

Universal Approach for Solving Real-World Problems Using Quantum Dynamics: Coherent States for Molecular Simulations (COSMOS)

Year 1 Report

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August 2024

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1 Introduction

In this programme grant we will develop transformative new QD simulation strategies that will uniquely deliver impact and insight for real-world applications across a range of technological and biological domains. The key to our vision is the development, dissemination, and wide adaptation of powerful new universal software for QD simulations, building on our collective work on QD methods exploiting trajectory-guided basis functions. The need for powerful QD simulations is demonstrated by experiments using modern laser technologies and new light sources. These look at quantum systems undergoing dynamic change to understand molecular function and answer fundamental questions relevant to chemistry, materials and quantum technologies. The software and methods this programme will deliver will enable the interpretation of these time-resolved experiments and so deliver new insights into the behaviour of matter on the quantum scale.

2 Objectives

Although the equations of quantum mechanics, which drive the dynamics of electrons and atoms, are well known, their solution for complex systems of direct technological and biological relevance is impossible using current and near-term new algorithms and simulations strategies are absolutely critical to jump the gap between simulation and experiment in order to provide new opportunities to understand and exploit quantum dynamics (QD). The central objective of our programme grant is to provide a new universal methodology and suite of software to perform QD simulations of complex systems, and demonstrate the game-changing ability this would provide for the understanding of fundamental processes involved in both light-driven chemical processes and quantum technologies.

Specific objectives are:

1. To develop new methods for QD simulations that span experimental, technological and biological ranges of time- and length-scales
2. To build a QD code that can be used by both experimental and computational researchers
3. To deploy our QD code to provide new insight into light-matter interaction in complex molecules and materials, demonstrating commonalities in seemingly disparate phenomena
4. To develop future quantum technology simulators, such as qubit-based quantum computers, for conventional computers
5. To provide community training in QD simulations, building new bridges across different application domains

To demonstrate the impact of QD simulations, we will employ our new code and new simulation strategies across a range of real-world applications with defined technological and healthcare impacts, offering a unique route to direct quantitative analysis of state-of-the-art experiments. Applications to be studied will be taken from five key domains spanning photochemistry, photocatalysis, time-resolved spectroscopy, photophysics, and quantum technologies. These studies will be focal points for interactions with world-leading experimental groups to demonstrate how the code provides a unique quantitative tool not only for interpreting existing experiments but also for designing new ones.

3 Milestones for the Initial Period

Fig. 1 shows the workplan for the first 3 years. The first year aimed to primarily set up the infrastructure required for the work to be performed. Progress against the milestones is detailed in the next sections.

3.1 Central Activity (CA). Lead: ES

3.1.1 Merge Codes

The aim is to bring codes together and provide the framework for collaborative development. This will be done in the community package Quantics, and controlled through a Gitlab repository.

1. Quantics, has been merged with the Heidelberg MCTDH code. Quantics was a modern update of the Heidelberg package, but development had continued on the old code. The differing features of the two programs have been brought together and future development of the MCTDH method will all be in Quantics.
2. A new version of the Zagreb Surface Hopping Code has been provided by the Došlić group and fully integrated as a Git submodule.
3. The AIMS code merger is underway (Daniel Hollas and Yorick Lassmann) and will combine FMS90 (Martinez's group) with Quantics, also opening an opportunity to combine the GPU-accelerated electronic structure code TeraChem to Quantics.

	Y1	Y2	Y3
CA	Merge Codes (All) DCA.1	QC Interface (BC, BFEC, DS, DCA.5)	Continuous Dev
		Sustainable Quantics Code (BC, GW, EPCC)	DCA.2a
	Web-site (BC, DCA.3)	GUI (BC, BFE(DCA.6)	Training Materials (All)
	Kick-off	File Format (BC, GW) DCA.2b	Optimise Quantics for HPC (BC)
WP1	Sampling Strategies (BFEC, DS)	D1.1a	
		External Perturbations (AK, TJP, GW)	D1.2
	ML / AI Potentials (SH, TJP)		D1.3a
WP2	Analysis Modules (TR-PES, TRXAS, TRXES)	(BFEC, SH, AK, TJP, D2.1	
		TR observables: photodamage/photoprotectio	D2.2a
		TR observables: photoredox catalysis (BFEC, D2.2b	
		TR observables: fluorophores for imaging (GV D2.2c	
		Design models for photoredox	
WP3	Electron dynamics in strong fields (AK, DS, GW)		D3.1a
		Spin-CS for coupled qubits (DS)	D3.2a
		Simulations of coupled (BFEC, DS)	D3.2b
		Electronic structure using Zombie CS (AK, DS)	
		Generalised Coherent States modules for Quantics cc (BC, AK, DS, GW)	

	Coding
	Theory
	Application
	Meeting

Figure 1: Planned work and activities for the first 3 years of the programme

3.1.2 Sustainable Quantics Code

The sustainable development will be based on the use of Gitlab which provides the main tools. The repository has been set up, and continuous integration tests now run to check updates to the code. Other tools to report and track work still need to be configured.

The second strand of sustainable development is through training. It is important that developers work in the same way. To start this process, an on-line workshop was run in Feb. 2024 to present the Quantics code and its development to the project members and partners. There were 42 attendees. The meeting was recorded and posted on the Quantics web-site (<http://www.chem.ucl.ac.uk/quantics>).

3.1.3 Web-site

The COSMOS web-site is up and running at <https://cosmosproject.gitlab.io/cosmos>. It is a site based on Hugoplate, a free starter template built with Hugo and TailwindCSS, designed and developed by Zeon Studio and released under the MIT code license. The website includes information about the COSMOS Team, a list of publications with minipages for each publication, latest news and events and information such as the code of conduct and ED&I. Each of these will continue to be improved and updated over the

course of the project.

Work has also started on updating and improving the Quantics web-site to provide a better platform for exchange of information on the code and how to use it.

3.2 Workpackage 1. New Methods for Quantum Dynamics. Lead GW.

3.2.1 Sampling Strategies

Including the effect of a laser pulse in the initial conditions for nonadiabatic molecular dynamics (BFEC)

The Curchod group has developed a strategy to include the effect of a laser pulse as part of the initial conditions in trajectory-based nonadiabatic molecular dynamics. The formalism, coined PDA (promoted density approach), uses as core component the Wigner pulse representation to calculate an (approximate) promoted nuclear density for the subsequent excited-state dynamics. Sampling the promoted density is the only additional step required in comparison to the standard approach invoking a vertical excitation. We have demonstrated the performance and possible limitations of the formalism by simulating the photoexcitation of NaI with surface hopping and PDA using a broad range of laser pulses, leading to excellent agreements with numerically-exact quantum-dynamics simulations including explicitly the laser pulse (see Fig. 2). The excellent performance of surface hopping+PDA contrasts with the poor performance of surface hopping when coupled to an explicit laser pulse, as reported in earlier works. We also derived the approximate PDAW formalism that sets the simpler energy windowing and intensity convolution strategy on firm ground. The applicability of the PDA approach to molecular systems (and its use as a postprocessing tool, that is, allowing to test the effect of various laser pulses using the same set of nonadiabatic trajectories) was demonstrated with the photoexcitation of protonated formalimine. PDA is implemented in a [user-friendly Python code available on GitHub](#), using as an input only the results of a spectrum calculation obtained with the nuclear ensemble method. Overall, the results of our simulations stress the importance of including the laser pulse in nonadiabatic molecular dynamics and the potential dangers of using the vertical (sudden) excitation. The manuscript of this work is available as a [preprint on arXiv](#) (submitted to J. Phys. Chem. Lett.) and code will be incorporated as a library in Quantics.

