



## Identification/Selection of E-CAM Quantum Dynamics Codes for

### Development

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## Executive Summary

As technologies reach atomic length and energy scales, the simulation of quantum effects acquires practical interest beyond basic science in areas ranging from sustainable energy, to medicine, to quantum computing. Brute force simulation of quantum dynamical properties, however, is currently out of reach due to the exponential scaling of its cost with the system size, and the development of approximate methods is an active field that must be coupled with the development of highly effective software to reach the computational capacity necessary to target significant applications. The goal of E-CAM's Work-package 3 "Quantum Dynamics" ([WP3](#)) is to develop software to contribute to this effort by implementing relevant algorithms and fostering the transition from in-house codes to reliable, modular, scalable and well documented community packages.

In this report, we first review current algorithms for the simulation of quantum dynamics, focusing in particular on approximate schemes that achieve satisfactory accuracy with manageable numerical cost and have good potential for massively parallel implementations. We then discuss software packages that make these methods available, focusing in particular on codes that enable to interface quantum dynamical algorithms with *ab initio* evaluation of the interactions in the system. Finally, we give an overview of the software modules to be developed within [WP3](#) of E-CAM.

# 1 Introduction

The laws of quantum mechanics describe matter at typical atomic length and energy scales. These laws are often counterintuitive and pose interesting conceptual and technical challenges for scientists. As our ability to design drugs and new materials reaches the atomic scales, quantum mechanics also acquires technological interest targeted at societal benefits unimaginable just a few years ago. Its laws are necessary, for example, to control the interaction of matter with light with the goal to engineer more efficient photovoltaic materials and fully harvest solar power as a sustainable energy source. Skin cancer drugs may be developed by understanding and preventing or counteracting the damage caused, via quantum mechanical effects, to DNA by the same power. Hydrogen, the most common element in the universe and a key player, for example, in the quest to replace oil as a sustainable energy carrier, is a quantum element. Quantum computers may one day increase exponentially our computational power and transform informatics and High Performance Computing (HPC).

Brute force, exact methods for quantum dynamical simulations, however, are condemned by their exponential scaling with the number of degrees of freedom in the system. This currently reduces the time and size scales accessible even on the most powerful available computers by several orders of magnitude compared to classical molecular dynamics. The challenging applications described above then motivate the development of approximate methods striving to combine optimal exploitation of HPC resources and methodological advances to reach performances of technological and academic interest. Current efforts in this direction are however hindered by the relatively early stage of development of the field, in which most of the available algorithms and codes are developed locally by research groups. Thus no well-established, user friendly tool exists that can be easily adapted to run user-driven calculations and/or can be efficiently ported to different architectures. WP3 in E-CAM contributes to fill this gap via the creation of a software and algorithmic infrastructure allowing a variety of approximate quantum dynamics methods to run efficiently on massively parallel platforms. This work is performed in collaboration with the other scientific WPs, and with WP6 "Software Infrastructure" and WP7 "Hardware considerations and the PRACE relationship" for the supervision of software and hardware considerations.

This intermediate report begins with an overview of the most relevant state-of-the-art algorithms for quantum dynamics, followed by a brief discussion of the capabilities of currently available software packages that incorporate (some of) these algorithms. The focus in this discussion will be mainly on combining approximate quantum schemes with accurate, but sufficiently cheap, methods for computing ground and excited electronic states and their coupling. Going beyond empirical models of the interactions is, in fact, often crucial to achieve the accuracy needed for comparison with experiments and for predicting and manipulating the system's properties, but poses a non-trivial computational challenge since it adds to the cost of the dynamics that of the electronic structure calculations.

In the final part of this document, we discuss the overall strategy for developing new software for quantum simulations in E-CAM, and describe a specific set of modules to be developed in WP3. The document is concluded with an outlook.

## 2 State of the art algorithms

Current computational methods in quantum dynamics are typically classified in three (overlapping) families:

- **Wave function based schemes**, in which attention is focused on pure state properties and where the time-propagation operates on the coefficients of an appropriate basis expansion of the quantum state, often chosen variationally to minimise size and numerical cost. These methods are used, for example, to understand and manipulate coherence and interference effects in quantum computing or to compute electronic properties relevant in photochemistry and photophysics. Typical system sizes are limited, for general Hamiltonians, to 10-20 degrees of freedom. Wave function propagation is performed most commonly on semiempirical models for the interactions and it is often restricted to the ground state. The most notable exception is the so-called Multi-Configurational Time-Dependent Hartree (MCTDH) approach, which allows to scale calculations up to a 1000 degrees of freedom, for appropriate potentials, and – for lower dimensions – can even be combined with *ab initio* methods.
- **Trajectory based schemes**, that combine sampling of the quantum statistical properties, and in particular of the thermal density matrix, with the classical evolution of an ensemble of trajectories. These methods are used to compute quantum correlation functions and, from these, macroscopic properties such as vibrational spectra, rate constants in chemical reactions, mass and charge transport coefficients. They find application, for example, in studying the properties or chemical processes involving hydrogen in biology (enzymatic reactions) or materials (hydrogen based fuel cells). Typical system sizes can reach 100-200 degrees of freedom. In this case too, the majority of calculations is performed on semiempirical models for the interactions and on the ground electronic state. Recently, however, the efficiency of some of these schemes has increased to the point where it is possible to couple them with *first principle* electronic structure calculations, typically at the level of Density Functional Theory (DFT).
- **Mixed quantum-classical schemes**, that go beyond the Born-Oppenheimer approximation, i.e. motion on a single electronic surface, and consider the coupled evolution of a small set of quantum degrees of freedom (e.g. electrons) and a large classical environment (e.g. nuclei). These methods are the only viable approach to simulate, for example, photochemistry and photophysics in relatively large, realistic, systems and find application in domains ranging from sustainable energy (e.g. in the investigation and mimicking of photosynthesis), to medicine (e.g. to investigate how DNA basis dissipate extra energy due to solar irradiation to prevent damage leading to skin cancer), to quantum computing (where the population of qubits is guided via interactions with appropriate electromagnetic pulses affecting the population of the quantum states). Typically, the quantum subsystem is modelled as a set of few (up to 10) states, while the size of the classical environment can reach hundreds of degrees of freedom. These methods are usually coupled with empirical models for the ground and excited quantum states. Recently, and importantly, however, approaches combining relatively cheap mixed-quantum classical schemes with *first principle* calculations of the electronic states, typically at the level of Time-Dependent Density Functional Theory (TDDFT), have appeared.

Below, we provide a brief overview of quantum dynamical methods belonging to these different families. The choice of the algorithms presented is guided by the extent of their use by the community and the problems addressed within E-CAM, as determined from discussions with academic and industrial counterparts in our State-Of-The-Art and Scoping Workshops, or from other contacts with new groups interested in collaborations with E-CAM.

### 2.1 Wave function based schemes

In these schemes, the state of the quantum system,  $|\Psi\rangle$ , is represented by an initially defined wave packet whose dynamics is governed by a specified Hamiltonian operator,  $\hat{H}$ , via the Time-Dependent Schrödinger Equation (TDSE). Available methods differ in the adopted representation, and in the specific method to compute the effect of the Hamiltonian at each time-step.

