Towards ab initio dynamical simulations of atoms, molecules, and clusters in femtosecond XUV pulses

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In this paper, we focus on a correct representation of electronic wavefunctions of the laser-driven systems. Out of various approaches developed for atoms and diatomics, making use of B-splines, numerical lattices, and basis sets, only the latter seem to be readily portable to other molecules due to an anisotropy resulting from the properties of the Coulomb potential. With the help of the Wigner representation, we will discuss numerical implications of a complex scaling transformation, which is used in order to properly account for ionization as well as to keep a feasible size of the dressed-states basis set [1]. Then we will demonstrate that Gaussian primitives that are optimized for a high accuracy of Rydberg states, happen to be unexpectadly beneficial for a numerical precision of complex scaling calculations [2]. Our conclusions will be demonstrated for example calculations of the field-free and driven helium atom [3,4]. Finally, we will briefly discuss the intended application of the Gaussian basis sets to other atoms and molecules.

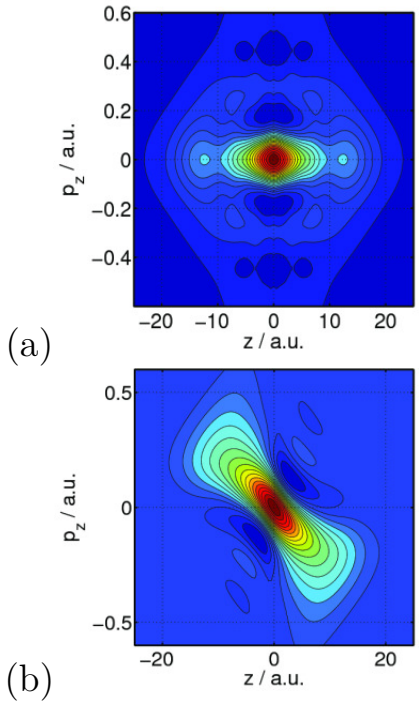

Figure 1: *Wigner distribution of the 5s state of hydrogen: (a) unscaled, (b) complex scaled.*

θ	aug-cc-pV5Z	ExTG5G
0	-2.903201	-2.903506
0.2	$-2.903230 + 10^{-4}i$	$-2.903505+2 \times 10^{-6}i$
0.6	$-2.904047 + 7 \times 10^{-3}i$	$-2.903509 + 7 \times 10^{-6}i$

Table 1: *Complex energies of the helium ground state obtain artifical non-zero imaginary parts for non-zero values of the complex scaling parameter θ due to insufficient basis sets. The second column shows results for a standard quantum chemistry basis set, while the third column for the new optimized Gaussian basis set.*

References

[1] P. R. Kaprálová-Žánská, J. Chem. Phys. **134**, 204101 (2011)
[2] P. R. Kaprálová-Žánská and J. Šmydke, J. Chem. Phys. **138**, 024105 (2013)
[3] P. R. Kaprálová-Žánská, J. Šmydke, and S. Civis, J. Chem. Phys. **139**, 104314 (2013)
[4] P. R. Kaprálová-Žánská and N. Moiseyev, submitted to J. Chem. Phys.