Comparative application of different approaches for band structure calculations on polyparaphenylene in the Pariser-Parr-Pople model: II. Moller-Plesset and coupled cluster methods. Forner, Wolfgang.

Abstract

An investigation on the calcn. of the band structure of polyparaphenylene using Moller-Plesset Perturbation Theory of 2nd order (MP2) to take into account correlation effects is presented. The basis for these calcns. is the PPP Hamiltonian to be able to ext. parameters from these calcns. for dynamical simulations. Different approaches to the application of MP2 to infinite system can be compared. In the ab initio case there are many calcns. on this level published which are all based on different Hartree-Fock (HF) program packages and thus use different cutoff schemes for the interactions and different basis sets. Therefore the results of these studies are not directly comparable and a thorough study of different approaches based on one and the same ref. is highly desirable. The PPP or the Hubbard model are well suited for such a purpose, since the correlation methods on top of HF, outlined earlier, use exactly the same formalisms as in the corresponding ab initio applications, although the numerical calcns. are much cheaper. Coupled cluster (CC) models, which are infinite order extensions of MP perturbation theory, are also discussed with respect to using localized orbitals. Polyparaphenylene is used as the model system because of its importance in diode technol. For an accuracy of the correlation corrections in the meV region 5-6 neighbors are needed, while more than 10 neighbors are required for μeV accuracies. Spectra calcd. from the correlated band structure are discussed.