How Many-Body Perturbation Theory (MBPT) has changed Quantum Chemistry.

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Abstract

Many-body perturbation theory (MBPT) was originally designed for nuclei or 'nuclear matter' in order to evaluate the interaction of nucleons by means of Rayleigh-Schrödinger perturbation theory (RS-PT). Since in the traditional formulation of RS-PT the extensivity (size-consistency) was not manifest order by order, an alternative access became popular, that was inspired by quantum electrodynamics (QED), and that is characterized by ingredients such a time-dependent theory for a time-independent problem and the use and manipulation of diagrams to represent contributions to the energy and the wave function. The extensivity is directly related to a linked-diagram theorem.

When it became obvious that MBPT is also applicable to atoms or molecules (electrons as well as nucleons are fermions), there was, for some time, a division of the AI-QC community into traditionalists and adepts of MBPT. Nowadays the competition between traditional ab-initio quantum chemistry (AIQC) and MBPT is history. The relevant aspects of MBPT have been integrated into AIQC, and play an important role. In many situations use of a Fock-space Hamiltonian is imperative. Extensivity (size consistency) has become a challenge of the same weight as to satisfy the variation principle. It is a general wisdom that a connected-diagram expansion is only possible if one is ready to include exclusion-principle-violating (EPV) diagrams. Many recent developments in AIQC like that of electron correlation for open-shell or multi-configuration reference states are manifestations of MBPT digested by AIQC, and liberated from irrelevant aspects such as the use of a time-dependent theory for a time-independent problem, or the insistance on perturbation theory.