Initial Conditions for CS MMethods (DS)

The exact way how the initial conditions of trajectory guided basis sets are sampled and guided is crucial for CS based methods. In the recent paper [J. Chem. Phys. 161, 064102 (2024)] by R. Brook, Ch.Symonds and D.Shalashilin it was demonstrated how the so called cloning technique, broadly used to improve convergence of Ab initio Multiple Cloning method can be used with the Multiconfigurational Ehrenfest version 1 (MCEv1) technique. MCEv1 uses interacting trajectories and demonstrates excellent convergence properties, but adding cloning to it allows to converge quantum dynamics in strongly quantum regimes, where CS basis sets guided my simple noninteracting classical or Ehrenfest trajectories fail. Good convergence of MCEv1 has been demonstrated at the example of analytical Spin-Boson model but direct “on the fly” dynamics version of MCEv1 can be developed in the future.

3.2.2 Machine Learning Methods for Quantum Dynamics

Gaussian Process Regression of Surfaces (GW)

The Quantics code contains routines for using Gaussian Process Regression (GPR) to fit a potential sur-

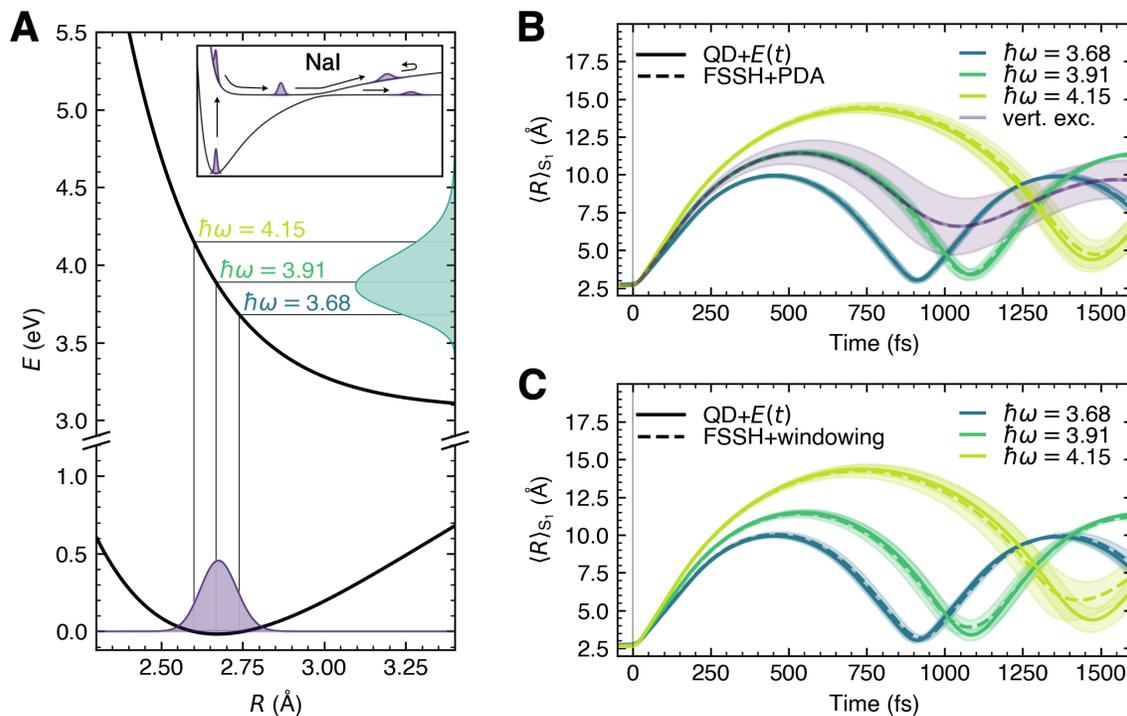


Figure 2: Photoexcitation of NaI with laser pulses of different frequencies, comparing QD with an explicit laser pulse and fewest-switches surface hopping (FSSH) with PDA. (A) Potential energy curves of NaI (full range with sketched nuclear wavepacket evolution is given in the inset) alongside the ground-state density (violet) and the absorption spectrum (green) calculated with the nuclear ensemble method. The different frequencies $\hbar\omega$ of the applied laser pulse are depicted. (B) Expectation values of the NaI bond length in S_1 for three different laser pulse frequencies, comparing quantum dynamics with an explicit 20-fs laser pulse (solid lines) and PDA combined with FSSH nonadiabatic dynamics (dashed lines). The shaded area represents $\langle \Delta R \rangle_{S_1} = \sqrt{\langle R^2 \rangle_{S_1} - \langle R \rangle_{S_1}^2}$ of the nuclear wavepacket (QD) or trajectories (FSSH). Simulations considering vertical excitation are provided as validation. (C) Same as in panel B but for FSSH using a simple windowing approach combined with a time convolution (dashed lines).

face. This code, however, is not general and can only be used in grid-based direct dynamics simulations. Work has started on tidying up this code and make it available for use in other simulation methods. This will not only provide a flexible form of potentials for direct dynamics (DD-vmCG), but as it is in a separable form can also be used in MCTDH simulations. It will also enable vmCG simulations with integrals better than presently provided by the local harmonic approximation.

Work has also been started in collaboration with Burghardt (Frankfurt) to implement a neural net fitting code suitable for QD potentials.

Excited State Potentials within the MACE Framework (TJP)

The MACE method, developed by Csányi and co-workers uses higher order equivariant message passing to provides fast and accurate machine learning interatomic potentials for ground state molecular dynamics simulations. Towards developing rapid approaches for simulating excited state potential energy surfaces, we have extended this model to predict excited state potentials within a single and multi-head framework. For the former, a network is trained on each excited state independently, while the latter

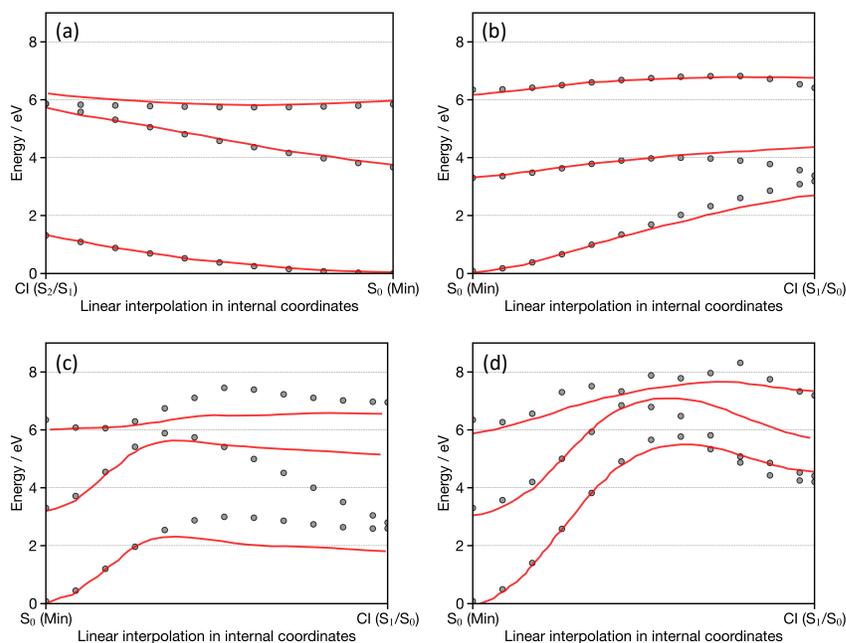


Figure 3: DFT/LR-TDDFT(PBE0)/aug-cc-pvdz (black dots) and MACE predicted (red) potentials along a linear reaction coordinate for cyclobutanone from (a) the Franck-Condon (FC) to the conical intersection (CI) between the S_2/S_1 states, (b) the FC geometry to C_α CI between the S_1/S_0 states (c) the FC geometry to C_β CI between the S_1/S_0 states and (d) the FC geometry to C_α, C_β CI between the S_1/S_0 .

(multi-head) predicts all excited state within a single network.

Figure 3 shows the MACE predicted (red) ground and excited (S_1 and S_2) potentials along key excited state reaction coordinates for cyclobutanone. This was achieved using the single-head framework trained upon 150 energies and gradients at randomly selected geometries obtained from excited state dynamics simulations. The performance is satisfactory for geometries in the region of the ground state (Franck-Condon) geometry (Figure 3a and Figure 3b), but for potentials which show a larger distortion from the ground state geometry, significantly larger errors are observed. Work is currently underway to assess the performance as a function of training set size. This will subsequently be extended to understand the performance with respect to the couplings between the potential energy surfaces.

