17.3: Moving from Qualitative to Quantitative Models

The preceding Chapters introduced, in a qualitative manner, many of the concepts which are used in applying quantum mechanics to electronic structures of atoms and molecules. Atomic, bonding, non-bonding, antibonding, Rydberg, hybrid, and delocalized orbitals and the configurations formed by occupying these orbitals were discussed. Spin and spatial symmetry as well as permutational symmetry were treated, and properly symmetry-adapted configuration state functions were formed. The Slater-Condon rules were shown to provide expressions for Hamiltonian matrix elements (and those involving any one- or two-electron operator) over such CSFs in terms of integrals over the orbitals occupied in the CSFs. Orbital, configuration, and state correlation diagrams were introduced to allow one to follow the evolution of electronic structures throughout a 'reaction path'.

Section 6 addresses the **quantitative and computational implementation** of many of the above ideas. It is not designed to address all of the state-of-the-art methods which have been, and are still being, developed to calculate orbitals and state wavefunctions. The rapid growth in computer hardware and software power and the evolution of new computer architectures makes it difficult, if not impossible, to present an up-to-date overview of the techniques that are presently at the cutting edge in computational chemistry. Nevertheless, this Section attempts to describe the essential elements of several of the more powerful and commonly used methods; it is likely that many of these elements will persist in the next generation of computational chemistry techniques although the details of their implementation will evolve considerably. The text by Szabo and Ostlund provides excellent insights into many of the theoretical methods treated in this Section.