1. PHD PROJECT DESCRIPTION (4000 characters max., including the aims and work plan)

Project title: Description of the attosecond nucleus-electron quantum dynamics of small atoms and molecules subject to intense laser pulses

Project goals :

1.Development and computational implementation of the time propagation method for solving the time-dependent Schrödinger equation using the Röthe method and explicitly correlated all-particle Gaussian functions with complex shifts without assuming the Born-Oppenheimer approximation.

2. Development of algorithms for calculating molecular integrals with complex all-particles explicitly correlated Gaussians in the n-dimensional case,$\psi(r) = \Sigma\, c\_k\, g(a\_k;r)$, where c_k are complex coefficients, and g is a general complex-valued Gaussian, with parameter vector a= a_k collecting all the coefficients of the exponent of the expression.

$$g(a\_k;\mathbf{r}) = \exp[-\tfrac{1}{2}(\mathbf{r}-\mathbf{q})^{T}(\mathbf{A}+i\mathbf{B})(\mathbf{r}-\mathbf{q}) + i\,\mathbf{p}^{T}(\mathbf{r}-\mathbf{q}) + (\zeta + I\,\eta)]$$

Thus, a consists of two real symmetric n x n matrices **A** and **B,** where **A** is positive definite, real n-vectors **q** and **p,** and real numbers ζ and η**.** In the Röthe time propagation, functional

$$|| (1+ih/2H(t_{n+1}))\ \psi_{n+1} - (1- ih/2H(t_n))\ \psi_n|| = \min$$

is minimized at every time step and the minimization is done for function $\psi_{n+1} \sim \psi_{t_(n+1)}$. An effective way to minimise is by employing an algorithm that uses the derivatives of the above functional with respect to the parameters of ψ_{n+1} . Thus, algorithms for calculating the derivatives will be developed in this project (i.e. the derivatives with respect to the complex exponents and the complex shifts of the Gaussians).

3.Using the software developed in this project to study the dynamics of the coupled electron-nucleus motion of small atomic and molecular systems. The motion involves the rotational, vibrational, and electronic degrees of freedom. Such dynamics can be probed using atto-second spectroscopy. Examples of possible dynamics simulations include the coupled rotational/vibrational/electronic dynamics of the LiH molecule, the He_2 cluster, the isotopologues of the H_3 cluster, etc. Collaboration with experimental groups performing atto-second experiments will be established and the results of the time simulations performed within this project will be compared with the experimental results.

Outline. With the advent of new technology for manipulating atoms and molecules with intense laser pulses there is an urgent need for accurate and reliable tools for their numerical simulation. Such simulations will guide the design of advanced spectroscopic experiments and their interpretation. In this PhD project the graduate student will develop systematically benchmarked accurate simulation tools for solving the time-dependent non-relativistic molecular Schrödinger equation, where all particles are treated on an equal footing without separation of electronic and nuclear degrees of freedom, i.e. without assuming the Born-Oppenheimer approximation.
To achieve high accuracy in the time propagation of the quantum wave packet representing the system, an approach that is both adaptive in space and time will be implemented. Mesh-free complex explicitly-correlated Gaussian functions with shifts, that are free to warp and roam in space, will be the main tool in the implementation. By making the Gaussian exponents and Gaussian shifts to be complex, evens that involve ionization/dissociation of the studied molecular system can be described. This work is an extension of our non-BO work on stationary states of small atoms and molecules that has been performed by the project supervisor and her students and collaborators using various forms of all-particles explicitly correlated Gaussians. For reliability, we will introduce computable error control certificates. We will develop and publish high-quality open-source computer codes that will be produced in this project.

Work plan This PhD project will last 3 years with a possible fourth-year extension. The complex explicitly correlated Gaussian formulation of non-BO quantum dynamics requires experience with both non-BO quantum mechanics and laser-induced quantum dynamics. The project supervisor possesses such experience. Finally, the ab initio molecular dynamics of WP4, led by Pedersen and Lasser, require experience with the efficient evaluation of forces and nonadiabatic couplings as well as experience with semiclassical nonadiabatic dynamics. All PIs have experience in leading multi-partner, synergetic research projects and possess the skills needed to divide the overall goals into manageable subtasks, and to distribute and coordinate activities among the partners. By far the largest part of the support requested from the ERC will be used to fund post-doctoral researchers and PhD student fellowships. Interaction between the partners will be secured through an active management and meeting structure (annual meetings and international workshops, regular PI (leader group) video meetings, as well as frequent, informal video meetings), extensive personnel exchange for junior and senior personnel involving all partners. All WPs will start in Month 1 and run until the end of the project.