



A Fast Algorithm for Generalized Van Vleck Perturbation Theory

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Abstract

Second order Generalized van Vleck perturbation theory (GVVPT2) in a recent revision has proven to be efficacious for many challenging molecular systems. ¹ An extension to third order (GVVPT3) has been demonstrated to be a close approximation to multireference configuration interaction including single and double excitations (MRCISD). ² To improve the computing efficiency, new GVVPT codes have been developed to take advantage of recently implemented configuration-driven configuration interaction (CI) with unitary group approach (UGA).

Partition of Space

$$L_M = L_P \oplus L_S$$

$$L = L_M \oplus L_Q$$

L_M – model space optimized by preceding multiconfiguration self-consistent field (MCSCF).

L_P – primary subspace spanned by targeted states.

L_S – secondary subspace complementary to L_P .

L_Q – external space related to model space by excitation.

General Flow Chart for Evaluation of sigma Vector in Configuration-driven UGA CI

Loops over bra macroconfigurations
Loops over ket macroconfigurations
Loops over ket configurations
Loops over bra configurations
Fetch and organize integrals
Calculate coupling coefficients on the fly
Loops over CSFs
Calculate Sigma vectors

Flow Chart for GVVPT2

Loops over Q1-external macroconfigurations
Loops over Q1-external configurations
Loops over model macroconfigurations
Loops over model configurations
Fetch and organize integrals
Calculate coupling coefficients on the fly
Loops over CSFs
Calculate X_{qp} or evaluate $(HX)_{qm}$

GVVPT2 Effective Hamiltonian

$$H_{PP}^{eff} = H_{PP} + \frac{1}{2} (H_{PQ} X_{QP} + X_{QP}^\dagger H_{QP})$$

$$H_{SP}^{eff} = H_{SQ} X_{QP}$$

$$H_{SS}^{eff} = H_{SS}$$

$$X_{qp} = - \frac{\tanh(\epsilon_q^p - E_p')}{\epsilon_q^p - E_p'} H_{qp}$$

Computation Times for Two GVVPT2 Codes

Molecule	NO ⁻	NO ⁻	N ₂	Cyclobutadiene	NiO ₂
Model CSFs	96	96	176	3,094	3420
Total CSFs	7,529,132	23,142,808	469,552	329,114,892	3,784,597,999
GVVPT2-UGACI	0.96 s	3.73s	0.28 s	73 s	611 s
GVVPT2-Table CI	27 s	124 s	17 s	14,368 s	--

GVVPT3 Effective Hamiltonian

$$H_{PP}^{eff} = U_{PP}^+ H_{PP} U_{PP} + U_{PP}^+ H_{PQ} U_{QP} + U_{PQ}^+ H_{QP} U_{PP} + U_{PQ}^+ H_{QQ} U_{QP}$$

$$H_{SP}^{eff} = H_{SQ} U_{QP}$$

$$H_{SS}^{eff} = H_{SS}$$

Optimized Structures and Automerization Barrier of Cyclobutadiene

Basis set: cc-pVTZ

Bond length in Å

Geometry	Method	R(C=C)	R(C-C)	R(C-H)	∠HCC
Rectangle	GVVPT2	1.355	1.565	1.080	134.9°
	MRCCSD(T) ³	1.354	1.564	1.079	134.9°
	MRAQCC ⁴	1.349	1.562	1.077	134.9°
Square	GVVPT2	—	1.450	1.079	135.0°
	MRCCSD(T) ³	—	1.451	1.078	135.0°
	MRAQCC ⁴	—	1.447	1.076	135.0°

Basis set: cc-pVDZ

Energy in kcal/mol

Energy Barrier	GVVPT2	GVVPT3	MRCCSD(T) ³	MRCISD ⁴	MRAQCC ⁴
	6.6	6.9	6.1	6.5	7.3

Conclusions

- ❖ This new GVVPT2 code is much faster than previous one. Speed up is more significant for molecular systems with larger model space.
- ❖ Memory requirements have been minimized for GVVPT2.
- ❖ GVVPT2 predictions of geometry for larger molecules are in excellent agreement with MRCCSD(T).
- ❖ New GVVPT2 code provides an efficient and reliable method for the study of relatively large molecules
- ❖ GVVPT3 is competitive as a potential alternative of MRCISD method.

References

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