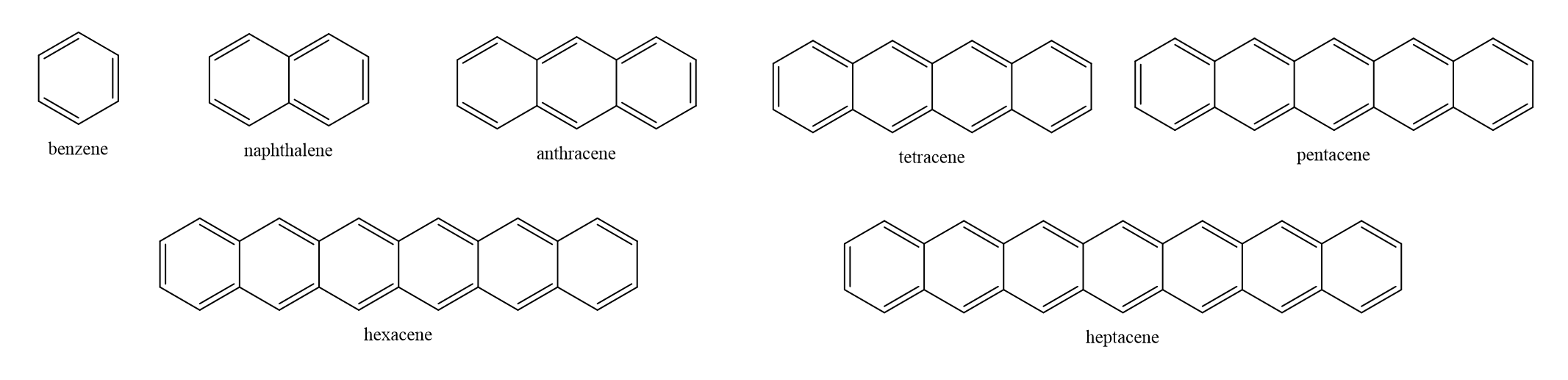
* What is the distribution of the possible fragmentation products?
* How does the size of the PAH influence the distribution of the fragmentation products?
* How does the geometry of the PAH influence the distribution of the fragmentation products?
* How does the energy of the excited photon influence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

In the first stage of the study, I will focus on linear PAHs: benzene, naphthalene, anthracene, tetracene, pentacene, hexacene and heptacene. By comparing different sizes of linear acenes, we will understand the effect of size on 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 not linearly fused. Specifically, we will study biphenyl and fluorene (containing two aromatic rings); phenantrene, [benzo[c]fluorene](https://en.wikipedia.org/wiki/Benzo(c)fluorene" \o "Benzo(c)fluorene) and phenalene (containing three aromatic rings); chrysene, triphenylene and [pyrene](https://en.wikipedia.org/wiki/Pyrene" \o "Pyrene) (containing four rings); perylene, benzo[a]pyrene and corannulene (containing five aromatic rings); and benzo[ghi]perylene (six aromatic ring), as well as coronene and ovalene (WP B2). To study how 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 great interest to the astrochemical community, as PAH 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 the fragmentation of PAHs that occurs 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 a 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, as shown in Scheme 1. Optimization will be performed using with the cc-pVTZ basis set as this is expected to yield accurate geometries. For each structure, we will perform the dynamic simulations in which the *ab initio* part is the ensemble DFT developed in WP A.