Machine-Learning Enhanced Propagation of vMCG Equations of Motion (TJP)

Gaussian-based quantum dynamics methodologies provide an accurate yet compact (sub-exponential scaling) representation of the time-dependent nuclear wavefunction. Despite these advantages the computational time remains significant computational challenge in propagating the trajectories. To overcome this, we have implemented a Long short-term memory (LSTM) neural network to predict the motion of the Gaussian basis functions. Here the objective is that the LSTM network will be trained alongside the propagation of the nuclear wavepacket to predictively map nonstationary wavepackets from a given current time to a target future time. Training will continue, until it has sufficient data to take-over in predicting the following steps.

The methodology of this project builds upon the proof-of-concept work described in [J. Phys. Chem. Lett. 12 (2021) 10654-10662]. Here, a Multi-Layer Perceptron neural network was used, with the data pre-processed in a manner to make it amenable to predicting time-series data. The network developed takes the potential (energy and force) as well as Gaussian-basis function (coefficient, position and momentum) information at each timestep as input to predict future position and coefficients of the basis functions.

Initial results suggest that the training time required increases significantly with the dimensionality of the problem at hand, meaning that long simulations are required before there is sufficient information of the LSTM network to take over from the first principles propagation. Work in this area continues to improve performance.

ML-driven design of functionalized maleimides as fluorescent probes (SH)

The Habershon group, in collaboration with the group of Prof. Rachel O'Reilly (Birmingham), have continued to study the use of ML strategies - notably artificial neural networks (ANNs) - to explore design integrated computational/experimental strategies for design of functionalized maleimides with targeted absorption and emission properties. By mining *experimental* absorption and emission data for known synthesized maleimides functionalised with different heteroatom functionalities, we have constructed an ANN to accurately predict maleimide photoproperties in very fast approach, with a good level of predictive performance (Fig. 4).

Following initial training on an experimental dataset of 200 maleimides, this ANN has been subsequently used to guide the exploration of chemical space in searching for maleimides with alternative absorption/emission profiles compared to those in the original training set. This has ultimately led to the synthesis and experimental characterization of a further 20 previously-unknown maleimides - simultaneously expanding the maleimide training set for a further iteration of maleimide design. This experimental/computational study is currently under review at *Chemical Science*.

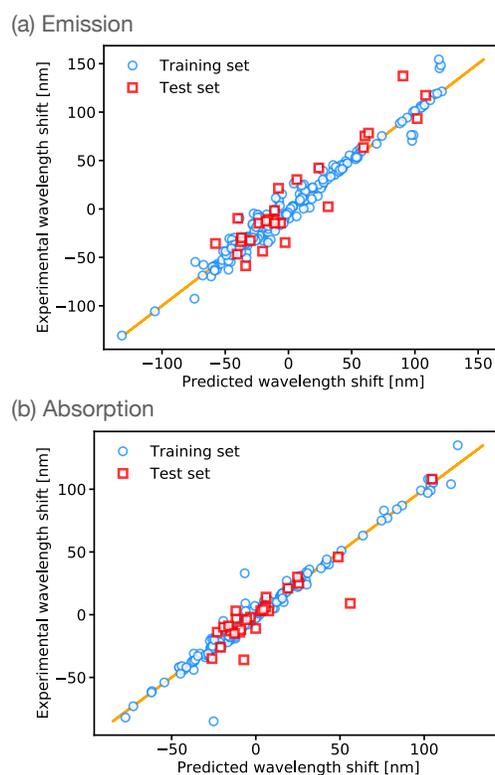


Figure 4: ANN prediction correlation plot of wavelengths for maleimide training-set (blue circles) and test-set (red squares). The ANN predictions and experimental wavelengths are given relative to the mean of the experimental dataset. Results are shown for prediction against (a) wavelength of maximum emission, and (b) wavelength of maximum absorption.

ML-inspired design of new time-dependent basis functions for quantum dynamics (SH)

The Habershon group have previously developed strategies for ‘on-the-fly’ quantum dynamics by coupling accurate wavefunction propagation strategies, such as MCTDH and v-MCG, with Gaussian process regression (GPR) and kernel ridge regression (KRR) [see, for example, *Acc. Chem. Res.*, **55**, 209 (2022); *J. Chem. Phys.*, **148**, 134116 (2018)]. An important learning-point from those studies is the impact of the choice of *kernel function* on the efficiency of representing potential energy surfaces (PESs). Specifically, we have shown how using *additive* Gaussian kernels means that a much lower number of target function evaluations are required to generate an accurate PES representation when compared to standard *product* Gaussian kernels.

This observation has now motivated a new study at Warwick to explore whether alternative functions - rather than standard product Gaussian wavepackets - could be used for representing time-dependent wavefunctions with better scaling with dimensionality. Starting with the appointment of a new post-doctoral research fellow in the Habershon group at Warwick (Lidice Cruz-Rodriguez), this project is in the early stages of confirming that low-dimensional-scaling functions can represent time-dependent wavefunctions generated by MCTDH. The next step will then be to develop a trajectory-based scheme founded on such basis functions; this is ongoing work.

3.2.3 New algorithms

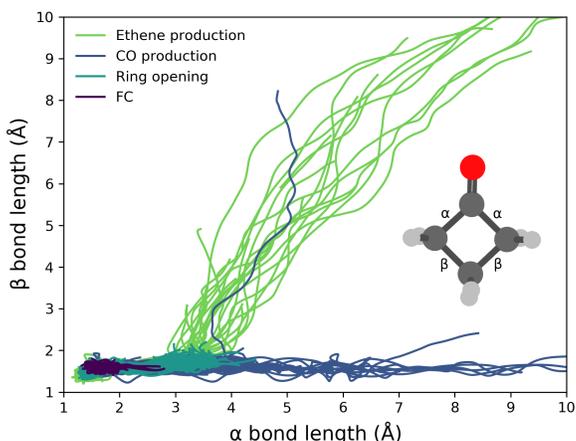


Figure 5: A 2D projection of all CC bond lengths in cyclobutanone across all trajectories obtained using the MASH approach to surface hopping. The CC bonds are partitioned according to the labeling on the inset. Each trajectory is clustered based on the final geometry of the trajectory, resulting in four channels: *i)* FC, *ii)* ring opening, *iii)* CO production and *iv)* ethene production.

New mapping algorithms for surface hopping (AK)

As part of the *Prediction Challenge* (see Section 3.3.3), we implemented and evaluated a new version of the trajectory surface hopping algorithm, known as *mapping approach to surface hopping* (MASH). This combines elements of mapping methods with standard surface hopping to attempt to achieve the best of both worlds. Hence, in contrast to the stochastic algorithm in fewest switches surface hopping, MASH uses a deterministic algorithm to evaluate the active state. Figure 5 shows a sample simulation result.

The evaluation of this methodology is ongoing, but some further details can be found in the following [publication](#), and the current plan is to integrate this methodology into the Quantics package.

3.3 Workpackage 2. Quantum Dynamics in Chemistry. Lead: BFEC.

3.3.1 Accurate and Rapid First Principles Model Potentials

Extending and Assessing Limits of the Linear Vibronic Coupling Hamiltonian (TJP)

The Linear Vibronic Coupling (LVC) Hamiltonian presents an accurate and accessible model approach for understanding the photophysics, including intersystem crossing of molecular systems. One of its main advantages is that the Hamiltonian can be derived using very few quantum chemistry calculations at the expansion geometry, usually the Franck-Condon geometry. However, this approach is only valid provided there are no large amplitude motions in the excited state dynamics. In recent work [Eng *et al.* PCCP **25** (2023), 7195-7204], we have introduced a metric to quantifying the breakdown of the linear vibronic coupling Hamiltonian.

