

QUANTUM MODELLING OF ORGANIC AND BIOLOGICAL MATERIALS FOR NANO-ELECTRONICS

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Organic materials (e.g. small conjugated molecules and conjugated polymers) and biological materials, such as DNA, have the potential to be used in nanoelectronic and molecular electronic devices as an active component. Although experimental research has greatly advanced our knowledge on the electronic properties of these materials, that research is not able to provide a deep understanding of their properties at molecular scale. Therefore, the intra-molecular properties of those materials which contribute for their overall conducting behavior remain controversial.

As in other areas, theoretical modelling can play an important role in understanding the experimental data and provide an insight into the physics underlying the processes involved. For organic and biological molecules which are flexible and have a strong coupling between the electronic and the atomic motion, methods combining molecular dynamics with self-consistent quantum mechanical methods need to be used. We have chosen to use the CNDO (Complete Neglect of Differential Overlap) method to perform the electronic structure calculations because it can handle biological and organic molecules of reasonable size, such as DNA and polymer molecules, and it has been tested and validated in previous calculations [1-7]. After the electronic structure calculations have been performed, atomic forces are calculated as the negative derivatives of the total self-consistent energy and atomic trajectories are obtained by solving Newton's equation of motion. Details concerning the computational implementation of the approach described above in the CHEMOS code is given in references [1,2,8].

In the work presented here, we used this self-consistent quantum molecular dynamics method to study the intra-molecular properties of the DNA and conjugated polymer molecules, concerning the injection of electrons and holes and their mobility along the molecules, as well as electron transfer between two metal electrodes (separated by a distance of approximately 2nm) through a single conjugated molecule (with and without spatial symmetry) bound to them.

Our results suggest that both electron and hole injection lead to charge-induced polaron-like defects in the polymer backbone, being the charge rearrangement amongst the polymer atoms not far from the defect site. The ionization potential is predicted to decrease whereas the electron affinity increases with the conjugation length but both converges to a nearly constant value for longer chains and their values for a chain of the same length depend on the polymer chemistry. We also found that the electric field dependence of intra-molecular charge mobility in conjugated polymer segments is quite different from the form derived for bulk materials. Based on our results, we suggest charge transport along the polymer segments for applied electric fields above the threshold for intra-molecular charge mobility can be realized by free-like carriers or charged polaron-like carriers depending on the number and sign of the injected charge, the conjugation length, the polymer chemistry, the strength of the applied field along the chain and the presence of twists or kinks between segments.

A significant difference in electron transfer through symmetric and asymmetric conjugated molecules was found to be due to molecular distortion and molecular vibrations along their axis. Because of the strong coupling between the motion of electrons and atoms in these molecules, both effects are expected to modify the charge transport through molecular devices, therefore the formulation of the transport in these molecules needs a self-consistent solution for both electronic and lattice time evolutions.

Our results for DNA molecules also show that the capturing efficiency of electrons and holes and the intra-molecular charge transport properties depend on molecular conformation and base sequence. In particular, both the backbone and the Guanine base seem to play an important role on charge transfer through poly(C)-poly(G) DNA molecule with B-type structure.

Results from these simulations provide useful information that needs to be considered for a further mesoscopic modelling aiming to improve charge transport efficiency in nanoelectronic devices based organic and biological materials.

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