



## Torsion barriers and atomic charges in OPVs

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**Abstract** –We investigate the effective atomic charges, obtained through different theoretical ab initio models, associated with the carbon atoms in the organic semiconductor poly-[para-phenylene-vinylene]. We analyse results obtained for small oligomers through the Löwdin, Hirshfeld and CHELPG schemes. We find that for this very well-studied system there are qualitatively conflicting results between these well-established methods.

The functionality of polymer films for new devices depends drastically on morphology issues, so theoretical models have to take this into account in order to predict electronic or optical properties. In order to do that for the complex systems in view, it is useful to adopt atomistic techniques within the classical molecular dynamics formalism, and in this case, since supra-molecular interactions are at the root of morphological arrangements, we must associate effective charges to each atom -or atom type- that will generate the electrostatic interaction field. Previous work on thiophenes [1] has pointed to the inadequacy of the classical charge equilibration scheme [2] that works so well for metals [3], and as such, it is important to validate it for each system that we want to investigate.

Here we focus on un-substituted poly[para-phenylene-vinylene] (PPV), a conjugated polymer that presents several technological applications in devices such as light-emitting diodes [4] and photovoltaic cells [5]. We perform theoretical calculations, at different levels of formalism, for the torsion energy barriers and corresponding charges of oligomers OPVs, small chains with 4 phenylene rings ( $P_4V_3$ ). Considering that the torsions of adjacent phenylene rings are independent, we have analyzed different geometries basically rotating the two internal phenylene rings about the vinylene central unit, with optimization of the other parameters. We use for that ab initio Hartree-Fock (HF) and Möller-Plesset second-order (MP2) calculations, and also Density Functional Theory in the Local Density approximation (DFT-LDA), always in combination with the 6-31G(d,p) polarized basis set, within the Gaussian 03 [6] package.

The first difference we note is that while DFT gives a correct planar equilibrium configuration, HF and MP2 yield a finite torsion for the molecule. Now, analyzing the charges, for the same molecule and conformation and through the same electronic structure formalism, we find that effective charges calculated according to the Löwdin and Hirshfeld methods are qualitatively different from those calculated through the CHELPG method. Surprisingly, while with the former methods (based directly on the wave-function distribution or charge density in real space) all C atoms are always negatively charged, with the CHELPG method (based on the effective electrostatic potential in real space) the  $\alpha$ -carbons of phenylene rings, linked to the vinylene group, are positively charged; even more surprisingly, this positive effective charge is also seen using the charge equilibration method. There are also quantitative differences, in the sense that values can differ by one order of magnitude. More work is still needed thus to validate one or other approach.

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