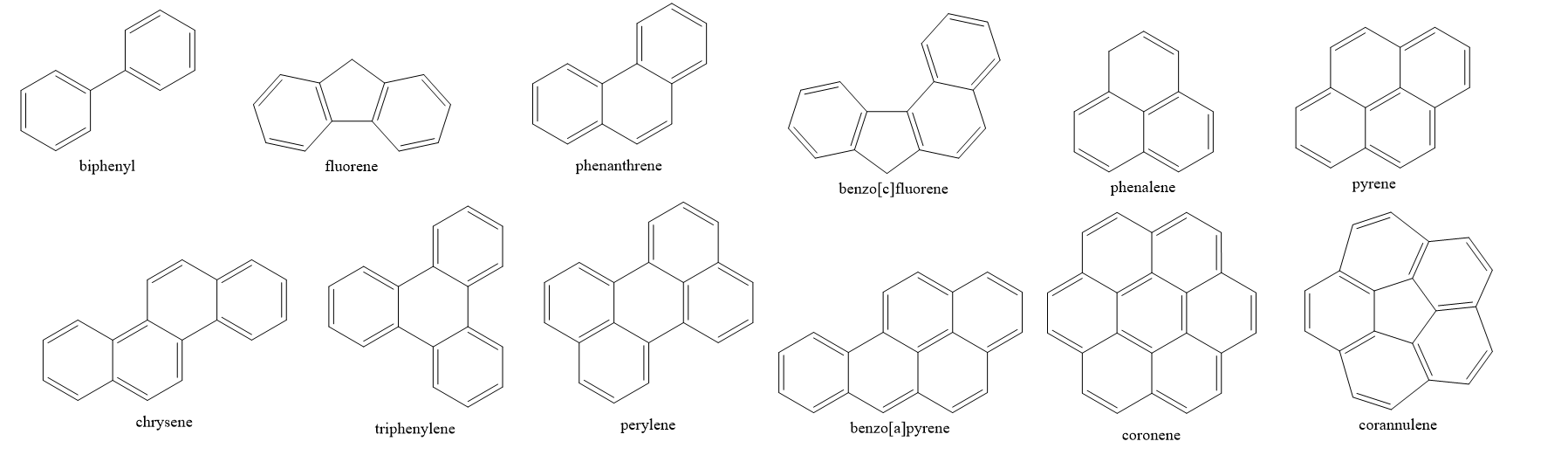
Scheme 1

The molecular dynamic simulations will run in the microcanonical (NVE) in which the energy is conserved. For each structure, we will run 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 the Maxwell–Boltzmann distribution. In addition, 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 economically sufficient. Moreover, we want to eliminate any dependence on the choice of the initial conditions.

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

**B2: Ensemble DFT studies on the fragmentation pathways of nonlinear 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 dynamic simulations. We will repeat the excited-state molecular dynamic simulations as performed in WP B1, in which our starting structures will be biphenyl, fluorene, phenantrene, [benzo[c]fluorene](https://en.wikipedia.org/wiki/Benzo(c)fluorene" \o "Benzo(c)fluorene), phenalene, chrysene, triphenylene, [pyrene](https://en.wikipedia.org/wiki/Pyrene" \o "Pyrene), perylene, benzo[a]pyrene, corannulene, benzo[ghi]perylene, coronene and ovalene, as shown in Scheme 2. The procedure for the performance of the NA-AIMD will be similar to those we employed in WP B1. Direct comparison of the results of WP B1 and WP B2 is expected to increase our understanding of the role played by geometry in fragmentation processes.



Scheme 2

**B3: Effect of excitation energy**

To quantify the effect of photon 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 occurring.

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

In this work package, I would like to study the photochemical reactivity of PAHs occurring in condensed environments. PAH fragmentation products, as well as PAHs, 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 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 occurring in these 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]. Therefore, I will use a hybrid approach, namely quantum mechanics/molecular mechanics (QM/MM) [92, 93]. The QM/MM part of the system (reactive part) is treated with quantum mechanics and the rest of the system (environment) is treated with force field-based molecular mechanics [92, 94]. Dividing the system into a 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 the first solvation shells surrounding it in the ice. This choice will allow the study of the photochemical reactions between the PAH and the molecules in close proximity. 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 newly implemented code. For realization of these calculations, force fields that 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 in which the description of the quantum part is by ensemble DFT developed in WP A. The simulations will be performed 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 mechanisms 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 the study of linear PAHs, and will continue with the nonlinear structures (WP C2). In WP B, we will study 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. Asscher’s research group performs experiments on ices of different compositions and has the ability to seed different organic molecules and to 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 will enable us to further verify our model and to produce a thorough study on 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 in regard to 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 the results of the accurate *ab initio* calculations modeling the ice environment. To model the bulk systems for parametrization purposes, plane-wave DFT that 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 VASP code [96] with (projector augmented wave method) PAW [97] pseudopotentials, in which the valence electron wavefunctions are smoothed near the atomic core, reducing computational time significantly.

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 determined. As the system involves an ice environment and organic molecules, dispersion forces are crucial; 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; therefore, they are able to consider 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 are obtained, we will create and use the data to optimize the different force fields using free ForceBalance software, 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 performed 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 studies on chemical reactions occurring 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). In addition, we will use PAH fragmentation products identified in WP B according to their abundance. The more abundant structures are more likely to be 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, in which for the QM part, we will use with the aug-cc-pVTZ basis set, as this is expected to yield accurate geometries; and for the MM part, we will use the force fields parametrized in WP C1. This study will provide insight into the effect of ice composition on PAH geometry. This, I anticipate, will interest the community and will result in a publication.

The next stage will be 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, I expect to achieve the following goals:

* Identifying possible products and intermediates. Once we identify the products forming during the simulations, we will proceed and calculate accurate PESs for their formation by optimizing the structures along the path (optimization can be performed on the ground electronic state and on the excited electronic state).
* Understanding 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 mechanisms, 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, which has the ability to radiate different ices at different wavelengths and will allow for a direct comparison between experiments and theory.

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

In this WP, I aim to quantify the effect of the radiation energy. Higher energy can alter either the distribution 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 the simulation from the second excited electronic state. Even if the result is a quick decay to a lower level, changes in the dynamics are expected. I expect the following changes:

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

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 plans to model the excited-state dynamics of large PAH systems. This is not a simple task and several obstacles may arise along the way, as summarized in 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 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 to be explicitly linear, some implicit nonlinear dependencies from the function will arise. | I 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 myself). In case our correction will not lead to satisfactory results, we will attempt other possibilities to achieve linearity with respect to the ensemble weights.  2. We will adopt a different approach: we will directly develop XC functionals for a correct description of static correlation by taking the existing functional forms and refitting the parameter to describe the problem at hand. |
| One of the main challenges when performing nonadiabatic molecular dynamic simulations is including decoherence effects, which are not properly described via the surface-hopping method and can lead to different populations in the different states and can thus provide spurious results in long-time dynamics. | 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 students and two postdoctoral fellows (sequential) will be hired from the requested budget. As the PI, I will dedicate 60% of my time to the realization of this project. I will closely supervise the two PhD students, 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; in 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 attempt 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 will have their own independent projects to carry out, they will all be in the same field working to achieve the same goal, which will enable the mutual exchange of knowledge. In 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 parametrized force fields. The availability of the force fields will allow performing the study on ice environments, 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 of NA-AIMD simulations. To achieve the goals of this proposal and perform the aforementioned calculations, substantial computational capabilities are needed beyond what I have at the moment. I thus request a computer cluster containing 35 nodes with high RAM memory that will be used solely to perform the NA-AIMD simulations of this project. In addition, 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 methods that we will implement in the realization of the proposed research will enable the study of systems whose size, as well as the computational cost of the available quantum chemistry methods, has previously prevented their study. The fact that we will enlarge the scope of capabilities of quantum chemistry will make this research 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 facilitate its use in many fields, from biology to material science.

**References**

1. Pety, J., D. Teyssier, D. Fossé, M. Gerin, E. Roueff, A. Abergel, E. Habart, and J. Cernicharo, *Are PAHs precursors of small hydrocarbons in photo-dissociation regions? The Horsehead case.* A&A, 2005. **435**(3): p. 885-899.

2. Peeters, E., L.J. Allamandola, J.C.W. Bauschlicher, D.M. Hudgins, S.A. Sandford, and A.G.G.M. Tielens, *Deuterated Interstellar Polycyclic Aromatic Hydrocarbons.* The Astrophysical Journal, 2004. **604**(1): p. 252-257.

3. Cui, W., B. Hadas, B. Cao, and C. Lifshitz, *Time-Resolved Photodissociation (TRPD) of the Naphthalene and Azulene Cations in an Ion Trap/Reflectron.* The Journal of Physical Chemistry A, 2000. **104**(27): p. 6339-6344.

4. Pachuta, S.J., H.I. Kenttamaa, T.M. Sack, R.L. Cerny, K.B. Tomer, M.L. Gross, R.R. Pachuta, and R.G. Cooks, *Excitation and dissociation of isolated ions derived from polycyclic aromatic hydrocarbons.* Journal of the American Chemical Society, 1988. **110**(3): p. 657-665.

5. Dibben, M.J., D. Kage, J. Szczepanski, J.R. Eyler, and M. Vala, *Photodissociation of the Fluorene Cation:  A Fourier Transform Ion Cyclotron Resonance Mass Spectrometric Study.* The Journal of Physical Chemistry A, 2001. **105**(25): p. 6024-6029.

6. Jochims, H.W., E. Ruhl, H. Baumgartel, S. Tobita, and S. Leach, *Size Effects on Dissociation Rates of Polycyclic Aromatic Hydrocarbon Cations: Laboratory Studies and Astrophysical Implications.* The Astrophysical Journal, 1994. **420**: p. 307.

7. Ekern, S.P., A.G. Marshall, J. Szczepanski, and M. Vala, *Photodissociation of Gas-Phase Polycylic Aromatic Hydrocarbon Cations.* The Journal of Physical Chemistry A, 1998. **102**(20): p. 3498-3504.

8. West, B., C. Joblin, V. Blanchet, A. Bodi, B. Sztáray, and P.M. Mayer, *On the Dissociation of the Naphthalene Radical Cation: New iPEPICO and Tandem Mass Spectrometry Results.* The Journal of Physical Chemistry A, 2012. **116**(45): p. 10999-11007.

9. Zhen, J., P. Castellanos, D.M. Paardekooper, H. Linnartz, and A.G.G.M. Tielens, *LABORATORY FORMATION OF FULLERENES FROM PAHS: TOP-DOWN INTERSTELLAR CHEMISTRY.* The Astrophysical Journal, 2014. **797**(2): p. L30.

10. Johansson, H.A.B., H. Zettergren, A.I.S. Holm, N. Haag, S.B. Nielsen, J.A. Wyer, M.-B.S. Kirketerp, K. Støchkel, P. Hvelplund, H.T. Schmidt, and H. Cederquist, *Unimolecular dissociation of anthracene and acridine cations: The importance of isomerization barriers for the C2H2 loss and HCN loss channels.* The Journal of Chemical Physics, 2011. **135**(8): p. 084304.

11. Kadhane, U.R., M.V. Vinitha, K. Ramanathan, A. S., J. Bouwman, L. Avaldi, P. Bolognesi, and R. Richter, *Comprehensive survey of dissociative photoionization of quinoline by PEPICO experiments.* The Journal of Chemical Physics, 2022. **156**(24): p. 244304.

12. Rodriguez Castillo, S., A. Simon, and C. Joblin, *Investigating the importance of edge-structure in the loss of H/H2 of PAH cations: The case of dibenzopyrene isomers.* International Journal of Mass Spectrometry, 2018. **429**: p. 189-197.

13. Burner, J., B.J. West, and P.M. Mayer, *What Will Photo-Processing of Large, Ionized Amino-Substituted Polycyclic Aromatic Hydrocarbons Produce in the Interstellar Medium?* The Journal of Physical Chemistry A, 2019. **123**(24): p. 5027-5034.

