Gaussian basis sets for complex scaling calculations

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The interest in complex scaling (CS) calculations is justified by calculations of atomic resonances – doubly excited states, atoms in strong laser fields, etc.. However, it is well known that CS calculations in conjunction with quantum chemistry methods often suffer from numerical instabilities that demonstrate itself, among others, in the emergence of complex ground state energies. In this contribution, we relate these numerical artifacts to inapropriate atomic basis sets and propose an optimization procedure for Gaussian basis sets which are resistant to the indicated problems.

First, the CS operator $\exp(-\theta \hat{x} \hat{p})$, being the foundation of the CS method, has been studied in the Wigner phase-space representation. It has been shown that this non-unitary transformation behaves similarly to the squeezing operator, rotating and amplifying Wigner quasi-probability distributions of the respective wavefunctions, where the deformation effect is mainly due to the scalar part of the respective phase-space operator, $\exp(-\sin 2\theta \, xp/\hbar) \exp(-\hbar \tan \theta \, \partial^2/\partial x \partial p \,/2)$ [1]. As a consequence, the basis sets for complex scaled wavefunctions generally require an increased number of basis functions to include larger momenta in the same extent of space.

Then, we have found that excited states are efficiently described by a set of virtual orbitals being defined as eigenfunctions of a non-redundant variant of the Fock operator [2]. This fact makes it possible to track many-electron wavefunctions in one-electron space and paves a natural way to an optimization of atomic basis sets based on the virtual energies. The robustness of the atomic basis sets in respect of CS is controlled by the required accuracy of the virtual energies.

The method has been applied for the atomic basis sets of helium atom. Calculations of helium doubly excited resonances illustrate the power of the method on a stability of the real and complex energies within a large interval of the CS parameter, which is incomparable with various standard basis sets [2]. Dynamical simulations of helium in strong XUV fields based on CS helium spectrum provide yet a more sensitive test to the basis sets, and still evidence a long-time independence of the calculated excitation yields on the CS parameter [3].

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[3] Kapralova-Zdanska, P. R., Smydke, J., and Civis, S., *J. Chem. Phys.*, submitted.