Numerical Instabilities in Pseudopotential Matrix Element Evaluation

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Every now and then, one hears rumours about possible numerical instabilities in the evaluation of effective core potential (ECP) matrix elements, that arise if steep high-angular momentum basis functions are located close to a nucleus carrying a core potential. Indeed, one easily finds examples where even Hartree-Fock energies are completely wrong. We have thus computed ECP matrix elements to high numerical accuracy for a model problem and compared the results to those from a standard quantum chemical computer code. These "experimental" results show where is the onset of inaccuracies that might compromise final results.

A mathematical analysis has been carried out that reveals that the numerical instability arises from the partial wave expansion that is performed. In other words, the accuracy of some intermediate quantities such as the angular and radial integrals [1] is *not* a problem. The partial wave expansion is not strictly necessary for the "type 1" matrix elements and could be avoided there in some cases. We were able to obtain analytical results for the numerical instability: if α is the Gaussian exponent of a normalized steep off-center basis function of angular momentum l, and if d is the distance to the ECP center, the relative accuracy of the intermediate quantities (machine precision at best), is amplified in the final result by a factor

$f \approx \frac{\left(16\alpha d^2\right)^l}{\left(2l-1\right)!!}$ (asymptotic result for large α) This factor reaches values larger than

10^{10} for parameter values that are encountered in *real life* quantum chemical calculations.

A method that does not explicitly use a partial wave expansion for the type 2 integrals relies on the resolution of the identity through an auxiliary basis set at the ECP center. This method will either be inaccurate for steep off-center basis functions, or the inversion of the overlap matrix of auxiliary basis functions will be unstable because the matrix is ill conditioned. The only way to alleviate the problem at least a little bit is to re-code the type 1 integrrals without making use of a partial wave expansion.

[1] L. E. McMurchie and E. R. Davidson, J. Comput. Physics **44**, 289 (1981)