

# Multireference Perturbation Theory with Four-Component General Multiconfigurational Reference Functions

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*Abstract:* The formulation and molecular applications of the multireference multi-state perturbation theory with four-component general multiconfigurational reference functions (relativistic GMC-QDPT) are presented. An efficient simplified form of the relativistic GMC-QDPT and its numerical results are also shown.

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## 1. Introduction

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. Several versions of MRPT are now included in various program packages such as GAMESS and MOLCAS. 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 recently proposed version of MC-QDPT 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.

In a previous paper [3], we have extended GMC-QDPT to a relativistic version with four-component general MC reference functions and applied it to the potential energy curves of I<sub>2</sub> and Sb<sub>2</sub>, and the excitation energies of CH<sub>3</sub>I, etc. These were the initial application of relativistic MRPT to molecular systems to the best of our knowledge. In the present paper, we present the formulation and some applications of the relativistic GMC-QDPT. We also show an efficient simplified form of the relativistic GMC-QDPT and its numerical results.

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## 2. Method

### 2.1. Relativistic GMC-QDPT

The effective Hamiltonian matrix  $H_{\text{eff}}$  of van Vleck perturbation theory with unitary normalization is given by

$$(H_{\text{eff}})_{MN} = \langle \Phi_M^{(0)} | H | \Phi_N^{(0)} \rangle + \frac{1}{2} \left[ \langle \Phi_M^{(0)} | HR_N H | \Phi_N^{(0)} \rangle + \langle \Phi_M^{(0)} | (HR_N VR_N H - HR_{N'} V | \Phi_{N'}^{(0)} \rangle \langle \Phi_{N'}^{(0)} | V | \Phi_N^{(0)} \rangle + (M \leftrightarrow N)^* \right] + \dots \quad (1)$$

with

$$R_N = \sum_{I \in \text{Ref}} | \Phi_I^{(0)} \rangle \langle E_N^{(0)} - E_I^{(0)} \rangle^{-1} \langle \Phi_I^{(0)} |, \quad (2)$$

where  $\Phi_M^{(0)}$  ( $\Phi_N^{(0)}$ ,  $\Phi_{N'}^{(0)}$ ) and  $\Phi_I^{(0)}$  are reference wave functions and a function in the complement space ( $Q$ ) of the reference space ( $P$ ), respectively, and  $E_N^{(0)}$  and  $E_I^{(0)}$  are zeroth-order energies of functions  $\Phi_N^{(0)}$  and  $\Phi_I^{(0)}$ .

Using the no-virtual-pair Dirac–Coulomb Hamiltonian

$$H_{\text{DC}}^+ = \Lambda^+ H_{\text{DC}} \Lambda^+ \quad (\Lambda^+ = \mathcal{L}^+(1) \mathcal{L}^+(2) \dots \mathcal{L}^+(N)), \quad (3)$$

where  $\mathcal{L}^+(i)$  are the projection operators to electronic states  $i$ , and general multiconfigurational reference functions and zeroth-order energies

$$| \mu \rangle = \sum_{A \in \text{GCS}} C_A^\mu | A \rangle, \quad E_\mu^{(0)} = \sum_p \langle \mu | p^+ p | \mu \rangle \varepsilon_p, \quad (4)$$

(GCS stands for *general configuration space*), we obtain the formal expression for the relativistic GMC-QDPT,

$$(H_{\text{eff}})_{\mu\nu} = E_\mu^{\text{GCS-Cl}} \delta_{\mu\nu} + \frac{1}{2} \left\{ \sum_{I \in \text{GCS}} \sum_{AB \in \text{GCS}} C_A^{\mu*} C_B^\nu \frac{\langle A | H_{\text{DC}}^+ | I \rangle \langle I | H_{\text{DC}}^+ | B \rangle}{E_\nu^{(0)} - E_I^{(0)}} + (\mu \leftrightarrow \nu)^* \right\} + \dots \quad (5)$$

In one of our implementations, the (second-order term) effective Hamiltonian is computed using a hybrid method of the diagrammatic and matrix element methods, i.e. the diagrammatic computational scheme

$$\begin{aligned} (H_{\text{external}}^{(2)})_{\mu\nu} &= \sum_{AB \in \text{GCS}} C_A^{\mu*} C_B^\nu \langle A | R H_{\text{DC}}^+ \frac{S}{E_\nu^{(0)} - H_{\text{DC}}^{+(0)}} H_{\text{DC}}^+ R | B \rangle \\ &= \sum_{AB \in \text{GCS}} C_A^{\mu*} C_B^\nu \langle A | O^{(2)} | B \rangle, \end{aligned} \quad (6)$$

( $R$  and  $S$  are the projectors for CAS and its complementary space, respectively;  $O^{(2)}$  is the diagrammatic expression of the operator) for the external excitations (including at least one core or virtual orbitals) and the matrix element scheme

$$(H_{\text{internal}}^{(2)})_{\mu\nu} = \sum_{I \in \text{CAS} \wedge I \notin \text{GCS}} \left[ \sum_{A \in \text{GCS}} C_A^{\mu*} (H_{\text{DC}}^+)_{AI} \cdot \sum_{B \in \text{GCS}} \frac{(H_{\text{DC}}^+)_{IB} C_B^\nu}{E_\nu^{(0)} - E_I^{(0)}} \right] \quad (7)$$

for internal excitations (including only active orbitals).

