

# Explicitly correlated molecular electronic wave functions: Energies and analytic derivatives

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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 F12 method will be discussed, which represents such an alternative. In the F12 methods, not only one-particle functions are used, but also two-particle functions (Slater-type geminals), which depend explicitly on the interparticle distances between the electrons in the molecule.

In previous work by Kordel *et al.*, we have discussed the implementation—in the Dalton program—of the analytic calculation of first-order molecular properties at the explicitly correlated second-order Møller–Plesset level, including nuclear gradients. In the present talk, we report our progress in the corresponding implementation in the Turbomole program. Results will be presented for the analytic calculation of relaxed first-order properties and nuclear gradients.

## Literature:

- E. Kordel, C. Villani, and W. Klopper, *J. Chem. Phys.* **122**, 214306 (2005).
- E. Kordel, C. Villani, and W. Klopper, *Mol. Phys.* **105**, 2565 (2007).
- S. Höfener, C. Hättig, and W. Klopper, *Z. Phys. Chem.* (in press).