14. Dyakov, Y.A., C.-K. Ni, S. Lin, Y. Lee, and A. Mebel, *Ab initio and RRKM study of photodissociation of azulene cation.* Physical Chemistry Chemical Physics, 2006. **8**(12): p. 1404-1415.

15. Johansson, H.A., H. Zettergren, A.I. Holm, N. Haag, S.B. Nielsen, J. Wyer, M.-B. Kirketerp, K. Støchkel, P. Hvelplund, and H.T. Schmidt, *Unimolecular dissociation of anthracene and acridine cations: The importance of isomerization barriers for the C2H2 loss and HCN loss channels.* The Journal of chemical physics, 2011. **135**(8): p. 084304.

16. Bouwman, J., A.J. de Haas, and J. Oomens, *Spectroscopic evidence for the formation of pentalene+ in the dissociative ionization of naphthalene.* Chemical Communications, 2016. **52**(12): p. 2636-2638.

17. Chuvilin, A., U. Kaiser, E. Bichoutskaia, N.A. Besley, and A.N. Khlobystov, *Direct transformation of graphene to fullerene.* Nature Chemistry, 2010. **2**(6): p. 450-453.

18. Zhou, J., X. Yu, S. Luo, X. Xue, S. Jia, X. Zhang, Y. Zhao, X. Hao, L. He, and C. Wang, *Triple ionization and fragmentation of benzene trimers following ultrafast intermolecular Coulombic decay.* Nature communications, 2022. **13**(1): p. 1-9.

19. Junfeng, Z., C. Tao, and G.G.M.T. Alexander, *Laboratory Photochemistry of Pyrene Clusters: An Efficient Way to Form Large PAHs.* The Astrophysical Journal, 2018. **863**(2): p. 128.

20. Kaiser, R.I., L. Zhao, W. Lu, M. Ahmed, V.S. Krasnoukhov, V.N. Azyazov, and A.M. Mebel, *Unconventional excited-state dynamics in the concerted benzyl (C7H7) radical self-reaction to anthracene (C14H10).* Nature Communications, 2022. **13**(1): p. 786.

21. Jose, J., A. Zamir, and T. Stein, *Molecular dynamics reveals formation path of benzonitrile and other molecules in conditions relevant to the interstellar medium.* Proceedings of the National Academy of Sciences, 2021. **118**(19): p. e2101371118.

22. Stein, T. and J. Jose, *Molecular Formation upon Ionization of van der Waals Clusters and Implication to Astrochemistry.* Israel Journal of Chemistry, 2020. **60**: p. 1-9.

23. Stein, T., P.P. Bera, T.J. Lee, and M. Head-Gordon, *Molecular growth upon ionization of van der Waals clusters containing HCCH and HCN is a pathway to prebiotic molecules.* Physical Chemistry Chemical Physics, 2020. **22**(36): p. 20337-20348.

24. Stein, T., B. Bandyopadhyay, T.P. Troy, Y. Fang, O. Kostko, M. Ahmed, and M. Head-Gordon, *Ab initio dynamics and photoionization mass spectrometry reveal ion-molecule pathways from ionized acetylene clusters to benzene cation.* Proc Natl Acad Sci USA, 2017. **114**(21): p. E4125-E4133.

25. Zamir, A. and T. Stein, *Isomerization of hydrogen cyanide and hydrogen isocyanide in a cluster environment: quantum chemical study.* The Journal of Chemical Physics, 2022. **156**(5): p. 054307.

26. Röder, A., J. Petersen, K. Issler, I. Fischer, R. Mitric, and L. Poisson, *Exploring the excited-state dynamics of hydrocarbon radicals, biradicals, and carbenes using time-resolved photoelectron spectroscopy and field-induced surface hopping simulations.* The Journal of Physical Chemistry A, 2019. **123**(50): p. 10643-10662.

27. Vogt, R.A. and C.E. Crespo-Hernández, *Conformational Control in the Population of the Triplet State and Photoreactivity of Nitronaphthalene Derivatives.* The Journal of Physical Chemistry A, 2013. **117**(51): p. 14100-14108.

28. Röder, A., J. Petersen, K. Issler, I. Fischer, R. Mitrić, and L. Poisson, *Exploring the Excited-State Dynamics of Hydrocarbon Radicals, Biradicals, and Carbenes Using Time-Resolved Photoelectron Spectroscopy and Field-Induced Surface Hopping Simulations.* The Journal of Physical Chemistry A, 2019. **123**(50): p. 10643-10662.

29. Marciniak, A., V. Despré, T. Barillot, A. Rouzée, M. Galbraith, J. Klei, C.-H. Yang, C. Smeenk, V. Loriot, and S.N. Reddy, *XUV excitation followed by ultrafast non-adiabatic relaxation in PAH molecules as a femto-astrochemistry experiment.* Nature Communications, 2015. **6**(1): p. 1-6.

30. Schirmer, J., L.S. Cederbaum, and O. Walter, *New approach to the one-particle Green's function for finite Fermi systems.* Physical Review A, 1983. **28**(3): p. 1237-1259.