#### 2.1.1 Exact solutions

Numerically exact solutions to the TDSE propagate an initially defined wave function forward in discretized time. The wave function and Hamiltonian operator are represented in a basis set that provides a grid, typically in configuration space, and the evolving wave function is a set of amplitudes on the grid. The basic problem can then be mapped in the solution of the evolution equation for these amplitudes. A number of efficient schemes have been developed to integrate these equations [1], among which we mention the Chebyshev, Lanczos, Split-Operator and Second Order Differencing methods. All these methods are stable and accurate, with results limited only by the quality of the potential functions used. However, they all suffer from an exponential growth of computational resources and are restricted

to 3-4 atom systems. Exact methods are then usually employed to provide benchmarks for approximate schemes. Exact solution methods are implemented, for example, in the package [QUANTICS](#) (see also Deliverable D3.1: Quantum Dynamics E-CAM modules I [2]).

### 2.1.2 MCTDH

In the [MCTDH](#) approach, the wave function for a multidimensional set of particles is expanded in a direct product of self-adapting time-dependent single-particle functions ([SPFs](#)) and the equations of motion for the expansion coefficients and the [SPFs](#) are obtained via a variational principle. These time-dependent basis functions are expanded in a discrete variable representation to effectively represent the evolving wavepacket and Hamiltonian on a multi-dimensional grid. The scaling of this representation is more favourable than that in exact solution methods, enabling to treat much larger systems [3]. The method is, however, limited in the form of the Hamiltonian that can be used, and care must be taken in converging the basis set for good results. At a final level, in the variational multi-configurational Gaussian method [4], the basis is a set of time-dependent Gaussian functions. This is a general and flexible ansatz which can be used with general potentials calculated on-the-fly by electronic structure programs. It is, however, numerically unstable and difficult to obtain converged results. MCTDH is implemented in the [QUANTICS](#) package [5] and provide a range of calculated properties as the full wave function is obtained as a function of time. Representative examples are the interpretation of the absorption spectrum of pyrrole [6], the electron transfer dynamics at a dye-semiconductor interface [7], or the calculation of the strongly anharmonic infrared spectrum of the protonated water dimer including all quantum effects [8].

## 2.2 Trajectory based schemes

This family of methods originates from the pioneering work of Van Vleck in the late 1920s [9]. In the following, we shall discuss it, as commonly done today, in the framework of the path integral formalism introduced by Richard P. Feynman [10]. In this language, the quantum propagator, i.e. the probability amplitude for the system to go from configuration  $x$  to configuration  $x'$  in a given time  $t$ , is expressed as a weighted sum over all possible paths connecting the two configurations in the allocated amount of time. A Feynman path is, in general, any possible sequence of configurations for the system and the weight associated to each path is a phase factor whose argument is the quantum counterpart of the classical action. Direct evaluation of the propagator is computationally intractable for two main reasons: First, for non-trivial problems, there is no systematic procedure to generate the full set of relevant paths; second numerical estimation of the weighted sum is severely hindered by the path's complex weight, a rapidly oscillating function that leads to exponential growth, with time and system size, of the number of paths necessary for a converged calculation.

Some important approximations can, however, be derived from the path integral expression of the propagator:

### 2.2.1 Stationary phase approaches

The path integral expression of the propagator is approximated via a second order expansion of the phase associated to each path [11]. This procedure isolates the most important (stationary) path and approximates the full propagator as a, weighted, sum over this subset. Notably, the stationary paths are classical trajectories and can be computed via standard molecular dynamics algorithms. Quadratic fluctuations around them are analytically known as determinants of matrices (the so-called monodromy matrices) that can be computed by propagating an auxiliary set of classical-like equations of motion. These determinants are the new weights associated with each path, together with the - mildly oscillating - exponential of the classical action. Stationary phase methods include wave function propagation and calculation of time-correlation functions and preserve quantum dynamical effects such as coherence. Different stationary propagators exist depending on the choice of the basis in the path integral expression. The most stable and efficient numerically is the so-called Herman-Kluk propagator [12], which employs to a basis of coherent states. The convergence of these calculations is complicated by the presence of the monodromy weights, which can vary over several order of magnitude and require to propagate a very large number of trajectories. Thus, stationary phase approaches are currently limited to systems with relatively few degrees of freedom (a few tenths) and are only very rarely combined with electronic structure calculations. No general software package exists for implementing these calculations.

### 2.2.2 Matsubara dynamics

This method [13] starts from the representation of quantum time-correlation functions in the Wigner formalism. In this framework, quantum operators are mapped, via the Fourier transform of their off-diagonal elements in the coordinate representation, as functions in phase space. The time evolution can then be expressed as a series in powers of Planck's constant (the terms of this series involve differential operators), the so-called Wigner-Moyal expansion. Truncating the series to zeroth order leads to classical dynamics, while higher order terms account for quantum effects. Recently, it was observed that a more accurate classical approximation can be obtained combining Wigner representation and path integrals and writing the Wigner-Moyal series in an appropriate basis of normal modes. The propagation is then restricted to the lowest, equispaced, frequency modes, known as the Matsubara modes. These modes have the property that their superposition produces a smooth distribution of the path integral coordinates. Furthermore, it can be shown that the quantum evolution of these modes is classical and conserves the quantum probability density for the system. Unfortunately, the evaluation of physical observables, such as time-correlations, requires to compute also time dependent phase factors whose averaging makes this scheme too expensive for applications to complex systems. In spite of this limitation, Matsubara dynamics is a very interesting starting point [14] for analysing connections and characteristics of several other approximate algorithms such as linearized methods, and ring polymer and centroid molecular dynamics (see below).

### 2.2.3 Linearized dynamics

In these methods [15, 16, 11], a set of initial coordinates and momenta is sampled from the exact quantum thermal probability density. Each initial condition is then propagated via classical molecular dynamics, time correlation functions are computed along each trajectory, and the quantum result is approximated as the average of the classically-evolved correlations. It can be shown that this algorithm derives from an expansion to second order in Planck's constant of the exact path integral expression of the time correlation function. In contrast to stationary phase approaches, the classical trajectories carry no extra weight and the numerical complexity of the calculation is confined to initial condition sampling. To obtain both coordinates and momenta, the quantum thermal probability is represented in the Wigner formalism. In this formulation quantum averages bear strong similarities with the classical case, at the cost of introducing a non-positive definite representation of the probability density. This hinders direct application of standard Monte Carlo sampling schemes and several approximations have been proposed to sample effectively. Of particular interest for E-CAM is the Phase Integration Method [17], in which a cumulant expansion of the Wigner density is employed in combination with advanced Monte Carlo algorithms. The unique advantage of this procedure is that the convergence of the sampling can be tested and systematically improved via a suite of control parameters. Linearized methods are usually employed in combination with empirical potentials and reach system sizes of the order of one hundred atoms or more. Their accuracy is limited to short times and they suffer from the so-called zero point energy problem (see 2.2.6), but they remain a popular and useful approach. The first community package for this type of calculations, PaPIM, is currently being developed within E-CAM (see Section 4 and Deliverable D3.3 [18]). Combining linearized dynamics with *ab initio* calculations of the forces can be envisioned for system of small size (10-15 degrees of freedom).

