Semiempirical models in quantum chemistry

Andriy Zhugayevych, zhugayevych@iop.kiev.ua

March 23, 2011

§1. Introduction

Having no rigorous definition *semiempirical* methods and models are intermediate between *ab-initio* quantum chemistry and *empirical* molecular mechanics (see [4] for an overview). There is no strict boundary between ab-initio and semiempirical approaches either methodologically or in the view of the accuracy. The use of parametrized pseudopotentials and density functionals and the choice of the basis set in ab initio approaches are essentially empirical. On the other side all the parameters of semiempirical models can be derived from first-principles calculations. Practically the differentiation between ab initio and semiempirical methods is made by two points. First, one- and two-electron integrals are calculated exactly for a given basis set in ab initio approaches and are parametrized or approximated in semiempirical methods. Second, in semiempirical methods the minimal basis set of one fixed Slater-type orbital (STO) per valence electron plus, possibly, polarization orbitals is used, in ab initio methods at least two contracted gaussian orbitals (GCO) or many plane waves per valence electron must be used to have acceptable accuracy without introducing empirical parameters.

It is important to understand that if a properly parametrized semiempirical method fails then so does any orbital-based ab-initio method. In an orbital-based quantum chemistry we presume that the Fock space built on a finite number of molecular orbitals (MO), namely, of the order of the number of the electrons, "includes" all the lowest-energy eigenfunctions of the exact Hamiltonian. In this case there exist a *minimal basis set* of atomic-like orbitals (AO) containing one function per electron plus few polarization orbitals per valence electron. This basis set can be obtained by the localization of MOs, see e.g. [2]. The latter are the eigenfunctions of the exact one-electron density matrix whose total occupation approximates the number of electrons (these orbitals are called natural orbitals [3]).

The weakest point of any kind of empirical methods is the parametrization transferability issue: parameters optimized for one geometry (or charge state etc.) may give wrong results for other geometry. The strongest point is that semiempirical methods provide the complete description of quantum and many-body effects for the minimal "price". In particular, and this gives the ground for the present paper, semiempirical models are amenable to analytic treatment.