

Numerical application of the coupled-cluster theory with localized orbitals to polymers: III. bond alternation in trans-polyacetylene. Knab, Reinhard; Foerner, Wolfgang; Ladik, Janos

Abstract

Calcns. are presented concerning all-trans-polyacetylene (t-PA), using localized orbitals for the calcn. of total correlation energies in an ab initio framework. Due to the localization properties of the localized Wannier functions, esp. the virtual ones, simultaneous interactions between three unit cells of a polymer must be included. However, if a larger no. of neighbors are taken into account the method is still faster than those using canonical HF orbitals. The LO approxn. is shown to be able to recover about 90% of the correlation energy obtained in the canonical orbital basis in the equil. geometry. A different approxn. which also reproduces potential curves very well is presented, although this variant recovers only about 80% of the total correlation energy per unit cell calcd. with a canonical orbital basis. This failure, however, leads only to a shift of the potential parallel to the canonical one, even in a very subtle case like that of the bond-alternation potential in t-PA which depends strongly on the quality of the correlation calcn. method used. For the equil. bond alternation u_0 (projected onto the polymer axis) of t-PA the coupled-cluster doubles method with localized orbitals yields values almost identical to those obtained with canonical Moller-Plesset perturbation theory of fourth order including single, double, triple and quadruple excitations.