

Energy bands and bond alternation potential in poly(para-phenylene vinylene): a comparative ab initio quantum chemical and density functional theory study. Forner, Wolfgang; Bogar, Ferenc; Knab, Reinhard.

Abstract

We present calcns. of the total energy per unit cell for different bond alternations of the C-C bonds bridging the distance between two arom. rings in poly(para-phenylene vinylene) (PPV), using two different parametrizations of the energy functional in the local d. approxn. (LDA) and the ab initio Hartree-Fock (HF) method. For the application of correlation corrections to the HF results the system is already too large. We find that even simple LDA methods are reliable alternatives to the ab initio HF method for the calcn. of potential surfaces in polymers with large unit cells. The results in turn can be used to det. parameters for model Hamiltonians necessary for theor. studies of the dynamics of nonlinear quasiparticles in the polymers. We further present the LDA band structures of PPV together with their HF and correlation (many body perturbation theory of 2nd order in Moller-Plesset partitioning, MP2) cor. counterparts. We find that the fundamental gap obtained is too large both with HF and with the correlation cor. band structure compared to expt. However, we use only a modest correlation method and a small basis set, which already brings us to the limits of the computers available to us. The LDA gaps on the other hand are too small which, however, could be cor. with the help of self interaction corrections. None of the latter methods would lead to exceedingly large computation times.