31. Meyer, H.-D., U. Manthe, and L.S. Cederbaum, *The multi-configurational time-dependent Hartree approach.* Chemical Physics Letters, 1990. **165**(1): p. 73-78.

32. Recio, P., S. Alessandrini, G. Vanuzzo, G. Pannacci, A. Baggioli, D. Marchione, A. Caracciolo, V.J. Murray, P. Casavecchia, N. Balucani, C. Cavallotti, C. Puzzarini, and V. Barone, *Intersystem crossing in the entrance channel of the reaction of O(3P) with pyridine.* Nature Chemistry, 2022.

33. Andersson, K., P.Å. Malmqvist, and B.O. Roos, *Second‐order perturbation theory with a complete active space self‐consistent field reference function.* The Journal of Chemical Physics, 1992. **96**(2): p. 1218-1226.

34. Roca-Sanjuán, D., F. Aquilante, and R. Lindh, *WIREs Comput. Mol. Sci. 2, 585 (2012)*.

35. Malmqvist, P.Å., K. Pierloot, A.R.M. Shahi, C.J. Cramer, and L. Gagliardi, *The restricted active space followed by second-order perturbation theory method: Theory and application to the study of Cu O 2 and Cu 2 O 2 systems.* The Journal of chemical physics, 2008. **128**(20): p. 204109.

36. Sauri, V., L. Serrano-Andrés, A.R.M. Shahi, L. Gagliardi, S. Vancoillie, and K. Pierloot, *Multiconfigurational Second-Order Perturbation Theory Restricted Active Space (RASPT2) Method for Electronic Excited States: A Benchmark Study.* Journal of Chemical Theory and Computation, 2011. **7**(1): p. 153-168.

37. Angeli, C., R. Cimiraglia, S. Evangelisti, T. Leininger, and J.-P. Malrieu, *Introduction of n-electron valence states for multireference perturbation theory.* The Journal of Chemical Physics, 2001. **114**(23): p. 10252-10264.

38. Angeli, C., R. Cimiraglia, and J.-P. Malrieu, *n-electron valence state perturbation theory: A spinless formulation and an efficient implementation of the strongly contracted and of the partially contracted variants.* The Journal of Chemical Physics, 2002. **117**(20): p. 9138-9153.

39. Gross, E.K.U., L.N. Oliveira, and W. Kohn, *Rayleigh-Ritz variational principle for ensembles of fractionally occupied states.* Physical Review A, 1988. **37**(8): p. 2805-2808.

40. Theophilou, A.K., *The energy density functional formalism for excited states.* Journal of Physics C: Solid State Physics, 1979. **12**(24): p. 5419.

41. Levy, M., *Excitation energies from density-functional orbital energies.* Physical Review A, 1995. **52**(6): p. R4313-R4315.

42. Ayers, P.W., M. Levy, and Á. Nagy, *Time-independent density functional theory for degenerate excited states of Coulomb systems.* Theoretical Chemistry Accounts, 2018. **137**(11): p. 152.

43. Ayers, P.W., M. Levy, and A. Nagy, *Time-independent density-functional theory for excited states of Coulomb systems.* Physical Review A, 2012. **85**(4): p. 042518.

44. Ayers, P., M. Levy, and Á. Nagy, *Communication: Kohn-Sham theory for excited states of Coulomb systems.* The Journal of Chemical Physics, 2015. **143**(19): p. 191101.

45. Senjean, B. and E. Fromager, *Unified formulation of fundamental and optical gap problems in density-functional theory for ensembles.* Physical Review A, 2018. **98**(2): p. 022513.

46. Filatov, M. and S. Shaik, *Chem Phys Lett 288: 689 <https://doi>. org/10.1016.* S0009-2614 (98), 1998: p. 00364-9.

47. Filatov, M. and S. Shaik, *Application of spin-restricted open-shell Kohn–Sham method to atomic and molecular multiplet states.* The Journal of chemical physics, 1999. **110**(1): p. 116-125.

48. Filatov, M. and S. Shaik, *A spin-restricted ensemble-referenced Kohn–Sham method and its application to diradicaloid situations.* Chemical Physics Letters, 1999. **304**(5): p. 429-437.

49. Filatov, M. and S. Shaik, *Diradicaloids: Description by the Spin-Restricted, Ensemble-Referenced Kohn− Sham Density Functional Method.* The Journal of Physical Chemistry A, 2000. **104**(28): p. 6628-6636.

50. Cremer, D., M. Filatov, V. Polo, E. Kraka, and S. Shaik, *Implicit and explicit coverage of multi-reference effects by density functional theory.* International Journal of Molecular Sciences, 2002. **3**(6): p. 604-638.

51. Moreira, I.d.P.R., R. Costa, M. Filatov, and F. Illas, *Restricted Ensemble-Referenced Kohn−Sham versus Broken Symmetry Approaches in Density Functional Theory:  Magnetic Coupling in Cu Binuclear Complexes.* Journal of Chemical Theory and Computation, 2007. **3**(3): p. 764-774.

52. Huix-Rotllant, M., M. Filatov, S. Gozem, I. Schapiro, M. Olivucci, and N. Ferré, *Assessment of Density Functional Theory for Describing the Correlation Effects on the Ground and Excited State Potential Energy Surfaces of a Retinal Chromophore Model.* Journal of Chemical Theory and Computation, 2013. **9**(9): p. 3917-3932.

