Charge transport in organic semiconductors: *Ab initio* charge carrier propagation schemes

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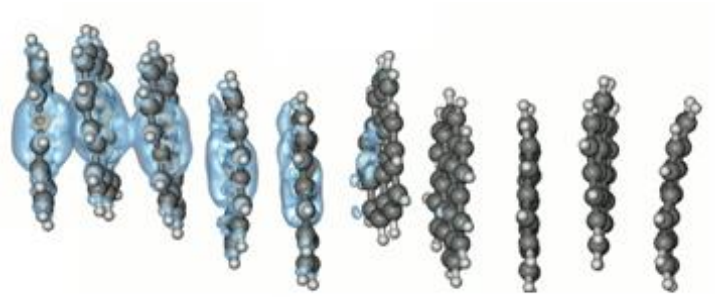
Although π-conjugated, organic semiconductors have been successfully tested in several electronic devices; *e.g.* organic photovoltaic cells [1], organic light emitting diodes [2], and organic field-effect transistors [3]; a full understanding of the precise nature of the underlying charge migration mechanisms is still lacking. In such systems, charge carrier mobilities are dramatically influenced by the structural fluctuations of the molecular stacks, which makes it necessary to take dynamic effects into account beyond purely perturbative treatments. As a result of this strong coupling of the electronic structure to dynamic degrees of freedom, charge transport cannot be described in terms of fully coherent or fully incoherent microscopic mechanisms within the molecular devices' operating temperature range (250 K to 350 K) [4].

In our studies, based on accurate and extensive benchmark calculations, two different propagation schemes are extended and applied to investigate the charge transport mechanisms of molecular systems: A kinetic Monte Carlo scheme based on semi-classical Marcus theory used for the evaluation of the charge transfer rates and a quantum dynamical scheme propagating the charge carrier wave function under explicit



consideration of charge effects on the dynamics and the electronic structure of the system. Herewith, charge carrier mobilities are computed for highly ordered molecular systems of different complexity in real-time in a fully *ab initio* matter. Our theoretical investigations open the possibility to achieve quantitative comparisons to transport experiments and are an essential basis for the development of a first-principle materials design.

References:

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