

Ab initio calculation of transfer integrals for polymer crystals

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Transport properties of organic conjugated materials are widely investigated, in view of their use in optoelectronic devices. While in the past organic layers were mostly disordered, recently crystalline films of oligomers have been proposed as a highly efficient alternative. However, there is still a fundamental need to understand the relationship between the solid-state packing of chains and the resulting charge transport. The first step would be to understand the properties of unrelaxed crystals, thereby neglecting polaronic effects as a first approximation. To this end we present a theoretical study of transport properties for a prototypical conjugated polymer, poly-*para*-phenylenevinylene, in two different possible crystalline packings. Our analysis is performed using density-functional electronic structure calculations and allows us to extract fundamental parameters such as the molecular transfer integrals (TI). These quantities are relevant both for coherent band-transport, in which they are used to calculate the transmittance in the Landauer-Büttiker formalism, and for incoherent hopping according to the Marcus theory. We obtained infinite-chain TI for polymer systems both from a tight-binding point of view and within a direct numerical calculation. The results obtained with these two approaches agree and indicate that interchain interaction plays a relevant role thus allowing one to use it as a tunable parameter for the design of efficient electronic devices based on organic materials.