

20.2: Ab Initio, Semi-Empirical, and Empirical Force Field Methods

Ab Initio Methods

Most of the techniques described in this Chapter are of the **ab initio** type. This means that they attempt to compute electronic state energies and other physical properties, as functions of the positions of the nuclei, from first principles without the use or knowledge of experimental input. Although perturbation theory or the variational method may be used to generate the working equations of a particular method, and although finite atomic orbital basis sets are nearly always utilized, these approximations do not involve 'fitting' to known experimental data. They represent approximations that can be systematically improved as the level of treatment is enhanced.

Semi-Empirical and Fully Empirical Methods

Semi-empirical methods, such as those outlined in Appendix F, use experimental data or the results of **ab initio** calculations to determine some of the matrix elements or integrals needed to carry out their procedures. Totally empirical methods attempt to describe the internal electronic energy of a system as a function of geometrical degrees of freedom (e.g., bond lengths and angles) in terms of analytical 'force fields' whose parameters have been determined to 'fit' known experimental data on some class of compounds. Examples of such parameterized force fields were presented in Section III. A of Chapter 16.

Strengths and Weaknesses

Each of these tools has advantages and limitations. **Ab initio** methods involve intensive computation and therefore tend to be limited, for practical reasons of computer time, to smaller atoms, molecules, radicals, and ions. Their CPU time needs usually vary with basis set size (M) as at least M^4 ; correlated methods require time proportional to at least M^5 because they involve transformation of the atomic-orbital-based two-electron integrals to the molecular orbital basis. As computers continue to advance in power and memory size, and as theoretical methods and algorithms continue to improve, **ab initio** techniques will be applied to larger and more complex species. When dealing with systems in which qualitatively new electronic environments and/or new bonding types arise, or excited electronic states that are unusual, **ab initio** methods are essential. Semi-empirical or empirical methods would be of little use on systems whose electronic properties have not been included in the data base used to construct the parameters of such models.

On the other hand, to determine the stable geometries of large molecules that are made of conventional chemical units (e.g., CC, CH, CO, etc. bonds and steric and torsional interactions among same), fully empirical force-field methods are usually quite reliable and computationally very fast. Stable geometries and the relative energetic stabilities of various conformers of large macromolecules and biopolymers can routinely be predicted using such tools if the system contains only conventional bonding and common chemical building blocks. These empirical potentials usually do not contain sufficient flexibility (i.e., their parameters and input data do not include enough knowledge) to address processes that involve rearrangement of the electronic configurations. For example, they can not treat:

1. Electronic transitions, because knowledge of the optical oscillator strengths and of the energies of excited states is absent in most such methods;
2. Concerted chemical reactions involving simultaneous bond breaking and forming, because to do so would require the force-field parameters to evolve from those of the reactant bonding to those for the product bonding as the reaction proceeds;
3. Molecular properties such as dipole moment and polarizability, although in certain fully empirical models, bond dipoles and lone-pair contributions have been incorporated (although again only for conventional chemical bonding situations).

Semi-empirical techniques share some of the strengths and weaknesses of **ab initio** and of fully empirical methods. They treat at least the valence electrons explicitly, so they are able to address questions that are inherently electronic such as electronic transitions, dipole moments, polarizability, and bond breaking and forming. Some of the integrals involving the Hamiltonian operator and the atomic basis orbitals are performed **ab initio**; others are obtained by fitting to experimental data. The computational needs of semiempirical methods lie between those of the **ab initio** methods and the force-field techniques. As with the empirical methods, they should never be employed when qualitatively new electronic bonding situations are encountered because the data base upon which their parameters were determined contain, by assumption, no similar bonding cases.

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