In this framework, the important intrastate coupling terms are derived using the gradient of the adiabatic state at the FC geometry, along the normal modes for each state involved. This is written:

$$\lambda_k^{mn} = \sqrt{\frac{|V_n - V_m|}{4} \left(\left. \frac{\partial^2 V_n}{\partial Q_k^2} \right|_{Q_0} - \left. \frac{\partial^2 V_m}{\partial Q_k^2} \right|_{Q_0} \right)}. \quad (1)$$

However, this two-state approach assumes the change in gradient along a normal mode for a given state is caused by only one other state, which is not always the case, especially for molecules exhibiting a high density of states. Importantly, in this Eq 1, the change in any two coupled states is expected to be equal and opposite. Consequently, and accounting for the underlying parabolic behaviour of the ground state, we can rewrite the equation to depend on only one state,

$$\lambda_k^{mn} = \sqrt{\frac{|V_n - V_m|}{2} \left(\left. \frac{\partial^2 V_n}{\partial Q_k^2} \right|_{Q_0} - \omega_k \right)} \quad (2)$$

The interstate coupling is then calculated by either Eq. 1 or Eq. 2 and differences can highlight an additional breakdown of the LVC model. This approach was used to study the excited state properties of a planar D_{3h} symmetric azatriangulenetrione, HTANGO, which has received significant interest due to its high solid-state phosphorescence quantum yield and therefore potential as an organic room temperature phosphorescent (ORTP) dye. Using a model linear vibronic coupling Hamiltonian in combination with quantum dynamics simulations, we observe that intersystem crossing (ISC) in HTANGO occurs with a rate of $\sim 10^{10} \text{s}^{-1}$, comparable to benzophenone, an archetypal molecule for fast ISC in heavy-metal free molecules. Our simulations demonstrate that the mechanism for fast ISC is associated with the high density of excited triplet states which lie in close proximity to the lowest singlet states, offering multiple channels into the triplet manifold facilitating rapid population transfer.

3.3.2 Analysis tools for observables

Rapid Predictions of X-ray Spectra using Physics-Inspired Neural Networks (TJP, BFEC)

The analysis of time-resolved observables is often time-consuming due to the need to perform a larger number of quantum chemistry simulations computing experimental observables at all time-steps required. The computational expense of this analysis can potentially be alleviated using machine learning algorithms. However, these are often highly contingent upon the architect's choice of input representation. We have recently introduced the partial density of states (p-DOS) descriptor: a novel, quantum-inspired structural representation which encodes relevant electronic information for machine learning models seeking to simulate X-ray spectroscopy. p-DOS uses a minimal basis set in conjunction with a guess (non-optimised) electronic configuration to extract and then discretise the density of states (DOS) of the absorbing atom to form the input vector. We demonstrate that while the electronically-focused p-DOS performs well in isolation, optimal performance is achieved when supplemented with nuclear structural information imparted *via* a geometric representation. p-DOS provides a description of the key electronic properties of a system which is not only concise and computationally efficient, but also independent of molecular size or choice of basis set. It can be rapidly generated, facilitating its application with large training sets. Its performance is demonstrated using a wide variety of examples at the sulphur K-edge, including the prediction of ultrafast X-ray spectroscopic signal associated with photoexcited 2(5H)-thiophenone. These results highlight the potential for ML models developed using p-DOS to contribute to the interpretation and prediction of experimental results *e.g. in operando* measurements of batteries and/or catalysts and femtosecond time-resolved studies, especially those made possible by emergent cutting-edge technologies, especially X-ray free electron lasers.

Towards Accurate and Rapid Simulations of Valence Excited Core-hole Spectra (TJP, BFEC)

First principles simulations of transient X-ray spectra are becoming increasingly important to interpret the wealth of electronic and geometric information contained within femtosecond X-ray absorption spectra recorded at X-FELs. However, because the transition dipole matrix elements must be calculated between two excited states (*i.e.* the valence excited state and the final core-excited state) of very different energies, this can be challenging and time-consuming to compute. To improve our description of these important experimental observables we have undertaken a detailed study seeking to establish the ability of *n*-electron valence state perturbation theory (NEVPT2), equation-of-motion coupled cluster theory (EOM-CCSD), linear-response time-dependent density functional theory (LR-TDDFT) and the maximum overlap method (MOM) to describe excited state X-ray spectra, with a particular focus on their behaviour away from the Franck-Condon geometry and around important topology features on excited state potential energy surfaces, namely conical intersections.

Figure 6 shows the ground state (black) and valence excited S_1 (green) oxygen K-edge X-ray spectra calculated along the LIIC from the optimized ground state to the S_1 minimum and then S_1/S_0 conical intersection for cyclobutanone. The main features are comparable between all four methods with the trends for coupled cluster, LR-TDDFT and MOM/LR-TDDFT in especially good agreement. In all four cases, the ground state and S_1 bands meet at the conical intersection geometry, and each spectral evolution follows the shape of the ground and excited state potential energy curves shown in Figure S1. Despite the general agreement, there are two key differences worth noting: firstly, the excited state feature is independent of geometry during the transition from the ground state to S_1 geometry for CCSD, LR-TDDFT, and MOM/LR-TDDFT; and secondly, the spectral changes in NEVPT2 are slightly larger than the shifts in potential energy surfaces. For the former, valence excitation corresponds to a HOMO \rightarrow LUMO ($n\pi^*$) transition while the final core-valence excited state exhibits a $1s\rightarrow$ LUMO from the reference ground state. Along the S_0 (min) to S_1 (min) potential, the primary change is an elongation of the C=O bond, which doesn't change the energy of the LUMO significantly, and the shape of the potential

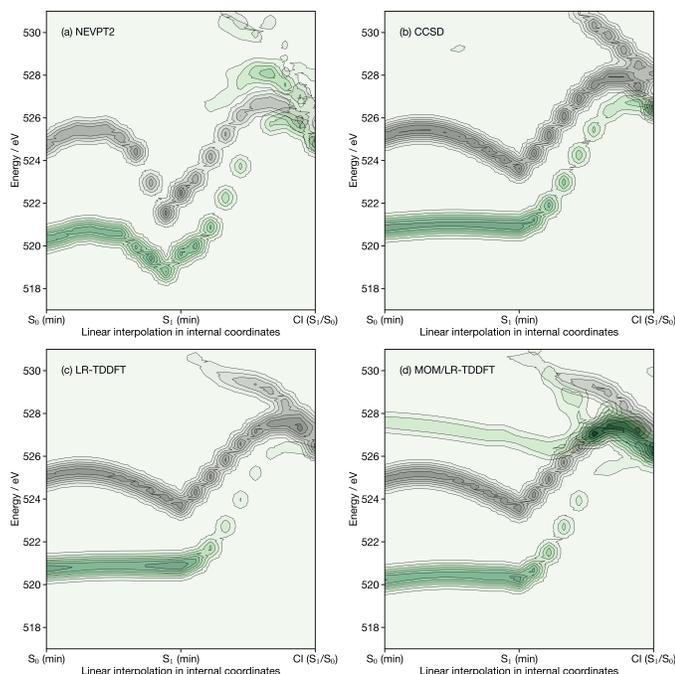


Figure 6: The oxygen K-edge X-ray spectra of cyclobutanone calculated using (a) NEVPT2, (b) CCSD, (c) LR-TDDFT and (d) MOM-TDFT along the LIIC from the optimised ground state to the S_1 minimum and then S_1/S_0 conical intersection for cyclobutanone. Black corresponds to the spectrum for the electronic ground state, while green is the spectrum for the S_1 state.

is driven by changes in the energy of the HOMO. In contrast, this feature in NEVPT2 shifts by ~ 2 eV, while the spectral features between the S_1 (min) and the S_1/S_0 conical intersection is ~ 4 eV, both greater than the change in the valence potential energy surfaces. This arises from configuration mixing by the multi-reference wavefunction.

Importantly, this work highlights the advantages and limitation of electronic structure methods of different accuracy for simulating transient X-ray spectra and therefore acts as an important benchmark in the field. It also provides the foundation to develop more accurate and computationally efficient approaches.

