Coupled cluster hierarchy based on the generalized doubles ansatz and the expectation value expansion.

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More than a decade ago, a coupled cluster (CC) ansatz with generalized two-body cluster (GCC) operator was proposed [1, 2]

$$|\Psi\rangle = e^{\hat{\mathcal{T}}}|\Phi\rangle \tag{1}$$

with

$$\hat{\mathcal{T}} = \tfrac{1}{4}\textstyle\sum_{p,q,r,s} \mathcal{T}^{pq}_{rs}\tilde{a}^{rs}_{pq}, \tag{2}$$

where $\mathcal{T}^{pq}_{rs}$ is an amplitude related to a replacement created by the related operator $\tilde{a}^{rs}_{pq}$ normal ordered with respect to the reference single determinant $|\Phi\rangle$ and $p,\ q,\ r,\ s$ denote arbitrary orbitals from an orthogonal one-particle basis. Generally, the constituting operators of $\hat{\mathcal{T}}$ (r.h.s. of Eq. (2)) do not mutually commute. Hence, unlike in standard CC approach, a similarity transformed hamiltonian

$$\bar{H}_N = e^{-\hat{\mathcal{T}}}H_N e^{\hat{\mathcal{T}}} \tag{3}$$

represents (at least formally) an infinite expansion. This fact disqualifies the use of $\bar{H}_N$ together with projection technique as a preferential method of determining the amplitudes of $\hat{\mathcal{T}}$. Moreover, the standard projection technique would provide a number of equations that is different from the number of parameters. Therefore, we have explored a possibility of using the ideas from the standard expectation value CC theory (XCC) that is based on the truncation of the expectation value CC expansion using an analysis stemming from the perturbation theory [3], whereas the parameters are obtained from stationarity condition for such a truncated functional. Indeed, a one to one correspondence with XCC(n) can be encountered. A feasibility of reduced scaling non-iterative corrections to standard CCSD as discussed in [4] has been investigated, too. The higher excitation non-iterative corrections from the standard CC can be exactly reproduced using the perturbation theory considerations based on the GCC ansatz. Though the scaling is formally reduced, the corrections are obtained in an iterative procedure that makes the approach less favorable. On the other hand, exact reformulation of CC with higher excitation ranks, such as with singles doubles and triples (CCSDT) is possible with such a reduced scaling and with no requirement of triple-excitation amplitudes storage during the iterative procedure.

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