

Abstract

We present a parametrization for the PPP Hamiltonian for the description of cis-polyacetylene (cPA). In contrast to trans-polyacetylene, we have to include symmetry breaking between neighboring sites into the Su-Schrieffer-Heeger-type one-electron part of the Hamiltonian. Our parametrization is based on correlated ab initio calcns. on cis-hexatriene and on the results of independent calcns. found in the literature. For open-shell systems (singly charged polarons) we use the annihilated UHF method to avoid the artificial spin contaminations inherent in UHF (unrestricted HF) calcns., which lead to the inclusion of fractions of the correlation energy in UHF total energies which cannot be controlled and are different for different systems and even for different geometries of the same system. Thus UHF is useless for the calcn. of potential hypersurfaces and thus in turn for dynamical simulations. We find that in cPA singly-charged polarons are formed, while in doubly-charged chains stable bipolarons are found, although of a quite large width. We further find that the charged polarons are mobile in the chain and thus we conclude that polarons and bipolarons can serve as charge carriers (the latter ones spinless) in doped cPA.