

Numerical application of the coupled cluster theory with localized orbitals to polymers. IV. Band structure corrections in model systems and polyacetylene. Forner, Wolfgang; Knab, Reinhard; Cizek, Jiri; Ladik, Janos.

Abstract

We present the formalism for the correction of the band structure for correlation effects of polymers in the framework of a localized orbital approxn., using the quasiparticle model. For this purpose, we use an ab initio framework Moller-Plesset perturbation theory in second order, the coupled cluster doubles method, and its linear approxn. The formalism is applied to a water stack and two different forms of a water chain as model systems to test the reliability of the approxns. involved. From our previous work we know that, e.g., in polyacetylene difficulties due to the localizability of the canonical crystal orbitals do not arise from the π or π^* bands, but from bands of σ symmetry. Thus we conc. in this work again on polyacetylene as an example of a realistic polymer. We find that the localized orbital approxn. is quite useful also in the case of band-structure corrections due to correlation effects. However, the coupled cluster calcn., in particular, turns out to be computationally very costly for infinite systems. But it seems to us that localized orbital approxns. are at the moment the only way to make coupled cluster calcns. on realistic polymers with covalent bonds between the unit cells possible at all.