### 2.2.4 Ring polymer molecular dynamics (RPMD)

The path integral approach offers also an elegant numerical approach to the evaluation of time-independent quantum average values. In this formalism, the quantum thermal probability (which can be interpreted as a propagator in temperature, instead that in time) is isomorphic to the classical Boltzmann density of a system in which each quantum particle is replaced by a classical polymer. The beads of this polymer interact via a nearest neighbours harmonic potential representing the action of the kinetic energy operator on the system, while the potential term induces interactions between beads on different polymers. This so-called classical isomorphism is exact in the limit of an infinite number of beads. In practice, convergence of the estimate of the average values against the number of beads provides a systematic assessment of its quality in given applications. The path integral thermal density can be sampled with classical schemes such as Metropolis Monte Carlo or molecular dynamics and enables exact calculations of quantum static properties at a numerical cost equal to that of the classical calculation times the number of beads.

RPMD takes this scheme a step further by assuming that the thermal paths can also be used to obtain dynamical information [19]. In this approach then, quantum time correlation functions are approximated as averages obtained along the, classical, evolution of the polymers. In this way, the standard methods for classical calculations can be directly translated to the quantum system. The approach cannot be formally justified for general system, though some interesting recent work in this direction exists [14], and suffers from some known limitations such as the appearance of spurious peaks in vibrational spectra. Due to its numerical convenience, however, RPMD, in its original version or with patches to mitigate some of its limitations, is a popular and effective method to assess the presence of quantum



nuclear effects in large systems, also when described via *ab initio* interactions, and it has been used for a variety of challenging applications [20].

### 2.2.5 Centroid molecular dynamics (CMD)

Thermal path integrals are the starting point also in **CMD**, an *ad hoc* but interesting proposal to compute dynamical quantum properties based on classical-like evolution of the polymers. The key variable in this scheme is the path centroid, i.e. the average position of the beads of each polymer. It can be shown that time-equilibrium averages over the paths can be exactly expressed as averages over the positions of the centroid and that, in the classical limit, the polymer collapses to the centroid's position. Several authors [21, 22, 23] have then suggested the use of the centroid also to obtain the time evolution. To that end, classical equations of motions for the centroid are imposed, but the quantum nature of the system is kept into account by prescribing that the force at each step of the trajectory is given by the derivative of an effective quantum potential. Due to the intuitive appeal and numerical efficiency of this prescription, CMD has become a popular tool in condensed phase calculations. However, although the algorithm is exact for harmonic systems and observables that depend linearly on the coordinates or momenta, the method lacks a rigorous justification and it can produce unexpected and pathological results. An interesting comparison of the performances of CMD and **RPMD** for condensed phase calculations suggests that they have similar capacities [24].

### 2.2.6 Quantum Thermal Bath (QTB)

**QTB** is an approximate method to simulate the quantum delocalization of nuclei using a generalized Langevin equation with a colored noise [25, 26]. In a classical Langevin dynamics, the power spectrum of the random force corresponds to a white noise with an amplitude proportional to the temperature. In QTB, this power spectrum is modified to match the average energy of a quantum harmonic oscillator, therefore taking into account the zero-point energy and associated zero-point motion in the stochastic dynamics. QTB provides an approximation to both static and dynamical properties and in contrast to path-integral methods, there is no need to introduce polymer beads, which lowers considerably the computational burden. The accuracy and exact domain of applicability of the quantum thermostats remain a matter of debate. In particular it has been shown to suffer -like other semiclassical methods- from zero-point energy leakage: to account for the zero-point motion of nuclei, high-frequency vibrational modes are thermalized at a higher effective temperature than low frequency modes. However, part of this additional vibrational energy leaks to the low frequency modes, changing the equilibrium configuration of the system and distorting the results. It was shown that this leakage imposes some constraints on the strength of the coupling with the quantum bath, which should be large enough for the QTB to be safely used (although this might not be sufficient for very anharmonic systems) [27, 28]. The very low computational cost, essentially equivalent to that of classical Langevin dynamics, makes QTB an appealing scheme to combine with *ab initio* forces, and different versions the method have been implemented into open source codes, such as Quantum Espresso or CP2K, and applied to a variety of systems [29, 30].

## 2.3 Mixed quantum-classical schemes (MQC)

These schemes are adopted to describe the coupled evolution of a set of relatively few degrees of freedom and of a larger system that can be effectively described at the classical level. The most common and important example is the case of electrons, represented as a set of discrete quantum states, and nuclei, approximated as classical particles for nonadiabatic phenomena, i.e. processes in which coupling with external perturbations (such as light) or with the environment causes transitions among the electronic states and the break down of the Born-Oppenheimer approximation.

**MQC** methods compute both wave functions and thermal properties. The most common starting point for wave function based methods is the TDSE for the whole system expressed in a basis with the nuclei in the coordinate representation, and the electrons in the so-called adiabatic basis (i.e. the same basis adopted to obtain the Born-Oppenheimer approximation). In this basis, the electronic states and eigenvalues depend parametrically on the nuclear coordinates. This leads to a set of coupled equations for the coefficients,  $\chi_\alpha(R, t)$ , which represent the probability amplitude to find the system at a nuclear position  $R$  and in the electronic state  $\alpha$  at time  $t$ . The modulus of these amplitudes is related to the occupation probability of the states and changes when nonadiabatic transitions occur. MQC methods are then obtained by assuming that the nuclear evolution is given by Newtonian dynamics, while retaining a quantum description for the electrons. The different available schemes differ in the way in which the two dynamics are coupled and, in particular, in the effect of nonadiabatic transitions on the nuclear motion. Thermal methods, on the other hand, are most conveniently obtained from the path integral or Wigner representation of the propagator of the full system. The

MQC in this case is derived via a controlled approximation on the nuclear propagation analogous to the linearization schemes.

The computational cost of mixed quantum-classical calculations is considerable, since they require as input not only the electronic ground state, but also excited states and couplings among them. These are most often modelled semi-empirically. However, recently important developments in excited states calculations - in particular in [TDDFT](#) - have enabled combining [MQC](#) with *first principle* electronic structure.

The most general nonadiabatic scheme for thermal properties is the Wigner-Liouville approach (section [2.3.1](#)), while several methods exist for nonadiabatic evolution of wave functions and we describe the most relevant in section [2.3.2](#) and following.

