CHAPTER OVERVIEW

6: Electronic Structure

Learning OBjectives

The subjects you should now be familiar with include

- The Hatree and Hartree-Fock models,
- Koopmans'theorem
- Atomic basis functions- Slater and Gaussian- and the notations used to describe them.
- Static and dynamic electron correlation.
- The CI, MPPT, CC, and DFT methods for treating correlation, as well as EOM or Greens function methods.
- The Slater-Condon rules.
- QM-MM methods.
- Experimental tools to probe electronic structures including methods for metastable states.
- Various contributions to spectroscopic line shapes and line broadening.

Electrons are the "glue" that holds the nuclei together in the chemical bonds of molecules and ions. Of course, it is the nuclei's positive charges that bind the electrons to the nuclei. The competitions among Coulomb repulsions and attractions as well as the existence of non-zero electronic and nuclear kinetic energies make the treatment of the full electronic-nuclear Schrödinger equation an extremely difficult problem. Electronic structure theory deals with the quantum states of the electrons, usually within the Born-Oppenheimer approximation (i.e., with the nuclei held fixed). It also addresses the forces that the electrons' presence creates on the nuclei; it is these forces that determine the geometries and energies of various stable structures of the molecule as well as transition states connecting these stable structures. Because there are ground and excited electronic states, each of which has different electronic properties, there are different stable-structure and transition-state geometries for each such electronic state. Electronic structure theory deals with all of these states, their nuclear structures, and the spectroscopies (e.g., electronic, vibrational, rotational) connecting them. In this Chapter, you were introduced to many of the main topics of electronic structure theory.

Contributors and Attributions

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