Exploring Molecular Properties through Cluster Perturbation Theory: Excitation Energy Benchmarking

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Cluster Perturbation Theory (CP) introduces an innovative approach in perturbation models by leveraging a correlated *zeroth-order* state. The innovative aspect of CP theory lies in its ability to truncate this state at various excitation levels, adeptly avoiding higher levels that have minimal impact on molecular properties. The real strength of CP theory is evident in its efficient computation of perturbation series, applicable to both ground-state and excitation energies. In CP's computational framework, the calculation of molecular properties involves meticulous computation of minor perturbation corrections. These corrections are deduced from the differences in energy and molecular properties observed between the parent and target states in coupled cluster (CC) calculations. What sets CP theory apart is its strategic treatment of the Jacobian of the CC parent state as the *zeroth-order* contribution. This approach is not just a feature of the methodology; it represents a significant leap forward in the field of CC perturbation theory, marking a new era of precision and efficiency in molecular property analysis.

In this study, we investigate the excitation energy of various molecules using different CC methods and compare the results with those obtained from the third-order CP model, CPS(D-3). This study contributes to the understanding of CP theory's capabilities in excited-state calculations, offering a critical evaluation of its potential for wider applications in molecular property analysis.