13th Strasbourg Seminar, September 2005

ADDITION BY SUBTRACTION IN COUPLED-CLUSTER THEORY: A RECONDSIDERATION OF THE COUPLED-CLUSTER/CI INTERFACE

Rodney J. Bartlett and Monika Musial
Quantum Theory Project
University of Florida
Gainesville, FL, USA

The complexity of the high-order coupled-cluster equations like CCSDT and CCSDTQ might appear to be overkill for many applications of the electron correlation problem. Instead, we take the viewpoint that we want the minimum number of diagrams, and no more, that are required to correctly describe physically important situations. For example, the simplest method that is exact for two-electrons need only retain the exclusion principle violating (EPV) diagrams. We call such a method nCCSD to indicate that it is exact for n electrons. Furthermore, unlike CISD, it is also exact for all products of two-electron units. Hence, the zeroth-order approximation to the correlation problem in chemistry is given by nCCSD, and this offers a vastly faster computation than the full CCSD method. Similarly, nCCSDT is exact for three electrons and all products of three electron units, as is nCCSDTQ for four electrons. Hence, we envision building the correlation problem up from such product wavefunctions. This also offers new insight into bond breaking and how that can be accomplished in CC theory.