

Third-order Generalized Van Vleck Perturbation Theory for Molecular Electronic Structure. Study of the ground and lowest excited states of C₂

Yuriy G. Khait, Wanyi Jiang, and Mark R. Hoffmann

*Chemistry Department, University of North Dakota,
Grand Forks, North Dakota, 58202-9024*

A revision of a second-order, multiconfigurational, multireference perturbation method for molecular electronic structure, based on generalized Van Vleck perturbation theory (GVVPT2), has been derived, implemented in sequential and now parallel computer codes, and is demonstrating itself to be a valuable new method for performing computational chemistry calculations. GVVPT is a mathematically well-defined approximation to the theoretically well-founded and robust self-consistent quasidegenerate perturbation theory (SC-QDPT), and retains many of the characteristics of the parent theory. In particular, GVVPT is both state-selective and of the "perturb-then-diagonalize" type of multireference perturbation theory. GVVPT2 is capable of a balanced treatment of nondynamic and dynamic electron correlation for even very challenging systems, while requiring only a relatively modest $O(n^5)$ scaling of computational effort.

Calculations of the potential curves of the ground ($X^1\Sigma_g^+$) and lowest two excited ($B^1\Delta_g$ and $B'^1\Sigma_g^+$) electronic states of C₂ were performed using a new third-order generalized Van Vleck multireference perturbation theory (GVVPT3), along with the GVVPT2 method and the CASSCF and MRCISD approaches, using the same 6-31G* basis set used in the Abrams and Sherrill full-CI study. Calculations in the range of 1.0 – 3.0 Å, which spans the equilibrium bond length and the crossing point of the $X^1\Sigma_g^+$ and $B^1\Delta_g$ curves, demonstrate that the deviations of the GVVPT3 curves from the full-CI curves for all states are comparable to MRCISD. GVVPT2 provides significant improvement relative to CASSCF, which already is much improved over even high-order single reference methods. Predictions of the challenging crossing point between the $X^1\Sigma_g^+$ and $B^1\Delta_g$ curves, in the vicinity of the $B'^1\Sigma_g^+$ avoided crossing with the ground state, is predicted to milliångstrom accuracy by MRCISD and GVVPT3, while GVVPT2 and CASSCF show deviations of about 0.07 Å.