10.S: Theories of Electronic Molecular Structure (Summary)

Other terms account for the interactions between all the magnetic dipole moments and the interactions with any external electric or magnetic fields. The charge distribution of an atomic nucleus is not always spherical and, when appropriate, this asymmetry must be taken into account as well as the relativistic effect that a moving electron experiences as a change in mass. This complete Hamiltonian is too complicated and is not needed for many situations. In practice, only the terms that are essential for the purpose at hand are included. Consequently in the absence of external fields, interest in spin-spin and spin-orbit interactions, and in electron and nuclear magnetic resonance spectroscopy (ESR and NMR), the molecular Hamiltonian usually is considered to consist only of the kinetic and potential energy terms, and the Born-Oppenheimer approximation is made in order to separate the nuclear and electronic motion.

In general, electronic wavefunctions for molecules are constructed from approximate one-electron wavefunctions. These one-electron functions are called molecular orbitals. The expectation value expression for the energy is used to optimize these functions, i.e. make them as good as possible. The criterion for quality is the energy of the ground state. According to the Variational Principle, an approximate ground state energy always is higher than the exact energy, so the best energy in a series of approximations is the lowest energy. In this chapter we describe how the variational method, perturbation theory, the self-consistent field method, and configuration interaction all are used to describe the electronic states of molecules. The ultimate goal is a mathematical description of electrons in molecules that enables chemists and other scientists to develop a deep understanding of chemical bonding, to calculate properties of molecules, and to make predictions based on these calculations. For example, an active area of research in industry involves calculating changes in chemical properties of pharmaceutical drugs as a result of changes in their chemical structure.

Study Guide

- What is meant by the expression *ab initio* calculation?
- List all the terms in a complete molecular Hamiltonian.
- Why are calculations on closed-shell systems more easily done than on open-shell systems?
- How is it possible to reduce a multi-electron Hamiltonian operator to a single-electron Fock operator?
- Why is the calculation with the Fock operator called a self-consistent field calculation?
- What is the physical meaning of a SCF one-electron energy?
- Why is the nonlinear variational method not used in every case to optimize basis functions, and what usually is done instead?
- Why is it faster for a computer to use the variational principle to determine the coefficients in a linear combination of functions than to determine the parameters in the functions?
- Identify the characteristics of hydrogenic, Slater, and Gaussian basis sets.
- What is meant by the Hartree-Fock wavefunction and energy?
- What is the difference between a restricted and unrestricted Hartree-Fock calculation?
- What is neglected that makes the Hartree-Fock energy necessarily greater than the exact energy?
- What is meant by correlation energy?
- What purpose is served by including configuration interaction in a calculation?

David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski ("Quantum States of Atoms and Molecules")