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Book Review

A. C. Hurley: Electron Correlation in Small Molecules: London: Academic Press 1977, 276 pp., price: £10.50/$23.00

The problem of electron correlation has played a dominating role in numerical quantum chemistry during the last ten or fifteen years, i.e. since the time when SCF calculations became routinely available and the merits and limitations of this approximation became apparent. A large number of different methods both for a qualitative and a quantitative treatment of correlation effects has been developed and applied and it is quite difficult even for the expert to keep track of this still rapidly increasing field.

In Hurley's monograph one of these methods is presented and described in full detail: The theory of electron pairs which has proved to be one of the most powerful tools for calculating molecular correlation energies to a high degree of accuracy, even up to what is sometimes called 'chemical accuracy'.

The first part of the book (62 pages) deals with the qualitative aspects of electron correlation: How can one obtain the proper dissociation of a closed-shell molecule into open-shell fragments? How can one describe a complicated molecular state for which an SCF wavefunction is not a reasonable zero order approximation? The author discusses the multi-configuration SCF and the separated electron pair theories for getting a qualitatively correct first-order wavefunction. The states of C_2 and the dissociation of ethylene are used as illustrative examples.

In the second part of the book (208 pages) the theory of separated electron pairs and its extensions is developed very systematically. The connection with CI-type wavefunctions, the advantages and disadvantages of all sorts of 'natural orbitals', the inclusion of 'unlinked clusters', the role of 'exclusion principle violating' terms etc. – all these ideas currently discussed and implemented into various computer programs for quantitative calculations of correlation energies are presented in full detail. Sometimes the presentation is a bit too lengthy and formal, but always lucid, correct and easy to follow. A lot of simple examples serve to illustrate the usefulness of the various concepts, in particular that of pair correlation energies.

It seems to be a disadvantage that Hurley confines his treatment almost exclusively to electron pair theories: The sections about interelectronic coordinates and about the transcorrelated wavefunctions are very short. Many-body perturbation theory and the direct CI scheme, methods which are very closely related to the topic of this book, are completely missing. Finally, as in the preceding part 'Introduction to the Electron Theory of Small Molecules' there are almost no references to publications later than 1971, though the progress in numerical applications between 1970 and 1976, has been enormous.

Despite of all this, Hurley's book has to be warmly recommended to all readers interested in a profound understanding of electron correlation effects or an application of numerical methods for the calculation of molecular correlation energies.

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