

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