### 2.3.1 Wigner-Liouville and linearized mapping dynamics

In its original formulation [31], the Wigner-Liouville method combined a Wigner representation for the nuclear degrees of freedom with a description of the electrons in the adiabatic basis. The evolution of the coupled system was expressed in mixed form, retaining only the zero order term in the Wigner-Moyal propagator for the nuclei, while leaving the electrons in full quantum mode. The corresponding algorithm entails legs of classical propagation of the nuclei interspersed with hops between electronic surfaces in regions of strong coupling. The method is targeted at the propagation of the thermal density of the mixed system and, interestingly, it approximates both diagonal and off-diagonal (coherences) elements of this operator in the electronic subspace. When computing diagonal elements, the nuclei move on a single electronic surface; when looking at coherences, they evolve on the mean of two electronic surfaces and the trajectory carries a phase. This phase enables to account for some quantum interference effects, but it also complicates numerical convergence. Another delicate element of the algorithm is the selection of the hopping times and surfaces. This is based on a generalised Monte Carlo scheme, which also implies a potentially unstable re-weighting of the averages. More recently, the Wigner-Liouville dynamics has been adapted to the so-called mapping form of the electronic states [32], a convenient representation in which the states are represented via a set of appropriate fictitious harmonic oscillators which simplify some aspects of the calculation. This representation is also commonly adopted in the so called Linearized Mapping methods [33], a family of algorithms which start from a full path integral representation of the system of nuclei and electrons and then obtain the classical limit via linearization in the nuclear variables. Recently, it was shown [34] that Wigner-Liouville and linearized Mapping methods are in fact completely equivalent approximations both from a theoretical point of view and in terms of results. These methods have been applied to study, in combination with empirical potentials, standard model problems such as the spin-boson system and two-level modellization of proton transfer in aqueous environment. More recently, applications to coherence effects in photosynthesis have also been made [35].

### 2.3.2 Surface Hopping

In Surface Hopping [36, 37], a swarm of classical, Newtonian, trajectories for the nuclei is propagated on the different adiabatic electronic energy surface. The force given on each surface is given by the derivative with respect to the nuclear positions of the corresponding energy eigenvalue. The number of nuclear trajectories on each state at a given time is tuned to be proportional to the quantum probability to find the system on that state. Changes in this probability are mimicked by allowing trajectories to hop from one state to another when nonadiabatic transitions become important. This is signalled in the algorithm by monitoring the evolution of the electronic states via an auxiliary [TDSE](#) which depends parametrically on the nuclear positions. Hops are governed by a stochastic procedure that mimics the effects of the quantum transition probability via an appropriate Monte Carlo algorithm. When an hop occurs, the forces experienced by the nuclei change discontinuously and the momenta are adjusted to enforce energy conservation. Surface hopping cannot be derived rigorously from the TDSE for the nuclei and electrons. In spite of this, it has proved a convenient and extremely cost effective tool to study nonadiabatic processes of great interest, such as photoreactions in complex environments (e.g. photoinduced proton-electron transfer at the heart of energy conversion reactions in photocatalysis, or photocatalytic water oxydation on  $\text{TiO}_2$  nanoparticles), and of biological interest (e.g. relaxation mechanisms of UV-photoexcited DNA and RNA nucleobasis). The low numerical cost, together with recent progress in electronic structure calculations for excited states, enables coupling surface hopping with *ab initio* calculations [38], and the algorithm is now available - directly or via interfaces - in several main stream packages (see Section [3](#) for details). Due to these features, Surface Hopping is the most used nonadiabatic method at present.

### 2.3.3 Ehrenfest dynamics

In this approach, the total wave function is represented as the product of an electronic and nuclear time dependent wave functions. In this factorisation, the electronic wave function does not depend (not even parametrically) on the

nuclear positions. This is the so-called single configuration ansatz, and it is an approximation that restricts the configurations accessible to the system compared to the exact solution. The TDSE can then be recast as a system of equations for these two wave functions in which both the electronic and nuclear parts depend on a mean potential generated by the other components. These average potentials are time-dependent and are responsible for the interaction and feedback between the electronic and nuclear components. The classical limit for the nuclear evolution is then obtained via an expansion to the first order in Planck's constant of the nuclear equation. The limit collapses the nuclear wave function into a single trajectory, evolving in the mean-field potential derived from the time evolution of the electronic wave function. This mean field is given by the expectation value, over the electronic wave function, of the electronic Hamiltonian which, in turn, depends on the nuclear coordinates thus preserving a feedback between the motions. Typical applications of Ehrenfest dynamics include modelling of radiation damage in metals and laser controlled dissociation reactions. The method is routinely combined with *ab initio* evaluation of the nuclear forces [39], and implemented in several electronic structure packages as described in Section 3.

### 2.3.4 Spawning

Full Multiple Spawning (FMS) [40, 41] employs a Born-Huang representation of the molecular wave function and portrays the nuclear dynamics by using a swarm of *coupled* frozen multidimensional Gaussians [42], indicated as Time Basis Functions (TBF). The Gaussians follow classical trajectories and their number can be adapted during the dynamics to ensure a proper support to the nuclear wavepacket propagation. The TDSE can be rewritten in the basis of the TBFs, leading to a set of coupled equations of motion for the complex coefficients of the expansion. The number of TBFs can be extended every time a nonadiabatic coupling is detected thanks to the *spawning* algorithm, ensuring an accurate description of the nuclear amplitude transfer between electronic states resulting from nonadiabaticity (more details on the spawning algorithms can be found in Ref. [41]). If a sufficiently large number of TBFs is used, FMS is formally exact. However, it requires the evaluation of multidimensional Gaussian integrals including electronic quantities like energies or nonadiabatic couplings, meaning that FMS is not directly suitable for *ab initio* nonadiabatic molecular dynamics. Ab Initio Multiple Spawning (AIMS) then proposes to approximate the coupling between TBFs in two different ways: the integrals are approximated by expanding any electronic quantity in a Taylor expansion of order zero (saddle point approximation) and the TBFs employed to describe the nuclear wavepacket at time  $t = 0$  (the parent TBFs) are considered uncoupled (independent first generation approximation, IFGA). AIMS has been coupled with different electronic-structure methods such as SA-CASSCF, MS-CASPT2, FOMO-CASCI, or linear-response TDDFT (LR-TDDFT) and employed to study a large number of molecules in their full configuration space and even predict experimental observables [41].

### 2.3.5 Exact Factorisation

The exact factorization of the electron-nuclear wave function [43] provides a prescription for decomposing the TDSE for a system of interacting electrons and nuclei into the coupled dynamics of the subsystems, i.e., the electronic and the nuclear. The idea is to factor the electron-nuclear wave function, solution of the molecular TDSE, into a time-dependent nuclear wave function and a time-dependent electronic factor, that depends parametrically on nuclear configurations. The electronic and nuclear contributions of the molecular wave function evolve according to coupled equations, where (i) the nuclear equation is a standard TDSE with time-dependent vector and scalar potentials [44, 45], including the effects of the electrons beyond the Born-Oppenheimer approximation, and (ii) the electronic equation contains explicitly the dynamical coupling to the nuclear subsystems [46]. The approximate solution of the nuclear TDSE can be constructed by generating classical trajectories according to a time-dependent force uniquely defined by the vector and scalar potentials [47]. Nuclear motion induces electronic nonadiabatic transitions and quantum decoherence [48], via the dependence of the electronic evolution equation on the classical nuclear momentum of the trajectories and on the, so-called, quantum momentum. The quantum momentum tracks the spatial spreading of the density and is responsible for quantum decoherence. To compute the quantum momentum, an ensemble of nuclear trajectories has to be evolved coupled to the electronic evolution equation. In order to perform excited-state molecular dynamics calculations on molecular systems, the electronic dynamics is represented in the adiabatic basis, and the classical nuclear dynamics needs to be interfaced with quantum-chemistry packages to perform on-the-fly electronic-structure calculations (for the nuclear geometries visited along the trajectories). Currently a preliminary implementation is available in CPMD [49] (sec. 3.2.1).

