

Convergence behaviour and convergence acceleration of molecular electronic wave functions

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In wave function-based quantum chemistry, molecular electronic wave functions are expanded in a basis of antisymmetrized products of one-particle functions, that is, orbitals. In practical calculations, this basis is incomplete, and basis-set truncation errors occur. The basis can be increased in a systematic and optimal fashion, but nevertheless, the basis-set truncation errors vanish only slowly as n^{-1} , where n is the number of orbitals per atom. This slow convergence represents a major obstacle for accurate wave function-based quantum chemistry, as computation times grow at least as n^4 . The convergence of computational results to the limit of a complete basis can be accelerated by utilizing extrapolation procedures or by seeking alternatives to the expansion in a basis of antisymmetrized products of one-particle functions. In the present talk, the R12 method will be discussed, which represents such an alternative. In the R12 methods, not only one-particle functions are used, but also two-particle functions, which depend explicitly on the interparticle distances between the electrons in the molecule.

References

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