Abstract

The aim of this work is the development and application of approximate methods to describe the electronic structure of molecular systems. *Tight-binding* methods are one way to approximate the very precise, but time consuming *ab initio* methods and yield the computaional speed up by an approximate determination of the Hamiltonian matrix elements. However, the common *tight-binding* schemes are restricted in their applicability, systems in which a large charge transfer occurs are usually not in the scope of those methods. Here, an extension to the traditional *tight-binding* scheme is introduced. This self-consistent *tight-binding* method is derived from density-functional theory. The broad applicability and high precision of this method is demonstrated by testing it for reaction energies, hydrogen bond energies, equilibrium geometries and vibrational frequencies of a large set of organic molecules.
To describe dynamical properties of conjugated hydrocarbon molecules, an O(N) method in combination with a *tight-binding* is used. The O(N) methodology leads to a linear increase of computation time with the size of the considered system. Test calculations for small polyenes document the applicability of the method in this context. This method is then applied to study the dynamics of breathers, neutral solitons and soliton collisions in trans-polyacetylene.