Recovering time-dependent photoproduct quantum yields from time-resolved diffraction techniques (BFEC)

A strategy was developed to extract the time-dependent population of photoproducts from time-resolved ultrafast electron diffraction signals. By simulating the time-resolved UED signal obtained for the photodynamics of thiophenone, it was shown that the UED signal corresponding to each photoproduct did not exhibit a significant time-dependence and a time-average can be used to produce photoproduct-dependent fitting basis functions for the experimental UED signal (Fig. 7). This strategy allowed to deduce the time-dependent photoproduct quantum yields for the early times dynamics of thiophenone, highlighted in particular the presence of an unexpected episulfide product – more information can be found in the corresponding [publication](#). This strategy is amenable to time-resolved x-ray scattering, with exciting preliminary results on the study of a Wolff rearrangement.

Molecular structure retrieval from scattering data (AK)

A method was developed to determine the molecular geometry from the large- q scattering, based on a recently developed simulated annealing approach for geometry retrieval. It makes it possible to identify deviations in the experimentally observed scattering signals from the independent atom model approximation and provides a tool for isolating the effect of valence electronic structure on the scattering signal. More information can be found in the corresponding [publication](#).

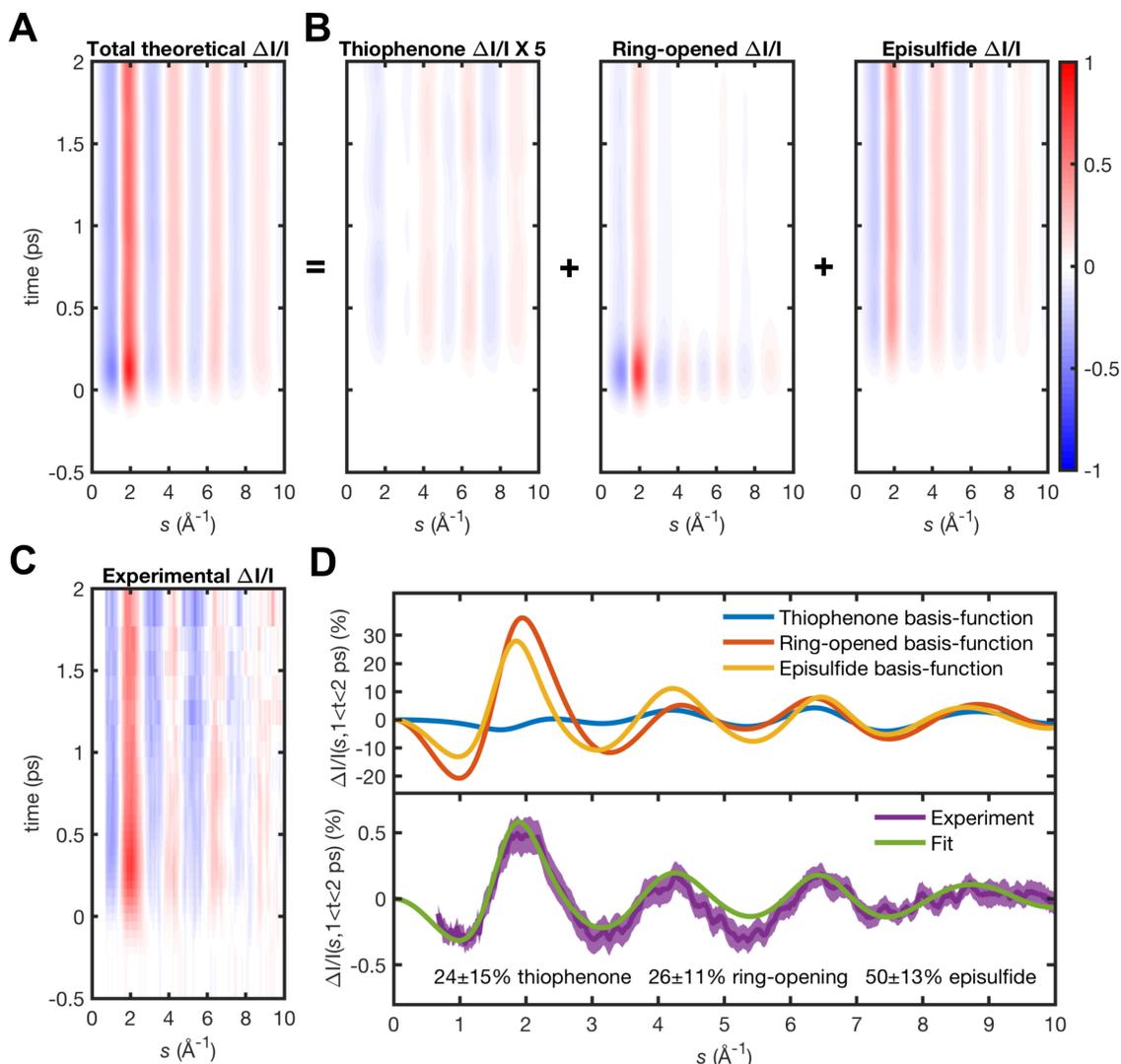


Figure 7: Decomposition of a theoretical UED signal (A) into its photoproduct contributions (B). Comparison with the experimental results (C) and (theoretical and experimental) time-averaged UED signals (D)

3.3.3 Simulating Time-resolved Experimental Observables: The Cyclobutanone Challenge (BFEC, GW, DS, AK, TJP)

The simulation of photochemical molecular dynamics has been a major challenge to theoretical chemistry because of the need to simultaneously describe quantum mechanical effects of both nuclei and electrons. Numerous advances have been made over the past decade and many would agree that excited state simulations have demonstrated their value in the interpretation of experiments. However, one can question whether these simulations have been unambiguously predictive. True predictive capabilities would pave the way to rational design of light-driven molecular systems, with revolutionary implications for renewable solar energy (directly to electricity or to fuels), bioimaging, optogenetics, and photochemical synthesis. Thankfully, new ultrafast diffraction experiments have come on-line which provide both spatio-temporal resolution on the atomic scale, *i.e.* molecular movies. This provides a novel opportunity — a double-blind test of the accuracy of excited state simulations.

Based on intensive discussions during a CECAM workshop in 2023, the COSMOS team and partners have arranged for such a test and challenged the community of computational photochemists to predict (i) the photochemistry of cyclobutanone (Fig. 8) in the gas phase and (ii) its resulting ultrafast electron diffraction signal in advance of an experiment. The participants could use any combination of methods of their liking, considering that they should submit a paper to the Journal of Chemical Physics with their prediction before the experiment was done, leaving them with six months for their prediction. This prediction challenge resulted in an unexpectedly large number of contributions (sixteen) with a much wider variety of methods for the electronic structure and nuclear dynamics than anticipated. The current status of the challenge is accessible on the [dedicated webpage of the Journal of Chemical Physics](#).

Yet, the publication of these predictions is only the beginning of the adventure, as the community now needs to analyze and thoroughly discuss these results to agree on their interpretation and lead to the publication of a fact-based roadmap for future developments in the field. The COSMOS team and partners have submitted a proposal for the organization of a CECAM workshop in 2025, where the computational results will be discussed in light of the experimental data, offering a clear, community-driven roadmap for future developments in nonadiabatic molecular dynamics.

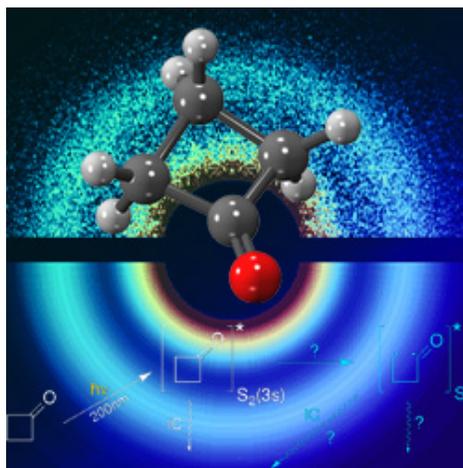


Figure 8: Prediction challenge – photochemistry of cyclobutanone and its ultrafast electron diffraction signal.