53. Filatov, M., *Spin-restricted ensemble-referenced Kohn–Sham method: basic principles and application to strongly correlated ground and excited states of molecules.* WIREs Computational Molecular Science, 2015. **5**(1): p. 146-167.

54. Kazaryan, A., J. Heuver, and M. Filatov, *Excitation Energies from Spin-Restricted Ensemble-Referenced Kohn−Sham Method: A State-Average Approach.* The Journal of Physical Chemistry A, 2008. **112**(50): p. 12980-12988.

55. Senjean, B., S. Knecht, H.J.A. Jensen, and E. Fromager, *Linear interpolation method in ensemble Kohn-Sham and range-separated density-functional approximations for excited states.* Physical Review A, 2015. **92**(1): p. 012518.

56. Yang, Z.-h., A. Pribram-Jones, K. Burke, and C.A. Ullrich, *Direct Extraction of Excitation Energies from Ensemble Density-Functional Theory.* Physical Review Letters, 2017. **119**(3): p. 033003.

57. Pribram-Jones, A., Z.-h. Yang, J.R. Trail, K. Burke, R.J. Needs, and C.A. Ullrich, *Excitations and benchmark ensemble density functional theory for two electrons.* The Journal of Chemical Physics, 2014. **140**(18): p. 18A541.

58. Pastorczak, E. and K. Pernal, *Ensemble density variational methods with self- and ghost-interaction-corrected functionals.* The Journal of Chemical Physics, 2014. **140**(18): p. 18A514.

59. Tasnádi, F. and Á. Nagy, *Ghost- and self-interaction-free ensemble calculations with local exchange–correlation potential for atoms.* Journal of Physics B: Atomic, Molecular and Optical Physics, 2003. **36**(20): p. 4073-4080.

60. Gould, T. and J.F. Dobson, *The flexible nature of exchange, correlation, and Hartree physics: Resolving “delocalization” errors in a “correlation free” density functional.* The Journal of Chemical Physics, 2013. **138**(1): p. 014103.

61. Gidopoulos, N.I., P.G. Papaconstantinou, and E.K.U. Gross, *Spurious Interactions, and Their Correction, in the Ensemble-Kohn-Sham Scheme for Excited States.* Physical Review Letters, 2002. **88**(3): p. 033003.

62. Oliveira, L.N., E.K.U. Gross, and W. Kohn, *Density-functional theory for ensembles of fractionally occupied states. II. Application to the He atom.* Physical Review A, 1988. **37**(8): p. 2821-2833.

63. Vosko, S.H., L. Wilk, and M. Nusair, *Accurate spin-dependent electron liquid correlation energies for local spin density calculations: a critical analysis.* Canadian Journal of physics, 1980. **58**(8): p. 1200-1211.

64. Kohn, W., *Density-functional theory for excited states in a quasi-local-density approximation.* Physical Review A, 1986. **34**(2): p. 737-741.

65. Nagy, A., *An alternative optimized potential method for ensembles of excited states.* Journal of Physics B: Atomic, Molecular and Optical Physics, 2001. **34**(12): p. 2363.

66. Andrejkovics, I. and A. Nagy, *Excitation energies in density functional theory: comparison of several methods for the H2O, N2, CO and C2H4 molecules.* Chemical physics letters, 1998. **296**(5-6): p. 489-493.

67. Gidopoulos, N.I., P.G. Papaconstantinou, and E.K. Gross, *Spurious interactions, and their correction, in the ensemble-kohn-sham scheme for excited states.* Physical review letters, 2002. **88**(3): p. 033003.

68. Glushkov, V.N. and A.K. Theophilou, *Application of the subspace density functional theory to the excitation energies of molecules.* Journal of Physics B: Atomic, Molecular and Optical Physics, 2002. **35**(10): p. 2313-2324.

69. Paragi, G., I.K. Gyémánt, and V.E. Van Doren, *Investigation of exchange potentials for excited states by parameter fitting.* Chemical Physics Letters, 2000. **324**(5): p. 440-446.

70. Gould, T. and S. Pittalis, *Hartree and Exchange in Ensemble Density Functional Theory: Avoiding the Nonuniqueness Disaster.* Physical Review Letters, 2017. **119**(24): p. 243001.

71. Gould, T. and S. Pittalis, *Density-Driven Correlations in Many-Electron Ensembles: Theory and Application for Excited States.* Physical Review Letters, 2019. **123**(1): p. 016401.

72. Gould, T., G. Stefanucci, and S. Pittalis, *Ensemble Density Functional Theory: Insight from the Fluctuation-Dissipation Theorem.* Physical Review Letters, 2020. **125**(23): p. 233001.

73. Gould, T., L. Kronik, and S. Pittalis, *Double excitations in molecules from ensemble density functionals: Theory and approximations.* Physical Review A, 2021. **104**(2): p. 022803.

74. Franck, O. and E. Fromager, *Generalised adiabatic connection in ensemble density-functional theory for excited states: example of the H2 molecule.* Molecular Physics, 2014. **112**(12): p. 1684-1701.

