

Rate of convergence of basis expansions in quantum chemistry

Werner Kutzelnigg,¹

¹*Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum, Germany*

Traditional expansions in an orthonormal basis of the type of a Fourier series are very sensitive to the singularities of the function to be expanded. Exponential convergence is only possible, if the basis functions describe the singularities of the expanded functions correctly. Otherwise only an inverse-power-law convergence is realized, which is usually slow. Example: the slow convergence of the CI expansion due to the correlation cusp. An improved convergence, though still of inverse-power type, can be achieved, if one augments the basis by functions that describe the singularities of the wave function correctly, like in the R12 method.

Alternative: a discretized integral transformation, as in the conventional expansion of wave functions in a Gaussian basis. Such expansions are surprisingly insensitive to singularities of the wave function to be expanded (e.g. the nuclear cusp). The rate of convergence is of a new type, with an error estimate $\sim \exp(-a\sqrt{n})$, if n is the basis size. For the expansion of the hydrogenic ground state function in an even-tempered Gaussian basis, simple closed expressions for the asymptotic error can be derived. This can be generalized to the relativistic case, where the convergence is qualitatively similar to the non-relativistic one, in spite of the stronger singularity in the relativistic wave function.

References:

- W. K, Int J. Quantum Chem. 51, 447 (1994);
Computational Quantum Chemistry: a Primer, by E. Cancès, M. Defranceschi,
W. Kutzelnigg, C. Le Bris, Y. Maday, Handbook of Numerical Analysis, Vol. X,
Elsevier 2003
W.K. J. Chem. Phys. 126, 201103 (2007) .
W.K. AIP conference proceedings, in press 2011

E-mail: werner.kutzelnigg@rub.de