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Book Reviews

P. Čársky and M. Urban: *Ab Initio* Calculations – Methods and Applications in Chemistry (Lecture Notes in Chemistry, Vol. 16) Berlin-Heidelberg-New York: Springer-Verlag 1980. 247 pp., soft cover, price: DM 35,60; approx. US $21.10

The aim of this publication is to fill the gap existing between textbooks and more advanced reports as far as recent applications of rigorous *ab initio* methods are concerned. The first part is devoted to technical details for the SCF matrix element calculations. It points out the care needed in choosing an appropriate AO basis (number of Gaussian- or Slater-type functions) not only for a reasonable determination of various equilibrium properties at the SCF level, but also its importance for the (correlated) wavefunction's quality and/or the degree of correlation energy accounted for, independent of the theoretical approach used. A discussion, limited to closed-shell cases, is given on how to solve the Schrödinger equation exactly, whereby a Hartree–Fock calculation is invariably improved by more or less equivalent ways of considering correlation effects. We would like to comment that the usual definition of $E_{corr} = E_{exact} - E_{HF}$ will lead into trouble if strictly applied to the case of closed-shell molecules along the whole dissociation range: at intermediate bond lengths, where the perturbational methods discussed are more difficult to apply, one can observe increases in $(E_{exact} - E_{HF})$, while in reality the true electronic correlation actually diminishes.

In addition a good insight is given into the contribution of different excitation classes to E_{corr} on the basis of a cluster expansion of the wavefunction, a general formalism from which the CPMET and CEPA methods are derived. Also the MB-RSPT technique (well known to the authors of this monograph) is nicely presented and analyzed in great detail. Finally, although the size-inconsistency of the single-reference CI-SD approach (and how to overcome it via correction formulas) is mentioned, it is not noted that this deficiency is partially resolved when higher than double excitations are explicitly considered as in various multi-reference singles and doubles CI methods currently used.

The last chapter covers some applications, with items such as ionization potentials and inter-molecular interactions. The study of extremal points on potential surfaces or molecular force fields by gradient techniques is only presented formally, since numerical results with correlated wavefunctions are still scarce, but progress is expected in the near future.

This book is pleasant to read, contains an extensive bibliography up to 1978, and provides a broad survey of the actual state of some methods, as exemplified by numerical data for closed-shell systems. Nonetheless the inclusion of available results in the fields of electron spectroscopy and photochemistry would give a more realistic picture of the present capability of *ab initio* methods to complement experimental information.

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