75. Perdew, J.P., R.G. Parr, M. Levy, and J.L. Balduz, *Density-Functional Theory for Fractional Particle Number: Derivative Discontinuities of the Energy.* Physical Review Letters, 1982. **49**(23): p. 1691-1694.

76. Stein, T., J. Autschbach, N. Govind, L. Kronik, and R. Baer, *Curvature and Frontier Orbital Energies in Density Functional Theory.* The Journal of Physical Chemistry Letters, 2012. **3**(24): p. 3740-3744.

77. Kronik, L., T. Stein, S. Refaely-Abramson, and R. Baer, *Excitation Gaps of Finite-Sized Systems from Optimally Tuned Range-Separated Hybrid Functionals.* Journal of Chemical Theory and Computation, 2012. **8**(5): p. 1515-1531.

78. Stein, T., L. Kronik, and R. Baer, *Reliable Prediction of Charge Transfer Excitations in Molecular Complexes Using Time-Dependent Density Functional Theory.* Journal of the American Chemical Society, 2009. **131**(8): p. 2818-2820.

79. Kraisler, E. and L. Kronik, *Piecewise Linearity of Approximate Density Functionals Revisited: Implications for Frontier Orbital Energies.* Physical Review Letters, 2013. **110**(12): p. 126403.

80. Kraisler, E., M.J.P. Hodgson, and E.K.U. Gross, *From Kohn–Sham to Many-Electron Energies via Step Structures in the Exchange-Correlation Potential.* Journal of Chemical Theory and Computation, 2021. **17**(3): p. 1390-1407.

81. Hodgson, M.J.P., E. Kraisler, A. Schild, and E.K.U. Gross, *How Interatomic Steps in the Exact Kohn–Sham Potential Relate to Derivative Discontinuities of the Energy.* The Journal of Physical Chemistry Letters, 2017. **8**(24): p. 5974-5980.

82. Mazzio, K.A. and C.K. Luscombe, *The future of organic photovoltaics.* Chemical Society Reviews, 2015. **44**(1): p. 78-90.

83. Wenderich, K. and G. Mul, *Methods, Mechanism, and Applications of Photodeposition in Photocatalysis: A Review.* Chemical Reviews, 2016. **116**(23): p. 14587-14619.

84. Cheng, Y.-C. and G.R. Fleming, *Dynamics of Light Harvesting in Photosynthesis.* Annual Review of Physical Chemistry, 2009. **60**(1): p. 241-262.

85. Middleton, C.T., K.d.L. Harpe, C. Su, Y.K. Law, C.E. Crespo-Hernández, and B. Kohler, *DNA Excited-State Dynamics: From Single Bases to the Double Helix.* Annual Review of Physical Chemistry, 2009. **60**(1): p. 217-239.

86. Rivero, P., C.A. Jiménez-Hoyos, and G.E. Scuseria, *Entanglement and polyradical character of polycyclic aromatic hydrocarbons predicted by projected Hartree–Fock theory.* The Journal of Physical Chemistry B, 2013. **117**(42): p. 12750-12758.

87. Plasser, F., H. Pašalić, M.H. Gerzabek, F. Libisch, R. Reiter, J. Burgdörfer, T. Müller, R. Shepard, and H. Lischka, *The Multiradical Character of One- and Two-Dimensional Graphene Nanoribbons.* Angewandte Chemie International Edition, 2013. **52**(9): p. 2581-2584.

88. Hachmann, J., J.J. Dorando, M. Avilés, and G.K.-L. Chan, *The radical character of the acenes: A density matrix renormalization group study.* The Journal of Chemical Physics, 2007. **127**(13): p. 134309.

89. Tully, J.C., *Molecular dynamics with electronic transitions.* The Journal of Chemical Physics, 1990. **93**(2): p. 1061-1071.

90. Schmidt, W., *Photoelectron spectra of polynuclear aromatics. V. Correlations with ultraviolet absorption spectra in the catacondensed series.* The Journal of Chemical Physics, 1977. **66**(2): p. 828-845.

91. Öberg, K.I., *Photochemistry and Astrochemistry: Photochemical Pathways to Interstellar Complex Organic Molecules.* Chemical Reviews, 2016. **116**(17): p. 9631-9663.

92. Warshel, A. and M. Levitt, *Theoretical studies of enzymic reactions: Dielectric, electrostatic and steric stabilization of the carbonium ion in the reaction of lysozyme.* Journal of Molecular Biology, 1976. **103**(2): p. 227-249.

93. Lin, H. and D.G. Truhlar, *QM/MM: what have we learned, where are we, and where do we go from here?* Theoretical Chemistry Accounts, 2007. **117**(2): p. 185-199.

94. Lin, H. and D.G. Truhlar, *QM/MM: what have we learned, where are we, and where do we go from here?* Theoretical Chemistry Accounts, 2006. **117**(2): p. 185.

