Cluster perturbation theory for energies and molecular properties

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We introduce a new class of perturbation models—the cluster perturbation (CP) models—where the major drawbacks of Møller-Plesset and coupled cluster (CC) perturbation theories have been overcome. In CP theory, we consider a target excitation space relative to the Hartree-Fock state and partition this target excitation space into a parent and an auxiliary excitation space. The zeroth-order state is a CC state in the parent space and the target state is the CC state in the target space. Perturbation series, leading from the zeroth-order, parent state to the target state, is in CP theory determined in orders in the similarity-transformed fluctuation potential, where the similarity transformation is carried out using a cluster operator describing the parent space. Perurbation series are in CP theory determined not only for the ground-state energy, but also for molecular properties, including excitation energies and frequency-dependent response properties, with the zeroth-order contribution in the series being the energy or the molecular property for the CC parent state and with the series formally converging to the energy or the molecular property for the CC target state. The applicability of CP theory to both the energy and molecular properties and the numerical results for the ground-state energy and excitation energies demonstrate the superiority of CP theory compared to previous perturbation models. Low-order corrections in the CP perturbation series may be expected to become state-of-the-art electronic structure models for determination of energies and molecular properties of target-state quality for single-configuration dominated molecular systems.

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