

# Analytic gradients for general non-iterative coupled-cluster approaches

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It is fair to say that the coupled-cluster (CC) approach popularized by Bartlett and his associates [1] in the field of computational chemistry became an inevitable tool for quantum chemists. The level of accuracy that can be achieved heavily depends on the truncation applied to the cluster operator. Due to the steep scaling of the CC( $n$ ) approach,  $n_o^n n_v^{n+2}$ , where the cluster operator truncated at  $n$ -tuple excitations and  $n_o$  is the number of occupied while  $n_v$  is the number of virtual orbitals, facilitated the development of the non-iterative [CC( $n$ )( $n+1$ )] methods where the highest excitations are treated approximately including the most important contributions only. Well-known methods such as the CC(2)(3) a.k.a. CCSD(T) and CC(3)(4) a.k.a. CCSDT(Q) approximations including non-iterative triples and quadruples excitations, respectively, belong to this category.

The calculation of energy for the CC( $n$ )( $n+1$ ) approximation has already been coded for arbitrary excitations using a string-based algorithm [2]. Nevertheless, the efficient calculation of first-order properties requires analytic gradients. Although analytic first derivatives are implemented for the general iterative CC( $n$ ) approaches they are not readily available for the non-iterative CC( $n$ )( $n+1$ ) methods. So far, analytic gradients have been developed for CCSD(T) only [7]. Here, we present the first general implementation of analytic gradients for the CC( $n$ )( $n+1$ ) approaches. It is coded into the development version of the MRCC suite of programs utilizing its general string-based formalism. The details of the implementation are presented as well as the performance of the CCSDT(Q) method for first-order molecular properties, such as equilibrium structures and dipole moments has been assessed investigating several small molecular systems and compared the results with those obtained by CCSD(T), CCSDT and CCSDTQ calculations.

[1] R. J. Bartlett *Ann. Rev. Phys. Chem.*, 32:359, 1981.

[2] MRCC, a string-based quantum chemical program suite written by M. Kállay. See also Ref. 3 as well as <http://www.mrcc.hu/>

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