The Pariser-Parr-Pople model for trans-polyenes. II. Parametrization and ground-state dynamics. Foerner, Wolfgang

Abstract

The parameter space of the PPP model was surveyed to fit the bond alternation potential of trans-butadiene obtained by ab initio Hartree-Fock and correlation calcns. Since no unique best fit parameter set could be found, ab initio Hartree-Fock geometry optimization results on (C21H23)+, C22H24 and (C22H24)2+ found in the literature were taken as addnl. data. The author found as resonance integral $\beta 0$ = -2.4 eV and as on-site Coulomb repulsion parameter $\gamma 0$ = 11.25 eV as optimum values in agreement with usually used values for these parameters. The electron-phonon coupling const. is found to be α = 1.9 eV/.ANG. much smaller than the Su-Schrieffer-Heeger value for α. Ground state soliton dynamics are presented and it is shown that dynamical properties are very sensitive to the parametrization. At the optimum parameter set, moving solitons exist in the system. From a dimerization potential a force const. is obtained which agrees with expt.