Coupled-cluster studies. I. Application to small molecules, basis set dependences.

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Abstract

For calcns. of mol. correlation energies with the coupled-cluster-doubles method, an algorithm was formulated in an ab-initio framework. The use of localized orbitals instead of the canonical Hartree-Fock (HF) MO's is possible. Potential curves for H_2, LiH, and NH_3, and correlation and total energies of the ground state of formaldehyde calcd. by using different at. basis sets showed reasonable agreement with expts. for bond lengths, for the force const. of LiH, and for the inversion barrier of ammonia. The usefulness of oscillatory orbitals, proposed by S. F. Boys (1966) as an alternative to Hartree-Fock virtual orbitals, was also investigated. In this way, correlation energies were considerably improved compared to the HF virtuals, and also parts of the core correlation would be taken into account. The LCAO expansion of oscillatory orbitals requires a large basis set, which leads to computational difficulties. Comparisons were made with previously published results obtained by using other methods.