

Abstract: In this thesis, a number of different projects were carried out to get a better understanding of electron correlation effects. For this purpose, new quantum chemical methods and analysis techniques were developed that provide detailed insights into electron correlation and how this is described at various quantum chemical levels such as Many Body Perturbation Theory (MBPT) in connection with the Møller-Plesset (MP) perturbation operator used up to sixth order (MP6) and considering single (S), double (D), triple (T), quadruple (Q), pentuple (P), and hextuple (H) excitations, Coupled Cluster (CC) theory with S, D, T, and Q excitations, quasi-degenerate perturbation theory based on the generalized valence bond approach and second order perturbation theory, and density functional theory (DFT) with various exchange-correlation functionals. Results of this work are summarized in twelve publications, ten of which constitute the basis of this thesis: (1) MP_n spectra provide an excellent analysis tool for studying electron correlation effects, in particular if atoms and molecules are grouped in class A and class B systems (systems with well-separated electron pairs and systems with electron clustering) and correlation effects for the complete basis set (CBS) limit can be determined. - (2) Based on (1), the differing importance of three- and four-electron correlation effects was determined for class A and class B systems at all levels of MBPT up to MP6. - (3) MP6 geometries determined for the CBS limit are the most accurate geometries, which one can obtain at the MBPT level, however they are not as accurate as CCSD(T)/CBS geometries. - (4) Recent claims that MP theory is physically not meaningful because of the reported divergence behavior of the MP_n series are unjustified as the observed divergence is just the result of the use of unbalanced basis sets. By using Feenberg scaling any divergent MBPT-MP_n series can be converted into a convergent series. - (5) The best (in terms of cost-efficiency considerations) way of covering three-electron correlation effects is provided by CCSD(T) or alternatively CCSDT-1 as was found by a detailed analysis of CC methods containing T excitations in a perturbative or iterative way. - (6) Size-extensive QCISDTQ and QCISDTQ(6) were developed as new methods for describing four-electron correlation effects, which turn out to be important for systems with strong electron clustering. - (7) Such a system is FOOF, the geometry of which can only be described in an approximate way by the presently available single determinant correlation corrected methods. Ways of solving the FOOF problem are discussed. - (8) It was proven that the UHF-CCSD wave function is free of any S+1 spin contamination because this is totally suppressed by infinite order effects in the SD space. A new \hat{S}^2 diagnostic was developed to correctly assess the reliability of the UHF-CCSD energy. - (9) The theory for spin projection in UHF-CC was developed, simple spin-projected UHF-CCSD and UHF-CCSD(T) methods were programmed and applied. - (10) It was clarified which correlation effects are covered by DFT.