Assessing the performance of ΔSCF and the diagonal second-order self-energy approximation for calculating vertical core excitation energies

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Vertical core excitation energies are obtained using a combination of the ΔSCF method and the diagonal second-order (D2) self-energy approximation. These methods are applied to a set of neutral molecules and anions. An assessment of the results with the inclusion of relativistic effects is presented. The importance of both correlation and relaxation contributions to the vertical core-excited state energies, the concept of local and non-local core orbitals, and the consequences of breaking symmetry are discussed.