### 3 Efficient methods and interfaces for coupling electronic structure and quantum dynamical calculations

Reflecting the variety and on-going development of methods described in the previous section, software production in quantum dynamics is less mature than, for example, in classical molecular simulations or electronic structure calculations, which include, for the most part, classical evolution for the nuclei on the electronic ground state. The field is however reaching the stage in which some methods are consolidated enough to enable the transition from in-house software to community level tools. This proceeds along three lines that are also the focus of E-CAM's software development strategy:

- creation of modular packages with excellent scaling properties, well defined benchmarks and complete documentation that provide an environment to which academic groups can add new features and that can be easily adapted to the needs of non-academic users. The two codes developed in this spirit in E-CAM are [PaPIM](#) and [QUANTICS](#);
- development of interfaces for quantum dynamical codes with packages for electronic structure calculations (in E-CAM, this work is performed in collaboration with [WP2](#) "Electronic Structure") and, in the longer term, with codes for multiscale simulations of quantum systems (in E-CAM, this work will be performed in collaboration with [WP4](#) "Meso- and Multi-scale Modelling");
- introduction of new quantum dynamical features into well-established, portable, and scaling codes for electronic structure calculations.

In this section, we provide an overview of codes that include quantum dynamics algorithms. Essentially all existing examples refer to nonadiabatic mixed quantum classical schemes. We consider separately the case of codes developed for nonadiabatic calculations and expanded to include an interface with an external provider of *ab initio* interactions, section 3.1, and that of electronic structure codes augmented by including nonadiabatic dynamics as an internal engine, section 3.2. In the next section, we then describe in some detail the core codes for E-CAM in this domain.

#### 3.1 MQC/Nonadiabatic dynamics softwares with interfaces to external quantum chemistry packages

Most of the Mixed Quantum-Classical (MQC) packages described below are based on the same architecture: The main program is responsible for the propagation of the nuclear degrees of freedom – using different MQC strategies. Such propagation relies on several electronic structure quantities: electronic energies, nuclear forces, nonadiabatic coupling terms, and even dipole moments if an external field is present or spin-orbit coupling needed to describe intersystem crossings. The electronic structure information of interest is requested by the package to an interfaced quantum chemical software such as Gaussian, GAMESS, Turbomole, Molpro, Molcas, etc. The most commonly employed communication scheme is the following: (i) the central code writes, at each nuclear time-step, the nuclear coordinates as well as some previous information related to the electronic structure calculation (orbitals or CI vectors, basis set, method, etc) into a formatted file, (ii) the central code launches the quantum chemical software that will read the information and perform the requested electronic structure calculation, (iii) once the calculation is done, the central code parses the output file generated by the quantum chemical code and extracts the relevant information, (iv) the nuclear propagation progresses by one step and the full process is repeated. Rarely is any MQC code parallelized (exceptions being few subroutines in ANT and SHARC, see below) and their overall performance depends on the scaling of the coupled external electronic structure code. Some codes, like FMS90, directly include the electronic structure code as a library or use SMP or MPI to communicate with an external quantum chemical code.

The tasks above are usually accomplished via a set of different codes and scripts, often merging different languages such as Fortran, C, and Perl. Communication bottlenecks and lack of combined optimization for the nonadiabatic driver and the electronic structure code typically still hinder the numerical efficiency of these packages, which are however quite popular for historical reasons. The most commonly used are described below (in alphabetical order). When appropriate, we list in Table 1 the electronic structure codes interfaced with the different packages.

##### 3.1.1 ANT

[ANT](#) is a molecular dynamics program package for adiabatic and nonadiabatic classical and semiclassical trajectory simulations. It is developed in the group of Prof. Donald Truhlar. ANT is written in Fortran 90 and features Ehrenfest (2.3.3) and surface hopping (2.3.2) methods. Only the wave function overlap subroutine for computing nonadiabatic couplings is parallelized in ANT (OpenMP parallelization), and its interface enables external electronic structure packages to be run in parallel environment.

### 3.1.2 COBRAMM

**COBRAMM** is a code for on-the-fly surface hopping nonadiabatic molecular dynamics (section 2.3.2) with an emphasis on the **QM/MM** dynamics, i.e., algorithms to partition the description of the interactions into an *ab initio* and semiempirical region. It is developed in groups of Prof. Marco Garavelli and Prof. Andrea Bottoni. COBRAMM is available upon request. It interfaces several electronic structure code with the **Amber** program package for (up to three level) hybrid QM/MM dynamics. It also features optimization and conical intersection search algorithms.

### 3.1.3 FMS90

FMS90 code implements the Ab Initio Multiple Spawning method (section 2.3.4). FMS90 is developed in the group of Prof. Todd Martinez and is available upon request. It is also implemented in the Molpro program package as the **AIMS** module[50]. As the AIMS module in Molpro package, Molpro electronic structure calculation subroutines are directly linked to AIMS as a library, which avoids computationally slow I/O communication via external files. Although the program was designed for nonadiabatic dynamics with CASSCF wave functions, it can be used generally for *first principles* molecular dynamics, provided that nuclear gradients are available. Optionally, the spawning can be disabled and the method will reduce to traditional first-principles classical molecular dynamics. A **QM/MM** scheme is also available within Molpro by utilizing the external **Tinker** code. FMS90 code also contains the interface to **TeraChem**, a **GPU** electronic structure program package, which enables the code to be executed on hybrid **CPU+GPU** systems.

### 3.1.4 NEWTON-X

**NEWTON-X** (GPL license) is a general-purpose program for molecular dynamics in the electronic excited states which includes nonadiabatic effects via the surface hopping procedure (for method description see section 2.3.2). It is maintained in the group of Prof. Mario Barbatti. NEWTON-X is composed of Fortran 90 and C subroutines and of Perl scripts. For the nonadiabatic coupling in dynamics, NEWTON-X uses either nonadiabatic coupling vectors, time-derivative couplings or the local diabatization method. NEWTON-X handles only nonadiabatic effect between states of the same multiplicity. It also includes decoherence correction, Lagrangean extrapolation of orbitals, Andersen thermostat. NEWTON-X can also compute Dyson orbitals and simulate steady and time-resolved photoelectron spectra. Other NEWTON-X capabilities can be found in its documentation. **QM/MM** hybrid dynamics is available by utilizing the **Tinker** program package in combination with COLUMBUS, TURBOMOLE and DFTB+ electronic structure codes. The NEWTON-X code is not parallelized, but its interface enables external electronic structure packages to be run in parallel (**SMP**, not **MPI**) environment.

