Advances in Generalized Van Vleck variant of Multireference Perturbation Theory

M. R. Hoffmann
Chemistry Department, University of North Dakota, Grand Forks, ND, U.S.A.

A new, second-order, multiconfigurational, multireference perturbation method for molecular electronic structure, based on Generalized Van Vleck Perturbation Theory (GVVPT2), has been suggested and computationally implemented [1,2]. Through use of a combination of a multireference extension to degeneracy corrected perturbation theory and nonlinear responses to perturbations, the method is in principle stable for any degree of quasidegeneracy and is rigorously continuous and thus can be used to describe entire potential energy surfaces. The formalism can use either complete or incomplete model (or reference) spaces, and is limited, in this regard, only by the capabilities of the MCSCF program. The third-order method, GVVPT3, has also been obtained and shown to be capable of describing well the very difficult electronic structure problems for which GVVPT2 is less accurate than usual. The method makes use of the recently introduced concept of macroconfigurations, which allows arbitrarily complex incomplete model spaces to be used efficiently. Exploiting the capability of using very large one-electron active spaces, the method has been applied to problematic ground and excited electronic states of unsaturated, highly strained ring systems, such as CF_2O_2 and CF_2N_2, and to the debated ground state of Co_2.

Recently, a Lagrangian based approach has been suggested to obtain analytic formulas for GVVPT2 energy nuclear gradients and nonadiabatic coupling terms [3]. Trial calculations were performed and compared with finite difference calculations on several molecules and demonstrate that the GVVPT2 gradients are accurate. Of particular interest, the suggested formalism can straightforwardly use state-averaged MCSCF descriptions of the reference space in which the states have arbitrary weights. This capability is demonstrated by some calculations on the ground and first excited singlet states of LiH, including calculations near an avoided crossing. The formalism for nonadiabatic coupling shares many structural features with the energy gradient formalism, with the use of a function that corresponds to the energy for the coupling.

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[2] W. Jiang, Y. G. Khait, and M. R. Hoffmann, *J. Phys. Chem. A,* **113**, 4374 (2009).
[3] D. Theis, Y. G. Khait, and M. R. Hoffmann, GVVPT2 energy gradient and nonadiabatic coupling terms using a Lagrangian formulation, *J. Chem. Phys.* (submitted).