Basis Set Optimization Method for Rydberg States – GTO Basis Sets for He and Be

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A new method to optimize basis sets suitable for Rydberg states investigation has been suggested and applied [1,2] to Gaussian basis of helium and beryllium atoms. It is based on a variational optimization of *the improved virtual orbitals* [3], which lead to dominant configurations in the CI excited states expansion and thus more properly describe excited states than the standard Hartree-Fock orbitals.

We have also introduced *the exponentially tempered Gaussian basis set* scheme (ExTG)

$$log_{10}\,\zeta_k = a\,10^{-bk} + c\,;\;\; k = 0\ldots(N-1) \tag{1}$$

which naturally emerged after a series of improved virtual orbitals had consecutively been optimized. Compared to *the even tempered Gaussian* scheme (ETG)

$$log_{10}\,\zeta_k = a\,k + b\,;\;\; k = 0\ldots(N-1), \tag{2}$$

the ExTG basis increases density of diffuse Gaussians and achieves the same quality with much smaller number of basis functions.

The calculated CI and EOM-CC excitation energies were compared to other basis set results and to experiment. The helium basis set was also employed in a complex scaled calculation of resonances with excellent results approaching quality of the Coulomb-Sturmian basis set.

References

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