### 3.1.5 SHARC

**SHARC** (GNU General Public License) is a general-purpose program for molecular dynamics in the electronic excited states which includes nonadiabatic effects via the surface hopping procedure (for method description see section 2.3.2). It is developed in the group of Prof. Leticia González. SHARC consists of Fortran 90 programs and of Python and Shell scripts. In addition to nonadiabatic dynamics with nonadiabatic coupling vectors, time-derivative couplings or the local diabatization, SHARC also includes the spin-orbit couplings for the description of inter-system crossings in the on-the-fly nonadiabatic dynamics. SHARC can also include the interactions with laser fields (in the long-wavelength limit) into the dynamics. For strong field applications, derivatives of the dipole moments can be included. SHARC can also compute Dyson norms for single-photon ionization spectra. **QM/MM** hybrid dynamics is available through **Tinker-Molcas** or **ADF** implementations. Other SHARC capabilities can be found in its documentation. Only the wave function overlap subroutine for computing nonadiabatic couplings is parallelized in SHARC, and its interface enables external electronic structure packages to be run in parallel environment.

Among less frequently use MQC softwares we mention **JADE** and **PYXAID** whose current interfaces with electronic structure codes are also listed in Table 1.

## 3.2 Electronic structure packages including quantum dynamical algorithms

Based on their characteristics, input from our user base and project for future module developments, the most relevant electronic structure packages that include **MQC** algorithm for E-CAM include (in alphabetical order):

Table 1: MQC dynamics softwares with their currently implemented interfaces to external quantum chemistry packages.

MQC program	Electronic structure program package												
	Turbomole	Columbus	GAMESS	Gaussian	Molpro	Molcas	ADF	TeraChem	ORCA	DFTB	DFTB+	MOPAC	Quantum Espresso
ANT				+	+							+	
COBRAMM	+			+	+	+			+	+			
FMS90		+	+	+		+		+					
JADE	+		+	+									
NEWTON-X	+	+	+	+						+	+		
PYXAID													+
SHARC	+	+		+	+		+						

### 3.2.1 CPMD

CPMD is a DFT plane-wave electronic structure package that allows for *ab initio* molecular dynamics using either Car-Parrinello or Born-Oppenheimer propagation. The code incorporates the trajectory Surface Hopping and Ehrenfest dynamics, both on the TDDFT level of theory. CPMD also incorporate highly-sophisticated QM/MM capabilities which can be used with all aforementioned nuclear dynamics methods. This functionality is crucial in view of applications to realistic systems (e.g. reactions in biomolecules and inorganic complexes in solutions). The code is based on modern Fortran, with fully dynamical memory allocation, and is highly parallelized employing both MPI and OpenMP. It is ported on a number of common architectures, including MacOS, Cray, IBM, and Linux platforms and it has been shown to scale to up to million of threads on the Blue Gene Q. CPMD is jointly owned by IBM and the Max Plack Institute (Stuttgart). The code has a large user and developer base and is well documented. CPMD is distributed free of charge to non-profit users under the CPMD Free Licence.

### 3.2.2 CP2K

CP2K is similar to CPMD in terms of methods available (including QM/MM), but it uses an hybrid plane-wave/localized basis set strategy for the electronic structure, allowing it to employ hybrid DFT functionals at a lower cost than a purely plane-wave-based code like CPMD. The code is written in Fortran 2003 and parallelised with both MPI and OpenMP standards. It includes a CUDA implementation thanks to which some of the most computer time demanding approaches can be run on GPUs. The input of CP2K is not trivial, but it is built in a way that allows modularisation and the addition of extensions in a seamless manner. The code is actively maintained and further optimised and extended, there is an increasing user base, and the developers can be reached via a discussion forum. The code is freely available under GPL licence. Currently, the only MQC method included in CP2K is Ehrenfest dynamics (section 2.3.3).

### 3.2.3 Octopus

Octopus (GPL license) is a pseudopotential real-space program package aimed at the simulation of the electron-ion dynamics of one-, two-, and three-dimensional finite systems subject to time-dependent electromagnetic fields. The program is based on TDDFT in the Kohn-Sham scheme and implements Ehrenfest dynamics for the nuclei (section 2.3.3). Octopus is written in Fortran 90, with additional subroutines in C/C++, and is parallelized using MPI and OpenMP. It also has support for GPUs through OpenCL and CUDA. Octopus features and benchmarks are given in its documentation page. Further Octopus capabilities and information on its scaling can be found in the on-line documentation.

### 3.2.4 Q-Chem

Q-Chem is a commercial quantum chemical program package for standard quantum chemical applications and implements HF, (TD)DFT, Møller-Plesset and coupled cluster based methods. It implements Born-Oppenheimer *ab initio* molecular dynamics and quasi-classical molecular dynamics which can be carried out in the ground or excited state potential energy surface. Langevin and Nosé-Hoover thermostat can be also included in the dynamics. For treatment of nonadiabatic effects Tully's surface hopping algorithm on CIS and LR-TDDFT level of theory can be employed, where nonadiabatic coupling vectors and their spin-flip analogues, between all electronic states are available on both

level of theory. Decoherence effects can also be included. Q-Chem is parallelized with [MPI](#) and OpenMP, and uses static and dynamic memory allocation. Performance and scaling analysis of Q-Chem SCF procedures on the number of processor cores was reported in [51].

### 3.2.5 TeraChem

[TeraChem](#) is a quantum chemistry software developed in the group of Prof. Todd Martinez. Its first commercial release by the Silicon Valley-based company PetaChem took place in 2010. The central motivation for TeraChem development resides in the use of streaming processors for calculations such as those found in [GPUs](#). A complete remodeling of quantum-chemical algorithms was necessary due to the different architecture between GPUs and conventional CPUs and allows TeraChem to fully benefit from the speedup offered by streaming processors. With this new paradigm for the implementation of electronic structure methods on GPUs, TeraChem developers could reach substantial speedups – 10x to 1000x depending on the system size – for methods like DFT using atom-centered basis functions. Such speedups pave the way for a more general usage of *ab initio* molecular dynamics for the study of molecular systems, in particular for excited-state dynamics with the recent development of GPU-accelerated LR-TDDFT and SA-CASSCF. TeraChem benefits from a direct interface with FMS90 to perform GPU-accelerated nonadiabatic dynamics with the Ab Initio Multiple Spawning strategy. Further TeraChem capabilities and scalings can be found in its documentation.

### 3.2.6 Turbomole

[Turbomole](#) is a commercial quantum chemical program package for standard quantum chemical applications and implements HF, (TD)DFT, Møller-Plesset and coupled cluster based methods. It was initially developed in the group of Prof. Reinhart Ahlrichs. It implements an *ab initio* molecular dynamics which can be carried out on the ground and excited state Born–Oppenheimer potential surface. It also enables treatment of nonadiabatic effects through Tully's surface hopping algorithm on the LR-TDDFT level of theory, but in the current implementation only switches between the first excited singlet state and the ground state are available. Total energies of higher excited states can be computed during the molecular dynamics simulations. Turbomole is parallelized with [MPI](#) and OpenMP, and uses static and dynamic memory allocation.

## 4 E-CAM quantum dynamics codes for development

Based on the outcome of the E-CAM state-of-the-art workshop on Quantum Dynamics, and following discussions with developers and users in the community, we have selected two core codes to develop and propose as a framework for modular development of scalable open source quantum dynamics software: PaPIM, targeted at calculation of thermal averages and observables from nuclear motion, and QUANTICS, targeted at wave function propagation (ground state and nonadiabatic dynamics). The current status of these codes and plans for further developments are briefly described in the following. In the next section, we also describe plans for additional modules proposed by the community with the goal to implement key new functionalities in other available software packages. This tentative list will be subject to reevaluation, updating and further additions based on future state-of-the-art and scoping E-CAM workshops and interactions with new academic and industrial partners.

