Four-component relativistic multireference perturbation theory

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Multireference perturbation theory (MRPT) based on multiconfiguration (MC) reference functions has become a basic and practical tool for studying the electronic structures of molecules and the potential energy surfaces of chemical reactions. MRPT takes account of both static and dynamic electron correlations and thus can obtain accurate relative energies, including reaction, activation, and excitation energies, within a chemical accuracy (i.e., a few kcal/mol).

We have developed an MRPT using MC functions that we call "multiconfigurational quasidegenerate PT (MC-QDPT)".[1]   It is a multiconfiguration basis *multi*-reference-state method based on van Vleck PT and includes multireference Møller–Plesset PT, a *single*-reference-state method based on Rayleigh–Schrödinger PT, as a special case. In particular, a version of MC-QDPT proposed later uses *general* multiconfiguration reference functions (GMC-QDPT or GMC-PT).[2]   GMC-QDPT imposes no restriction on the reference space, so it is much more compact than complete active space (CAS)-based MRPT.   In addition, since it can avoid unphysical multiple excitations, it is numerically stable.

Several years ago, we extended GMC-QDPT to a relativistic version with four-component general MC reference functions and applied it to the potential energy curves of I_2 and Sb_2, and the excitation energies of CH_3I, etc.[3,4]   These were the initial application of relativistic MRPT to molecular systems to the best of our knowledge.

In the presentation in ISTCP7, we present some applications to the excited states of several heavy-element complexes. The calculated excitation energies for $[PtCl_4]^{2-}$, $[PtBr_4]^{2-}$, and $[PtCl_6]^{2-}$, for example, were in very good agreement with available experimental data. The maximum and average deviations were 0.18 and 0.08 eV, respectively, which were better than time-dependent density functional theory results. We also present an efficient simplified form of GMC-QDPT and a Kramers unrestricted simplified MCSCF method.

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