3.3.4 Molecular benchmarks in nonadiabatic molecular dynamics (BFEC, GW, SH)

COSMOS members Graham Worth, Scott Habershon, and Basile Curchod participated in a CECAM workshop on '[Standardizing nonadiabatic dynamics: towards common benchmarks](#)' in May 2024. The goal of this workshop was to discuss the creation of an adequate benchmark set for methods in nonadiabatic dynamics that can be used with any type of nonadiabatic molecular dynamics methods. The workshop was organized by COSMOS project partners Federica Agostini and Sandra Gómez, as well as Lea Maria Ibele and Antonio Prlj (both former members of the Curchod group). The participants of this workshop are currently writing a Roadmap article (to be submitted to the Journal of Physical Chemistry A), identifying the different identified key ingredients to consider when developing benchmarks for nonadiabatic dynamics to ensure their uptake by the broad community.

3.4 Workpackage 3. Simulating Quantum Technologies. Lead: DS.

3.4.1 Electron Dynamics in Strong Fields

Coherent States for Electron Dynamics (DS)

Although the methods which use the grids of trajectory guided Gaussian Coherent States have been developed predominantly for description of nuclear dynamics they can also be applied to the dynamics of electrons.

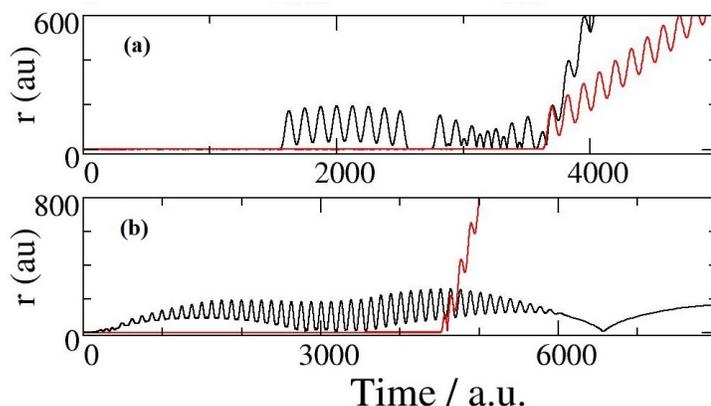


Figure 9: Two-electron dynamics for single and double ionisation in strong fields. Note the large radius electronic motions involved in the process. Trajectory guided basis efficiently follows this large amplitude motion .

The figure (Fig. 9) illustrates trajectories of electronic Gaussian Coherent States basis functions describing the motion of electrons in He atom subjected to strong laser electric field. These two trajectories illustrate the parts of the total 2-electron wave function responsible for double ionization via recollision or sequential double ionization. . The trajectory-guided Gaussian CSs are particularly effective for large amplitude motion dynamics, where regular grids quickly become too large to be tractable, while the adaptive grid employed here has succeeded to simulate double ionisation. Our ambition is to provide an accurate numerical solution of TDSE for multielectron systems for the cases when large amplitude electronic motion plays a role.

3.4.2 Generalised Coherent State Modules for Quantics

Coherent States for Qubit Simulations (DS)

Gaussian Coherent States are extremely efficient for the description of coupled oscillators and therefore for simulations of nuclear motion in chemical dynamics. However other types of CSs exist, such as SU(2) CSs describing 2 level systems. We are now using them to simulate the dynamics of coupled qubits. These calculations are meant to simulate quantum computers on a classical machine and belong to the class of quantum inspired classical algorithms.

Also, we are exploring a new class of recently introduced fermionic SU(2) states, called Zombie Coherent States, and develop a new approach to electron dynamics and electronic structure. The ZS techniques address the problem of dimensionality in electronic structure which is manifested by a huge number of electronic configurations required by standard electronic structure calculations. ZSs describe spin-orbitals as occupied by simultaneously “dead or alive” electrons or put it differently allow random fractional occupations of spin-orbitals. We prepared a publication, which demonstrates that a multielec-

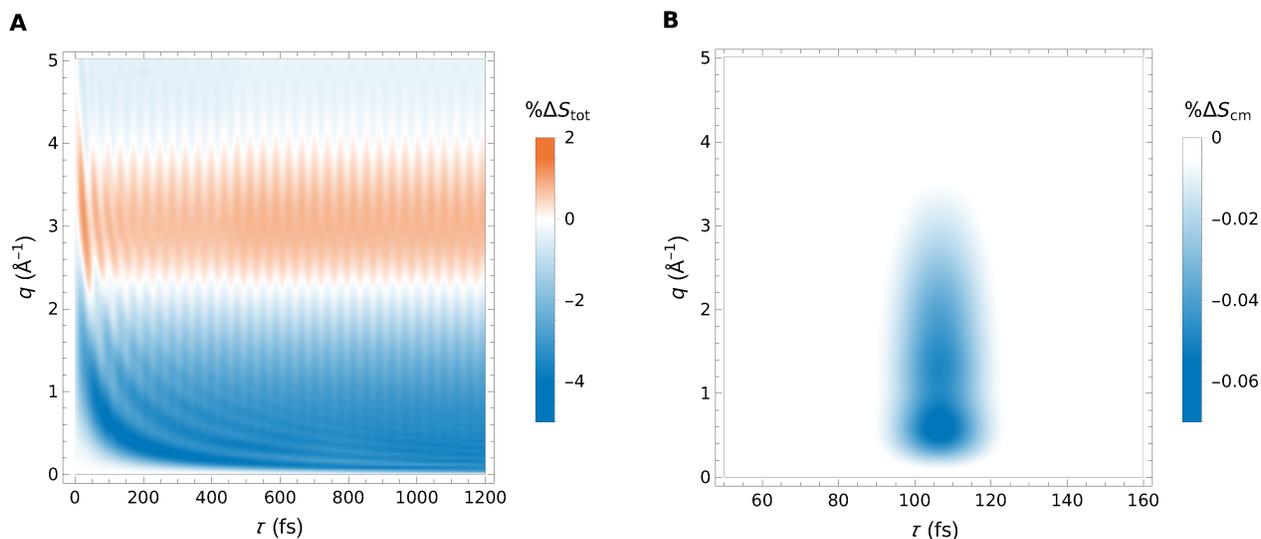


Figure 10: The total (**A**) and coherent mixed (**B**) percent-difference scattering signals of photoexcited LiF probed by a hard X-ray pulse as a function of momentum transfer q and pump-probe delay time τ , based on accurate quantum dynamics simulations.

tron ground state of a molecule can be represented with a superposition of a small number of ZSs whose parameters are globally optimised.

3.4.3 Transient electron dynamics induced by nonadiabatic effects

Accurate quantum dynamics simulations in a molecular model system (AK)

Nonadiabatic transitions at conical intersections and avoided crossings play a pivotal role in shaping the outcomes of photochemical reactions. Using the photodissociation of LiF as a model, our theoretical study demonstrated how gas-phase nonresonant ultrafast x-ray scattering could map nonadiabatic transitions at an avoided crossing, utilising a part of the scattering signal which probes electronic coherence directly. The predictions are based on numerically exact propagation of the LiF wavepacket and uses two- rather than one-electron densities, to obtain accurate scattering cross sections which inherently account for *all* possible electronic transitions. The results are shown in Fig. 10. The approach provides quantitative predictions of the experimental signals, thereby facilitating future experimental endeavors to observe nonadiabatic effects and coherent electron dynamics with ultrafast x-ray scattering. More information can be found in the corresponding [publication](#).

4 Workshops and Training Activities

4.1 Cohort Building and EDI. Lead: TJP.

The first cohort of PDRAs and PhD students have now been recruited (see Sec. 9). Daniel Hollas (Bristol) will chair a PDRA committee and will join the management committee (MC) to represent the early career researchers (ECRs). The PDRAs will meet soon to discuss how they want to interact and be supported as the project progresses.

