GVVPT2 Descriptions of Electronic Structures of Metalloid Oxides

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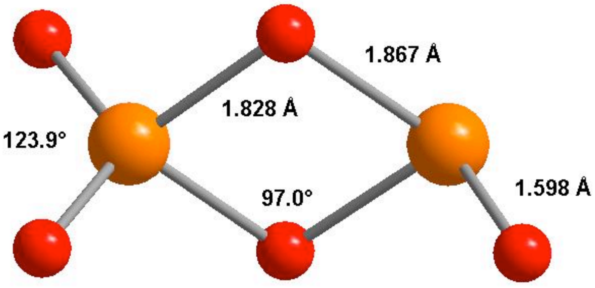

The second-order Generalized van Vleck variant of multireference perturbation theory (GVVPT2) for the description of molecular electronic structure [1] has been shown to be versatile and robust. Recently, the method has been used to elucidate the ground and low-lying electronic structures of metalloid oxides (e.g., Se_nO_m [2], As_nO_m, Sb_nO_m, where n=1,2 and m=1–5) and dimers of first and second row transition metals (e.g., Cr_2 [3], Mo_2). Such molecules have proven elusive for many methods of electronic structure theory primarily because of the subtle interplay of short-range (i.e., dynamic) and long-range (i.e., nondynamic or static) electron correlation.

GVVPT2 is capable of describing complicated molecular electronic structures because of two complementary features. First, GVVPT2 uses an intermediate Hamiltonian structure to separate energetically perturbing functions from zero-order descriptions of the functions of interest. Second, a nonlinear resolvent

$$X_{qp} = \frac{\tanh\left(\tilde{H}_q^{(0)}(p) - E_p^{(0)}\right)}{E_p^{(0)} - \tilde{H}_q^{(0)}(p)} H_{qp},$$

where $\tilde{H}_q^{(0)}(p) = \frac{1}{2}\left(H_q^{(0)}(p) + E_p^{(0)}\right) + \frac{1}{2}\sqrt{\left(H_q^{(0)}(p) - E_p^{(0)}\right)^2 + 4\sum_{q'\in m}\left(H_{q'p}\right)^2}$ is an effective zero-order energy of perturbing state q for primary (or reference) function p, avoids remaining intruder states. As a consequence, potential energy surfaces are rigorously continuous. Because the current implementation supports incomplete model spaces and utilizes a GUGA formulation for evaluation of Hamiltonian matrix elements [4], molecules that were not previously accessible on the basis of computational resources can now be addressed.

[1] Khait, Y. G., Song, J., Hoffmann, M. R. *J. Chem. Phys.*, 117:4133–4145, 2002.

[2] Mokambe, R. M., Hicks, J. M., Kerker, D., Jiang, W. Theis, D., Chen, Z., Khait, Y. G., Hoffmann, M. R. *Mol. Phys.*, DOI: 10.1080/00268976.2013.809163.

[3] Tamukong, P. K., Theis, D., Khait, Y. G., Hoffmann, M. R. *J. Phys. Chem. A*, 116:4590–4601, 2012.

[4] Jiang, W., Khait, Y. G., Hoffmann, M. R. *J. Phys. Chem. A*, 113:4374–4380, 2009.