

Coupled cluster studies. IV. Analysis of the correlated wave function in canonical and localized orbital basis for ethylene, carbon monoxide, and carbon dioxide. Foerner, Wolfgang

Abstract

An a posteriori anal. of the correlated wavefunctions of 3 small mols. using canonical and localized orbitals shows that, while more excitations are nearly zero for canonical orbitals than for localized ones, in the latter case a straightforward way exists for a priori selection of negligible excitation. The same observation is made in the case of a larger mol. cytosine. However, in this case 99% of the correlation energy is obtained already with $\approx 10\%$ of the excitations when localized orbitals are used, while $\approx 36\%$ of them are necessary in canonical basis. Using localized orbitals, the excitations can be split into subsets which can be calcd. individually. A simple derivation of the orbital invariant formalism of Pulay and Sabo (1986) for the calcn. of Moeller-Plesset correlation energies is given.