4.2 Workshops Held 2023-2024

- Worth and Curchod organised a [Theory Workshop on Computational Photochemistry](#) for the consortium of the EPSRC Programme Grant 'Ultrafast Photochemical Dynamics in Complex Environment', Apr. 5, 2024.
- On-line Workshop on code structure and development, Feb. 22, 2024. Forty two people attended and presentations were made on developing the code and how it looks to run simulations from the user perspective.
- A one-day meeting was held in Leeds on Mar. 22, 2024. COSMOS participants and their group members met, and external speakers presented two talks: "Probing dynamics of chemical bonds in organic chromophores by X-ray spectroscopies" by Dr. Sergei Tretiak from Los Alamos National Laboratory and "Theoretical and Computational Photochemistry of Light-Sensitive Biosystems" by Prof. Anastasia Bochenkova from Moscow State University.
- The First Project Meeting was a 2 day meeting held in Newcastle on Sep. 25-26 2024 with the whole COSMOS team and a number of project partners. There were 43 attendees on-site, and a further 6 joined on-line. There were presentations on key topics and ideas, including a presentation from Andy Turner of the EPCC on novel HPC architectures and how to use them. The second day was devoted to talks and ideas from the project partners and ECRs. Throughout were also posters presenting work from various groups. Chi Onwaruh, Newcastle MP and chair of the government Select Committee on Science and Technology, also visited and presented the new governments position on science, along with a short Q+A session on how the government could support science research.

4.3 Planned

- Quantics training day, Nov. 2024
- ECR Training in Presentation Skills.
- Joint COSMOS - UPDICE meeting, Summer 2025
- Proposal submitted in July 2024 to organise a CECAM Workshop on the Prediction Challenge. The outcome is expected in December 2024, for a workshop taking place in 2025.

5 Exchange visits between groups and project partners

1. Worth visited the partner group of Sanz-Sanz (Madrid) Nov. 6-8 2023. Discussion of possible projects.
2. Worth visited the partner group of Gómez (Salamanca) Nov. 9-10 2023. Discussion of possible projects.
3. Worth visited the partner group of Vendrell (Heidelberg) 26 Feb. - 1 Mar. 2024. Merging of Heidelberg MCTDH package and Quantics.
4. Sanz-Sanz (Madrid) visited Worth May-Jul 2024. New code for Surface hopping including spin-orbit coupling was added to Quantics.

6 Presentations at International Meetings and University Symposia

Worth has presented work related to COSMOS at:

1. High-Dimensional Quantum Dynamics. 8th International Workshop, DESY, Hamburg, Germany, Jul 16-19 2024.
2. Cecam Workshop: Standardizing nonadiabatic dynamics: Towards Common Benchmarks, Orsay, Paris, France, May 21-24 2024.
3. Modern Methods for Differential Equations of Quantum Mechanics, BIRS, Banff, Canada, Apr. 21 - 26 2024.
4. AMOC24: Atoms, Molecules and Clusters in Motion, Marne-La-Vallée, Paris, France, Apr 15-18 2024.
5. Cecam Workshop: Theoretical and Experimental Advances in Atmospheric Chemistry, Lausanne, Switzerland, Mar 26-28 2024.
6. CHAMMPS Workshop on Electron and Nuclear Dynamics in Phase Space, Bristol, UK, Jan 8-10 2024.
7. Structure and Dynamics: Spectroscopy and Scattering (SDSS-2023), Kolkata, India, Oct 5-8 2023.
8. DESY, Hamburg, Germany, Jan 18 2024.
9. NYU Shanghai University, China (On-line), Dec 1 2023.
10. University of Salamanca, Spain, Nov 9 2023.
11. Autonoma University of Madrid, Spain, Nov 8 2023.

Penfold has presented work related to COSMOS at:

1. Marseille University, France, Apr. 2024
2. ESRF User Meeting 2024, Grenoble, France, Mar. 2024
3. Rutgers University, USA, Feb. 2024
4. University of Sheffield, UK, Nov. 2023
5. University of Edinburgh, UK, Oct. 2023

Curchod has presented work related to COSMOS at:

1. 2024 Computational Chemistry GRC, Maine (USA), 22 July 2024.
2. Quantum Dynamics Seminar, MPI, Dresden (Germany), 4 July 2024.
3. ESCMQC 2024, Copenhagen (Denmark), 26 June 2024.
4. RSC Prize Lecture, Sheffield (UK), 5 June 2024.
5. UK XFEL Townhall, Sheffield (UK), 5 June 2024.
6. CECAM/Psi-k conference on excited states, Lausanne (Switzerland), 27 May 2024.
7. CECAM workshop on nonadiabatic dynamics, Paris (France), 21 May 2024.
8. Chemistry seminar, Université Gustave Eiffel (France), 18 April 2024.
9. AMOC 2024, Paris (France), 16 April 2024.
10. QETLab Seminar, University of Bristol (UK), 11 April 2024.
11. ACS Spring Meeting 2024, New Orleans (USA), 17 March 2024.
12. ViRAPID 2024 Workshop, Vienna (Austria), 27 February 2024.
13. Quantum Information Theory Seminar, University of Bristol (UK), 7 February 2024.
14. Chemistry Seminar, Warwick University (UK), 25 October 2023.
15. Telluride Meeting on Nonadiabatic Dynamics, Telluride (USA), 2 October 2023.

Shalashilin has presented work related to COSMOS at:

1. Telluride Meeting on Nonadiabatic Dynamics, Telluride (USA), 2 October 2023.
2. Gaseous Electronics Conference, Ann Arbor (USA), 9 October 2023.
3. Quantemol Plasma Chemistry workshop, London (UK), 10 May 2024.
4. Challenges 2024 International School and Conference "Current Challenges in Chemical Physics and Theoretical Chemistry", Moscow (Russia) 1 July 2024.
5. Tokyo Electron Plasma Chemistry workshop, Albany (USA), 21 October 2024.

Habershon has presented work related to COSMOS at:

1. Royal Society of Chemistry Spectroscopy and Dynamics Interest Group Annual Meeting, Keynote lecture, Leicester (UK), January 2024.
2. American Chemical Society National Meeting, Denver, CO (USA), August 2024.

Kirrander has presented work related to COSMOS at:

1. International Conference for High-Resolution Spectroscopy, Plenary lecture, Bologna (IT), September 2024.
2. Central Laser Facility, Invited seminar, Rutherford (UK), July 2024.
3. Danscatt 2024 XFEL meeting, Invited talk, University of Aarhus (DK), May 2024.
4. The Path of Quantum Chemistry into the 21st Century, Invited talk, ETH (CH), February 2024.
5. DOE Basic Sciences Division PI meeting 2023, Group presentation, Washington D.C. (USA), October 2023.
6. Oxford Photonics Day 2023, Invited talk, Oxford (UK), October 2023.

7 Outreach Activities

1. Worth presented at talk to the ADM Mathematical Society, UCL, Mar. 20 2024.
2. Curchod presented a talk at [Pint of Science](#), Bristol, May 13, 2024.
3. Kirrander hosted the Master of St. Peter's College, Prof. Judith Buchanan, for a high-level introduction to the research projects in COSMOS, March 20, 2024.