95. Shao, Y., Z. Gan, E. Epifanovsky, A.T.B. Gilbert, M. Wormit, J. Kussmann, A.W. Lange, A. Behn, J. Deng, X. Feng, D. Ghosh, M. Goldey, P.R. Horn, L.D. Jacobson, I. Kaliman, R.Z. Khaliullin, T. Kuś, A. Landau, J. Liu, E.I. Proynov, Y.M. Rhee, R.M. Richard, M.A. Rohrdanz, R.P. Steele, E.J. Sundstrom, H.L. Woodcock, P.M. Zimmerman, D. Zuev, B. Albrecht, E. Alguire, B. Austin, G.J.O. Beran, Y.A. Bernard, E. Berquist, K. Brandhorst, K.B. Bravaya, S.T. Brown, D. Casanova, C.-M. Chang, Y. Chen, S.H. Chien, K.D. Closser, D.L. Crittenden, M. Diedenhofen, R.A. DiStasio, H. Do, A.D. Dutoi, R.G. Edgar, S. Fatehi, L. Fusti-Molnar, A. Ghysels, A. Golubeva-Zadorozhnaya, J. Gomes, M.W.D. Hanson-Heine, P.H.P. Harbach, A.W. Hauser, E.G. Hohenstein, Z.C. Holden, T.-C. Jagau, H. Ji, B. Kaduk, K. Khistyaev, J. Kim, J. Kim, R.A. King, P. Klunzinger, D. Kosenkov, T. Kowalczyk, C.M. Krauter, K.U. Lao, A.D. Laurent, K.V. Lawler, S.V. Levchenko, C.Y. Lin, F. Liu, E. Livshits, R.C. Lochan, A. Luenser, P. Manohar, S.F. Manzer, S.-P. Mao, N. Mardirossian, A.V. Marenich, S.A. Maurer, N.J. Mayhall, E. Neuscamman, C.M. Oana, R. Olivares-Amaya, D.P. O’Neill, J.A. Parkhill, T.M. Perrine, R. Peverati, A. Prociuk, D.R. Rehn, E. Rosta, N.J. Russ, S.M. Sharada, S. Sharma, D.W. Small, A. Sodt, T. Stein, D. Stück, Y.-C. Su, A.J.W. Thom, T. Tsuchimochi, V. Vanovschi, L. Vogt, O. Vydrov, T. Wang, M.A. Watson, J. Wenzel, A. White, C.F. Williams, J. Yang, S. Yeganeh, S.R. Yost, Z.-Q. You, I.Y. Zhang, X. Zhang, Y. Zhao, B.R. Brooks, G.K.L. Chan, D.M. Chipman, C.J. Cramer, W.A. Goddard, M.S. Gordon, W.J. Hehre, A. Klamt, H.F. Schaefer, M.W. Schmidt, C.D. Sherrill, D.G. Truhlar, A. Warshel, X. Xu, A. Aspuru-Guzik, R. Baer, A.T. Bell, N.A. Besley, J.-D. Chai, A. Dreuw, B.D. Dunietz, T.R. Furlani, S.R. Gwaltney, C.-P. Hsu, Y. Jung, J. Kong, D.S. Lambrecht, W. Liang, C. Ochsenfeld, V.A. Rassolov, L.V. Slipchenko, J.E. Subotnik, T. Van Voorhis, J.M. Herbert, A.I. Krylov, P.M.W. Gill and M. Head-Gordon, *Advances in molecular quantum chemistry contained in the Q-Chem 4 program package.* Molecular Physics, 2015. **113**(2): p. 184-215.

96. Kresse, G. and J. Furthmüller, *Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set.* Physical review B, 1996. **54**(16): p. 11169.

97. Blöchl, P.E., *Projector augmented-wave method.* Physical review B, 1994. **50**(24): p. 17953.

98. Bernal, J.D. and R.H. Fowler, *A Theory of Water and Ionic Solution, with Particular Reference to Hydrogen and Hydroxyl Ions.* The Journal of Chemical Physics, 1933. **1**(8): p. 515-548.

99. Singer, S.J., J.-L. Kuo, T.K. Hirsch, C. Knight, L. Ojamäe, and M.L. Klein, *Hydrogen-Bond Topology and the Ice $\mathrm{VII}/\mathrm{VIII}$ and Ice $\mathrm{I}h/\mathrm{XI}$ Proton-Ordering Phase Transitions.* Physical Review Letters, 2005. **94**(13): p. 135701.

100. Steinmann, S.N. and C. Corminboeuf, *Comprehensive Benchmarking of a Density-Dependent Dispersion Correction.* Journal of Chemical Theory and Computation, 2011. **7**(11): p. 3567-3577.

101. Steinmann, S.N. and C. Corminboeuf, *A generalized-gradient approximation exchange hole model for dispersion coefficients.* The Journal of Chemical Physics, 2011. **134**(4): p. 044117.

102. Perdew, J.P., K. Burke, and M. Ernzerhof, *Generalized Gradient Approximation Made Simple.* Physical Review Letters, 1996. **77**(18): p. 3865-3868.

103. Wang, L.-P., T.J. Martinez, and V.S. Pande, *Building Force Fields: An Automatic, Systematic, and Reproducible Approach.* The Journal of Physical Chemistry Letters, 2014. **5**(11): p. 1885-1891.

104. Subotnik, J.E., *Fewest-Switches Surface Hopping and Decoherence in Multiple Dimensions.* The Journal of Physical Chemistry A, 2011. **115**(44): p. 12083-12096.