

Resolution-of-Identity State-Average-CASSCF Analytic Gradients and Non-Adiabatic Coupling Vectors

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The fast computation of analytic gradients and non-adiabatic coupling vectors is the brick stones upon which we today can simulate non-adiabatic processes as encountered in photochemistry and chemiluminescence. The inner-projection technique, as championed by Per-Olov Löwdin, has been instrumental to our understanding and development of techniques for wave function theories. This technique was extended to the treatment of two-electron integrals by Beebe and Linderberg - Cholesky decomposition of two-electron integrals - but did for a long time get no attention. Recently Koch and co-workers showed the ability of the approach to facilitate large coupled-cluster simulations. Subsequent work by F. Aquilante, T. B. Pedersen and R. Lindh showed the close connection between the popular Resolution-of-Identity (RI), or as it is also called Density Fitting, and the Cholesky decomposition technique. This connection enable techniques from the two methods to be combined. For example, it allowed for a strict derivation of so-called on-the-fly auxiliary basis sets to be developed and implemented. Aquilante and co-workers has since showed how these techniques, with minimal loss of accuracy, can be extended to virtually all types of wave function models and the associated gradients. This has in particular been facilitated by efficient treatment of the exchange integrals - the LK approach. Developments of Pair-Atomic RI (PARI) suggest that this bottleneck can be further reduced/eliminated. In this presentation we would like to report the use of these methods for the computation of analytical gradients and non-adiabatic coupling vectors for the State-Average (SA) CASSCF wave function. In the presentation we will use a number of molecular systems to demonstrate the tractability of the approach, in combination with standard techniques (especially projected-constrained optimization), to efficiently locate, characterize the conical intersection and to explore the conical seam for large molecular systems in conjunction with large active spaces. We expect this work in combination with so-called DMRG technique and efficient corrections for dynamic electron correlation to pave the way for simulations of non-adiabatic processes with qualitative and quantitative accuracy.