Fundamental models of quantum chemistry

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§1. Introduction

Having no rigorous definition *semiempirical* methods and other models are intermediate between *ab initio* quantum chemistry and *empirical* molecular mechanics (see [5] 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 parameterized 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 basis set: in ab initio approaches we try to achieve basis set convergence, whereas in empirical approaches we use a minimal basis set enough to grab essential physics of a given quantum system. Consequently, in ab initio approaches all Hamiltonian matrix elements are calculated exactly, whereas in semiempirical methods well-parameterized model Hamiltonians are used. For example, in PM7-like methods the basis set consists of one fixed Slater-type orbital (STO) per electronic shell including valence electrons (s,p) and optionally