Nonlinear charge carriers in polyacetylene. Forner, Wolfgang; Utz, Wolfram.

Abstract

Conjugated org. polymers are intrinsically semiconductors but become conducting upon doping and photoconducting after optical excitation. In the low doping regime they show usually conduction without an assocd. spin transport. Thus as charge carriers in this regime nonlinear quasiparticles are assumed, such as charged solitons in materials with a degenerate ground state like e.g. trans-polyacetylene or pernigraniline. In the case of materials with a non-degenerate ground state the situation is often less clear but it is assumed that charged polarons or bipolarons are the charge carriers in them. We present a theor. model for the description of the dynamics of such quasiparticles which yields also information on their mobility, their nature and stability, as well as their spectral properties. The model is based on a π-electron Hamiltonian including electron-electron interactions. On the basis of the prototype material polyacetylene it is demonstrated how such a model can be parametrized with the help of correlated ab initio or d. functional calcns. and applied. We discuss in some detail the dynamics of the pristine material, as well as of doped and of electronically excited polyene chains. With the help of these dynamics a scenario for the conduction mechanism assumed for polyacetylene is given. Further we calc. optical spectra from the dynamics for charged solitons and for excited chains which are in fair agreement with expts. The thermal mobility of neutral solitons is also studied. Further we show how the model can be extended for applications to polymers different from polyacetylene. Such modifications could yield informations about the nature of nonlinear quasiparticles involved in the process of charge transport in cases where the question is not completely solved. This is the case in cis-polyacetylene where recent literature suggests that bipolarons should be instable.

However, we could show that both charged polarons and bipolarons are stable in the material with bipolarons favored over charged polarons. Due to the fact that the model can be extended to other polymers, also to chem. structures not yet synthesized, it could gain also predictive poser after further development.