### 4.1 PaPIM

PaPIM is a high performance code for calculating time correlation functions of systems in thermal equilibrium. The code can be adapted to implement all the trajectory based methods described in section 2.2, but it currently provides an implementation of linearized methods specifically designed for high scaling on HPC machines. PaPIM provides an environment to assemble efficiently the complementary functionalities of independent E-CAM modules, into a Fortran 90/95 MPI parallelized package. A detailed description of the current status of the code, which includes documentation, test and benchmark cases, can be found in Deliverable 3.3, Section 2.3 [18]. A performance analysis of the code has been performed by the E-CAM team in collaboration with the EINFRA5 CoE POP (see Deliverables D7.4 [52] and D3.3, section 2.3.2 [18]). The analysis has shown very good scalability of the code. A few bottlenecks, in particular unequal load balance between processing cores, have also been identified and possible solutions to mitigate them indicated. Details of the modules composing PaPIM can be found in the corresponding description on the [E-CAM GitLab](#). Planned developments of the code include

- implementation of further performance optimisation following the analysis performed in this reporting period;
- further parallelization of the current scheme for Wigner sampling via the introduction of an OpenMP restructuring of the path integral part of the calculation;
- expansion of the current library of time-correlation functions to enlarge the set of computable observables;
- addition of new phase space sampling procedures based on generalised Langevin equations for the Wigner density to enable more flexible generation of the initial conditions and to provide direct access to dynamical quantities already at the sampling stage (collaboration with Dr. Simon Huppert, Université Pierre et Marie Curie Paris);
- implementation of a new module for the QTB approach (collaboration with Prof. Fabio Finocchi, Université Pierre et Marie Curie Paris);
- development of an interface to external *ab initio* codes (collaboration with Dr. Ari Seitsonen, Ecole Normale Supérieure Paris). The prototype will be developed and tested for interfacing with the CP2K package, see below for more details.

#### 4.1.1 Interfacing PaPIM with CP2K

Given the focus of this report on methods for interfacing quantum dynamics with electronic structure codes, we provide a few more details on the planned development of the prototype PaPIM-CP2K interface. The choice of CP2K was motivated by the large variety of methods to calculate forces, ranging from empirical to *ab initio* to QM/MM schemes, available in this package, and from the fact that the code already provides a well written, flexible interface to call the software from an external program. This interface enables efficient usage of CP2K as a library. Furthermore, given that CP2K contains several models and levels of sophistication of interaction between the atoms and it is trivial to switch between those, one can easily use a computationally lighter interaction model for the development and initial testing of the PaPIM driver program calling CP2K and can then return to the target model of interaction at the appropriate advanced level of development of the interface. Finally, the scaling properties of this package have been analysed in E-CAM (see Deliverable D7.2 [53]), providing a good basis for further developments. Specifically, the planned PaPIM-CP2K interface is targeted for efficient and flexible use of the latter via appropriate calls in PaPIM. It will consist of three main calls: (1) The initialisation of the force field model, where the force environment (model of interaction between the atoms, parallel environment, basis sets etc.) is set up for later use; (2) the evaluation of the forces on the nuclei using the formerly initialised force environment; (3) destruction of the force environment when it is no longer needed. The second step, evaluation of the forces, can be repeated at different atomic configurations, for example



during a molecular dynamics run at each time step. Because the force environment had been initialised at an earlier step, the overhead at each evaluation is predicted to be small. Two main development steps are foreseen: (1) preliminary, implementation of a parallelization scheme such that all processing cores are involved in the parallel evaluation of the forces in CP2K; (2) general and flexible parallelization scheme enabling to split the current parallelization over the number of classical trajectories from that of the force calculation and to choose separately the number of tasks allocated to each instance of CP2K.

## 4.2 QUANTICS

The QUANTICS package simulates quantum nuclear motion by solving the time-dependent Schrödinger equation and propagating wave-functions. It implements a number of algorithms, including exact solution schemes, but the focus of the package is the MCTDH algorithm. As discussed in section 2, MCTDH is the most powerful and general method for wave function propagation, a determining factor in our choice of this code for development.

QUANTICS originates from a code for MCTDH first developed in Heidelberg, and its main developer is currently Prof. G. Worth (University College London), a key participant to E-CAM's WP3. The code can propagate the system in the ground or in a manifold of several excited electronic states necessary to model the nonadiabatic processes. QUANTICS is a Fortran 90 code with full dynamical allocation of memory. Several parts of the code are parallelized using OpenMP and MPI. QUANTICS is able to use quantum chemistry programs to calculate the potential surfaces on the fly during calculations of the dynamics. At present the code can use the Gaussian, Molpro and Molcas programs. An initial assessment of the package scalability has been performed within E-CAM and is reported in Deliverable D7.4[52]. The first modules developed within E-CAM targeted expanding and improving the efficiency of the integration schemes for exact wavefunction propagation (see also Deliverable 3.1 [2]). Future software development plans include

- improvement of code parallelization;
- development of an interface with an existing surface hopping code (collaboration with the group of Prof. Nada Došlić, Rudjer Boskovic Institute, Zagreb);
- development of an interface with the Q-Chem package for *ab initio* quantum chemistry.

### 4.2.1 Interfacing QUANTICS with Q-Chem

The Quantics-Qchem-Interface module will grant access, in particular, to the Time-Dependent Density Functional Theory module of the electronic structure program Q-Chem. This program contains state-of-the-art methods for computing ground and excited electronic states, including non-adiabatic couplings. It has been chosen, in particular, because it already includes in its developer version the Spin-Flip variant of the Algebraic-Diagrammatic Construction method for computing polarization propagation, ground and excited state calculations, including gradients and couplings. The full release of these features, crucial for an accurate modelling of the photoreactions of interest in E-CAM, will be available soon. The structure of the planned interface consists of creation of an appropriate input file from the nuclear configuration, initialization and execution of the Q-Chem calculations, reading of the Q-Chem output and its storage in the QUANTICS database.

## 5 Modules to be developed in Work Package 3

Module development in [WP3](#) is planned based on input from our industrial partner, requests from participants in our growing network of academic collaborations, and the goal to favour transition to community packages within the developers and user base in quantum dynamics. In connection to this last point, in particular, an increase of the number of state-of-the-art algorithms coded as efficient, portable and scalable modules is planned. All module production is discussed with the E-CAM Software Manager and the leader of [WP7](#) to assess [HPC](#) aspects.

Modules in [WP3](#) fulfil the E-CAM requirements for software development (see deliverables D6.1 [54] and D11.5[55]). In particular, E-CAM software modules need to be: open source; free for academic use; scale well when ported to massively parallel platforms; frequently updated to the most recent parallel environments and platforms; ideally well accepted by the community; and, finally, the software needs to be reasonably readable at a source code level. More concretely, E-CAM needs to be able to:

- modify available existing code to build E-CAM modules;
- exploit available code for input, testing & benchmarks;
- exploit available code where E-CAM modules are in effect plug-ins; and,
- use the module creation also for advanced training in the development and application of advanced scientific software.