8 Publications

1. Prediction through quantum dynamics simulations: Photo-excited cyclobutanone; O Bennett, A Freibert, K. E. Spinlove and G. A. Worth, *J. Chem. Phys.*, 2024, 160, 17, 174305
2. Valence shell electronically excited states of norbornadiene and quadricyclane; J. C. Cooper, D. M. P. Holland, R. A. Ingle, A. Kirrander, D. Rolles, *et al.*, *J. Chem. Phys.*, 2024, 160, 6, 064305
3. On the multiphoton ionisation photoelectron spectra of phenol; D. Dey, J. L. Woodhouse, M. P. Taylor, H. H. Fielding and G. A. Worth, *Phys. Chem. Chem. Phys.*, 2024, 26, 4, 3451
4. The Photochemistry of Rydberg Excited Cyclobutanone: Photoinduced Processes and Ground State Dynamics; J. Eng, C. Rankine and T. Penfold, *arXiv*
5. Monitoring the Evolution of Relative Product Populations at Early Times during a Photochemical Reaction; J. P. Figueira Nunes, L. M. Ibele, S. Pathak, B. F. E. Curchod, *et al.*, *J. Am. Chem. Soc.*, 2024, 146, 6, 4134
6. Predicting the photodynamics of cyclobutanone triggered by a laser pulse at 200 nm and its MeV-UED signals—A trajectory surface hopping and XMS-CASPT2 perspective; J. Janoš, J. P. Figueira Nunes, D. Hollas, P. Slavíček and B. F. E. Curchod, *J. Chem. Phys.*, 2024, 160, 14, 144305
7. Rigid and planar π -conjugated molecules leading to long-lived intramolecular charge-transfer states exhibiting thermally activated delayed fluorescence; S. Kuila, H. Miranda-Salinas, J. Eng, C. Li, M. R. Bryce, T. J. Penfold and A. P. Monkman, *chemRxiv*
8. Ultrafast electron diffraction of photoexcited gas-phase cyclobutanone predicted by *ab initio* multiple cloning simulations; D. V. Makhov, L. Hutton, A. Kirrander and D. Shalashilin, *J. Chem. Phys.*, 2024, 160, 16, 164310
9. Partial Density of States Representation for Accurate Deep Neural Network Predictions of X-ray Spectra; C. Middleton, B. F. E. Curchod and T. J. Penfold, *Phys. Chem. Chem. Phys.*, 2024, in press.
10. Extracting the electronic structure signal from X-ray and electron scattering in the gas phase; T. Northey, A. Kirrander and P. M. Weber, *J. Synchrotron Rad.*, 2024, 31, 2, 303
11. Synthesis, Photophysical and Electronic Properties of a D- π -A Julolidine-Like Pyrenyl-*o*-Carborane; J. Krebs, L. Brändler, I. Krummenacher, A. Friedrich, H. Braunschweig, M. Finze, B. F. E. Curchod, T. B. Marder, *Chem. Eur. J.*, 2024, 30, e202401704.
12. On the Topological Phase around Conical Intersections with Tamm–Dancoff Linear-Response Time-Dependent Density Functional Theory; J. Taylor, D. J. Tozer, B. F. E. Curchod, *J. Phys. Chem. A*, 2024, 128, 5314.
13. Perspective on Theoretical and Experimental Advances in Atmospheric Photochemistry; B. F. E. Curchod, A. J. Orr-Ewing, *J. Phys. Chem. A*, 2024, 128, 6613.

14. Using a multistate mapping approach to surface hopping to predict the ultrafast electron diffraction signal of gas-phase cyclobutanone; L. Hutton, A. Moreno Carrascosa, A.W. Prentice, M. Simmermacher, J. E. Runeson, M. J. Paterson, A. Kirrander, J. Chem. Phys., 2024, 161, 064102.
15. Ultrafast x-ray scattering and electronic coherence at avoided crossings: complete isotropic signals; E. M. Liane, M. Simmermacher, A. Kirrander, J. Phys. B, 2024, 57, 145602.

9 Early Career Researchers on the Project

Dates	Name	Institution	Status	Employed on grant?
Oct. 2023 - Now	Eryn Spinlove	UCL	Programme Manager	Y
Jan. 2024 - Now	Sarbani Patra	UCL	PDRA	Y
Oct. 2024 - Now	Alice VanHaeften	UCL	PDRA	Y
Oct. 2023 - Now	Leon Cigrang	UCL	PhD	N
Oct. 2023 - Now	Jaymee Coonjobeeharry	UCL	PhD	N
Jul. 2024 - Now	Daniel Hollas	Bristol	PDRA	Y
Jun. 2024 - Now	Vera Brieskorn	Bristol	PhD	N
Jul. 2024 - Now	Yorick Lassmann	Bristol	PhD	N
Jan. 2024 - Now	Julien Eng	Newcastle	PDRA	Y
Apr. 2024 - Now	Thomas Pope	Newcastle	PDRA	N
Oct 2023 - Now	Clelia Middleton	Newcastle	PhD	N
Oct 2024 - Now	Leon Ashley	Newcastle	PhD	N
Oct 2024 - Now	Lidice Cruz-Rodriguez	Warwick	PDRA	Y
Oct 2023 - Now	Zahra Bhatti	Warwick	PhD	N
Oct 2023 - Now	Dmitry Makhov	Leeds	PDRA	Y
Oct 2023 - Now	Andrés Moreno Carrascosa	Oxford	PDRA	N
Oct 2023 - Now	Lewis Hutton	Oxford	PDRA	N
Oct 2023 - Now	Jakub Kara	Oxford	PhD	N
Oct 2023 - Now	James Merrick	Oxford	PhD	N

10 Members of the Project

The project has a group of international partners and associated researchers, listed below.

1. Federica Agostini, University Paris-Saclay
2. Mikhail Ivanov, Max-Born-Institute Berlin
3. Peter Weber, Brown University
4. Jakob Andreasson, ELI Beamlines
5. Matthias Kling, SLAC National Accelerator Laboratory
6. Eli Zysman-Colman, University of St. Andrews

7. Javier Segarra-Martí, University of València
8. Sergei Tretiak, Los Alamos National Lab
9. Hans Jakob Wörner, ETH Zürich
10. Nada Došlić, Ruđer Bošković Institute
11. Sandra Gómez, Universidad de Salamanca
12. Morgane Vacher, Nantes Université
13. Julia Weinstein, University of Sheffield
14. Olof Johansson, University of Edinburgh
15. Terry Frankcombe, UNSW Canberra
16. Shirin Faraji, Heinrich Heine University Düsseldorf / Rijksuniversiteit Groningen
17. Josh Vura-Weis, University of Illinois Urbana-Champaign
18. John Marangos, Imperial College London
19. Fabrizio Santoro, iCCOM Pisa
20. Sara Bonella, EPFL CECAM
21. Martin Centurion, University of Nebraska-Lincoln
22. Kenneth Lopata, Louisiana State University
23. Michael Minitti, SLAC (MeV-UED)
24. Daniel Rolles, Kansas State University
25. Cristina Sanz-Sanz, Universidad Autonoma de Madrid
26. Benjamin Lasorne, ICGM Montpellier
27. Albert Stolow, University of Ottawa
28. Michael Schuurman, University of Ottawa Pascal Mieville, EPFL
29. Artur Izmaylov, University of Toronto
30. Oriol Vendrell, University of Heidelberg
31. Daniel Pelaez-Ruiz, ISMO Université Paris-Saclay
32. Irene Burghardt, Goethe University Frankfurt
33. Helen Fielding, University College London
34. Rebecca Ingle, University College London
35. Vas Stavros, University of Warwick

Explicit work with the partners has been carried out as follows.

1. The Došlić group have provided an updated version on the Zagreb Surface Hopping code (ZagHop).
2. Nov. 2023. Worth visited Sanz-Sanz in Madrid and Gómez in Salamanca. This led to a 3 month visit by Sanz-Sanz to the Worth group funded by a grant from the Spanish Government for the development of new code (added to the ZagHop code) to run surface hopping calculations including spin-orbit coupling.
3. Feb. 2024. Worth visited the group of Vendrell in Heidelberg to sort out the merging of the old Heidelberg MCTDH package with QUANTICS.
4. June 2024. Kirrander visited the group of Weber at Brown to discuss software developments for the inversion of experimental scattering data.
5. A number of the partners will be joining us at the first official meeting in Newcastle, Sep 2024: Gómez, Sanz-Sanz, Ivanov, Lasorne, Bonella, Santoro, Došlić (represented by Sapanur), Agostini (represented by Ibele) and Pelaez-Ruiz .

11 Management Group Meetings

Meetings of the PIs on the project and Programme Manager have been held monthly. Discussions have been held on progress and and future work, along with organisational details of meetings and ECR employment. Minutes of these meetings are available on request.