THE DEVELOPMENT AND APPLICATION OF FULL AND EXTENDED CI METHODS

JEPPE OLSEN, *Dept. of Chemistry, University of Aarhus*.

This talk will report recent advances and applications of full and extended CI calculations. The calculations serve either as benchmarks for other methods or to provide definite answers to complicated electronic structure problems.
It is currently feasible to perform selected as well as full CI calculations using upto 10 billion Slater determinants. As an example of recent FCI calculations, we report the determination of geometry, spectroscopic constants and electric moments for HF in the cc-pVTZ basis. This calculation containing about four billion determinants was performed on a single node IBM 590 workstation.
To extent the use af accurate CI calculations to larger molecules, the included determinants must be selected from the huge list of FCI determinants. This selection should be realized by the computer, so that the errors compared to the corresponding FCI calculation is below user-specified thresholds. Even when only the important determinants are included, accurate CI calculations still require several hundred millions of determinants for rather simple polyatomic molecules. The power of this approach is also demonstrated by a clculation on ozone, where we obtain the FCI energy with an estimated error of less than .0001 Hartree, although the FCI expansion contains about than 10^{16} Slater determinants.
As an example how modern CI program can provide definite answers to intricate correlation problems, we will discuss calculations on pyrrole, where the has been a significant uncertainty in the assignment of the spectrum.