Coupled cluster method tailored by Configuration interaction

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The correlation energy is defined as the difference between the full CI and Hartree-Fock energies. According to the nature of the correlation, it can be classified into the non-dynamic and dynamic energies. In general, the CI method can treat the former and the CC method covers the latter. In this study, we developed the CC method combined with the CI method, to take the advantages of both the methods. This method is named as Tailored CC (TCC). The computational procedure of the TCC consists of two calculation steps. First, we perform the CI calculation. The wave function which is produced in CI calculation is expected to describe the non-dynamic correlation well. The CI coefficients are used to construct the corresponding cluster amplitudes according to the relation between the CI and CC expansions. Second, we solve the CC equations to incorporate dynamic correlation with the cluster amplitudes obtained in previous step fixed. When the reference function is not adequate for the exact wave function (as in the case of quasi-degenerate systems), the conventional CC method often fail in describing the potential energy surface (PES) even qualitatively. The reason is that the low-lying excitations responsible for the non-dynamic correlation are not adequately treated. In contrast, the TCC can avoid this problem and treat quasi-degenerate systems. We calculated several molecular PECs with the TCC and showed that the TCC yields improved PECs both qualitatively and quantitatively, compared with those obtained with the conventional CC method.