Theoretical study of bipolaron dynamics in polyparaphenylene: I. Derivation of the formalism and density functional (DFT) calculations on neutral and charged model systems. Forner, Wolfgang.

Abstract

The authors have derived the rather lengthy formalism for time simulations in polyparaphenylene, treating the rings as semi-rigid rotors. To this end an Euler-Lagrange formalism was used. As one of the model systems to parametrize a PPP Hamiltonian, the authors have chosen an asym. cationic dimeric system in model of the geometry, which allows the rings to move between arom. A-phase and quinoidal B-phase structures. A cation was chosen, to avoid the presence of an unpaired spin in the model. Further, anionic models would require more extended basis sets in D. Functional (DFT) calcns. The asym. structure of the model allows to scan the total potential surface between arom. and quinoidal structures. The cation shows only one min. on the quinoidal side. To make sure that this is not only due to the charge, around the expected min., the authors also performed calcns. on a quinoidal B-phase model dimer and on an arom. A-phase model dimer (biphenyl). However, since geometrical model is based on the central unit of the trimer, the authors do not find double min. potentials in dimers, which consist of just two terminal units. But the potentials still can serve as the basis of a parameterization of the model Hamiltonian for the π-electrons, while in longer chains one has to replace the terminal units by ones which have a more appropriate geometry. The calcd. DFT potentials will be compared in a forthcoming paper with the corresponding PPP potentials to allow a parameterization of the PPP Hamiltonian and subsequently bipolaron structure optimizations as well as simulations of the dynamics of the system. The formalism needed to this end is derived and outlined. It is currently under programming.