An additional desirable attribute is that E-CAM modules should be able to function, where appropriate, across more than one of the scientific work-packages of E-CAM.

In the following, we provide a list of future WP3 modules, explaining their provenance and giving a provisional time-frame for development.

### 5.1 Modules for quantum computing

Within the [Pilot Project on Quantum Computing](#) (collaboration with IBM R uschlikon), we will develop a toolbox of subroutines and functionalities that implements the Local Control Theory (LCT) used for construction of control pulses for tuning universal logical quantum gates in quantum computers. These modules respond to the needs of our industrial partner, who is developing a universally programmable quantum computer designed on superconducting transmon qubits. These qubits are mutually coupled to a tunable coupler which operates as a specific logical gate between selected qubits based on the inputted control electromagnetic pulse. The module is intended to shape state preparation pulses as well as logical gate control pulses in ideal and realistic model systems which include decoherence effects. The theory and implementation are general and can be used in any similar quantum computer design. In the upcoming future, new modules with advance optimization techniques will be developed, including an upgraded parallelization scheme which will enable more efficient utilization of [HPC](#) resources when searching an optimal control pulse. The first batch of modules is expected to be ready by the end of 2017.

### 5.2 Modules for implementation of the exact factorisation [MQC](#) dynamics

An independent module to perform quantum-classical nonadiabatic simulations based on the exact factorization of the electron-nuclear wave function will be developed in collaboration with Dr. Federica Agostini (Universit  Paris Sud). Within this scheme, trajectories are used to mimic the evolution of the nuclear degrees of freedom and are coupled to electronic dynamics involving excited states. Ground-state and excited-state electronic properties, i.e., potential energy surfaces and nonadiabatic couplings, will be represented on a grid in the adiabatic basis, and read as input. The initial conditions for the nuclei will be obtained via sampling of the Wigner density as provided either directly (for wave functions properties), or by [PaPIM](#) (for thermal properties). Efficient integration of the module within [PaPIM](#) will be considered. The possibility to directly include the module also in [CPMD](#), to avoid the grid representation of the electronic properties, will be investigated. Modules will be initiated in spring 2018 with an expected delivery in 2019.

### 5.3 Modules for implementation of Wigner-Liouville [MQC](#) dynamics

A set of modules will be developed in collaboration with Dr. Donal MacKernan (University College Dublin) to develop, for the first time, a highly scalable advanced implementation of the Wigner-Liouville scheme. These modules will implement, in particular, effective tools to circumvent the convergence problems of the method with respect

to the strength of the nonadiabatic coupling. Interfacing of Wigner-Liouville modules, based on the propagation of large sets of independent or correlated trajectories with initial conditions sampled from the Wigner thermal density, with the [PaPIM](#) package will be considered. Module production is expected to start in late 2017 and conclude in late 2018.

## 5.4 Cross-WP collaboration

We also indicate two projects to be developed in collaboration with other E-CAM WPs.

### 5.4.1 Integrating WP3 software development in E-CAM multi-scale modelling codes

Development of software for AdResS multi-scale approach is an on-going activity in E-CAM WP4, and in particular of the activities at Freie Universität Berlin (see deliverable D4.3 [56]). The AdResS code already incorporates the [RPMQ](#) method. Development of a [QTB](#) set of modules for multi-scale simulations to be included in this code is planned. QTB offers a distinct computational advantage compared to RPMQ, eliminating the need to propagate the dynamics of a number of replicas of the system. Inclusion of the method will thus greatly enhance the accessible system size. This work will be performed in collaboration with Prof. Luigi Delle Site and Dr. Christian Krekeler (Freie Universität Berlin), Dr. Simon Huppert and Dr. Etienne Manaud (Université Pierre et Marie Curie Paris), and Dr. Sara Bonella (EPF-Lausanne). Module development will start in mid 2018, with delivery expected for 2019.

### 5.4.2 Integrating WP3 software development with E-CAM task-based parallelization approaches

As discussed above, several state-of-the-art quantum dynamics algorithms rely on the propagation of large set of trajectories. The parallelization efforts deployed, for example in [PaPIM](#), strongly rely on this feature and bear similarities with methods in other areas of interest in E-CAM. Thus, a future direction for module developments in WP3 will explore how to integrate WP3 efforts with other work in E-CAM on parallelization. In particular, work is currently underway to implement a task-based parallelization approach for OpenPathSampling, a package under development in [WP1](#). Like PaPIM, OpenPathSampling involves running many independent trajectories, so the same parallelization approach will be relevant to PaPIM as well (see Deliverable D7.4[52]). The overall approach will be the subject of an [upcoming E-CAM Extended Software Development Workshop \(ESDW\)](#) in intelligent high throughput computing for scientific applications, which will include instruction on several possible frameworks: [Dask.distributed](#), [PyCOMPSs](#), and [MDStudio](#). PaPIM could benefit from integration with one or more of these frameworks for task-based, high throughput computing. The same tools could be beneficial to the modules described in [5.2](#) and [5.3](#).

## 6 Conclusion

One of the central objectives of WP3 of E-CAM is the creation of software modules for the calculation of quantum time dependent properties. This report gives an overview of currently available algorithms, provided in section 2. In section 3 a description of relevant software packages is given, with particular focus on codes combining *ab initio* calculation of the electronic structure with approximate quantum dynamical methods. This is followed, section 4, by the description of two core codes selected for specific development in E-CAM, and of the plans for further modular development of these packages. In section 5, we present additional modules to be developed based on input from our current industrial partner, and current and perspective academic collaborators. Additional modules may be developed based on the needs of the user base of WP3.

## References

### Acronyms Used

<b>HPC</b>	High Performance Computing
<b>MPI</b>	Message Passing Interface
<b>SMP</b>	Symmetric Multiprocessing
<b>QM/MM</b>	Quantum Mechanics/Molecular Mechanics
<b>MCTDH</b>	Multi-Configuration Time-Dependent Hartree
<b>MQC</b>	Mixed Quantum-Classical
<b>TDSE</b>	Time-Dependent Schrödinger Equation
<b>DFT</b>	Density Functional Theory
<b>TDDFT</b>	Time-Dependent Density Functional Theory
<b>CPU</b>	Central processing unit
<b>GPU</b>	Graphics processing unit
<b>RPMD</b>	Ring Polymer Molecular Dynamics
<b>CMD</b>	Centroid Molecular Dynamics
<b>QTB</b>	Quantum Thermal Bath
<b>WP3</b>	Quantum Dynamics
<b>WP6</b>	Software Infrastructure
<b>WP7</b>	Hardware Considerations and the PRACE Relationship
<b>FMS</b>	Full Multiple Spawning
<b>TBF</b>	Time Basis Functions
<b>AIMS</b>	Ab Initio Multiple Spawning
<b>WP2</b>	Electronic Structure
<b>WP4</b>	Meso- and Multi-scale Modelling
<b>WP1</b>	Classical Molecular Dynamics
<b>SPFs</b>	single-particle functions
<b>ESDW</b>	Extended Software Development Workshop

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