### 2.2. Simplified Form of Relativistic GMC-QDPT

The expression of relativistic GMC-QDPT, Eq. (5), includes the energy denominators that depend on the energies of the reference states  $E_\nu^{(0)}$ . This state dependence prevents the valence-universal computation of the effective Hamiltonian operator. An approximation is introduced in the energy denominator of Eq. (5) for utilizing the valence-universal effective Hamiltonian

$$E_\nu^{(0)} - E_I^{(0)} \approx E_B^{(0)} - E_I^{(0)}. \quad (8)$$

We can compute the effective Hamiltonian matrix to the second-order approximately as

$$(H_{\text{eff}}^{(0-2) \text{ Sim}})_{\mu\nu} = E_\mu^{\text{GCS-Cl}} \delta_{\mu\nu} + \sum_{AB \in \text{GCS}} C_A^{\mu*} C_B^\nu (H_{\text{eff}}^{\text{QDPT}(2)})_{AB}, \quad (9)$$

where  $H_{\text{eff}}^{\text{QDPT}(2)}$  is the effective Hamiltonian of the conventional quasidegenerate (QD) PT. This is very similar to Eq. (5), but is much more efficient. The second-order term can be reduced to the products of the transition density matrices  $\langle \mu | p^+ r^+ \dots s q | \nu \rangle$  and the effective Hamiltonian matrix elements in orbital indices  $(H_{\text{eff}}^{\text{QDPT}})_{pr\dots sq}$ .

Compared to the original form, this simplified form is very weak in the intruder states as in the case of the conventional QDPT. Thus the intruder state avoidance treatment is crucial. A simple replacement of the energy denominators,  $\Delta E^{-1} = 0$  (if  $\Delta E < \delta$ ), is effective according to our experiences. A typical value of  $\delta$  is 0.03 a.u.

### 3. Applications

Examples of the relativistic GMC-QDPT and its simplified form are presented in this section. We calculated excitation spectra of tetrachloroplatinate(II) ion  $[\text{PtCl}_4]^{2-}$  and methyl iodide  $\text{CH}_3\text{I}$ , which are examples of original and simplified relativistic GMC-QDPT, respectively.

#### 3.1. Excitation spectra of $[\text{PtCl}_4]^{2-}$

In the previous paper [3], we reported the ground state potential energy curves of the  $\text{I}_2$  and  $\text{Sb}_2$  molecules and the excitation energies of  $\text{CH}_3\text{I}$  and the C, Si, and Ge atoms. Here we present the excitation spectra of  $[\text{PtCl}_4]^{2-}$ . The 16 excited states mainly due to 5d-5d transition, as well as the ground state, were the target states. The active space used was of MRS type constructed from 20 electrons and 30 spinors. The spinors with 5d component were selected as active orbitals for taking account of the spinor relaxation effect. Dyall's double-zeta basis set [4] was used.

Table 1 shows the results of GMC-QDPT. The TDDFT [5] and experimental values [6] are also listed. Ref-CI stands for the reference space CI, i.e. the first-order energies. GMC-QDPT results well reproduced the experiment. In particular,  $1A_{1g}$  to  $2A_{2g}$  states were in good agreement with the peak values. The reference weight means the fraction of the zeroth-order (reference) wave functions in the zeroth plus first order wave functions, and is a measure of the quality of reference wave functions. The computed weights are all in the range of 76–77%. These very close weights indicated almost equal quality of the target states, supporting the computed excitation energies.

Table 1: Vertical excitation energies of  $[\text{PtCl}_4]^{2-}$  in eV.

State	Ref-CI	GMC-QDPT	Ref. weight <sup>a</sup>	TDDFT	Band	Exp. ( $\nu_{\text{max}}$ )
$1A_{1g}$	1.96	2.03	76.6%	2.30	1	2.06–2.14 (2.12)
$1A_{2g}$	2.05	2.14	76.6%	2.34		
$1E_g$	2.09	2.18	76.7%	2.38		
$1B_{2g}$	2.19	2.42	76.9%	2.49	2	2.16–2.29 (2.24)
$1B_{1g}$	2.45	2.53	76.6%	2.59	3	2.42–2.60 (2.57)
$2E_g$	2.50	2.59	76.7%	2.69		
$2A_{1g}$	2.99	2.78	76.0%	2.98	4	2.84–3.05 (2.97)
$3E_g$	3.05	2.93	76.3%	3.03		
$2A_{2g}$	3.37	3.24	76.0%	3.19		
$2B_{2g}$	3.48	3.43	76.6%	3.43	5	3.08–3.33 (3.23)
$4E_g$	3.80	3.77	76.3%	3.50	6	3.41–3.91 (3.67)
$2B_{1g}$	3.81	3.91	76.7%	3.53		
$5E_g$	–	–	–	3.53		
$3B_{2g}$	–	–	–	3.71		
$3B_{1g}$	–	–	–	3.74	7	4.09– (4.53)

<sup>a</sup> The reference weight for the ground state is 76.9%.

#### 3.2. Excitation spectra of $\text{CH}_3\text{I}$

Table 2 shows the excitation energies computed with the simplified form of the relativistic GMC-QDPT. The values of the original relativistic GMC-QDPT and SO-MCQDPT [7], a two-component method, are also listed for comparison. The basis set and the active spaces were the same as those used in the previous paper.[3] The results of simplified form were very close to the original GMC-QDPT. The maximum deviation was 0.07 eV. On the other hand, the speedup in CPU time was 40.1 and 21.3 for MRS(12,24) and MRS(12,36), respectively.

Table 2: Vertical excitation energies of methyl iodide CH<sub>3</sub>I in eV.

State	MRS(12,24) + Sel.( $ C_l  > 10^{-3}$ )			MRS(12,36) + Sel.( $ C_l  > 10^{-3}$ )			SO-MCQDPT	Exp.
	Ref-CI	GMC-QDPT	Simplified form	Ref-CI	GMC-QDPT	Simplified form		
1E	4.73	4.06	4.09	4.45	4.07	4.12	4.16	–
2E	4.92	4.23	4.27	4.63	4.23	4.29	4.30	4.13
1A <sub>2</sub>	5.33	4.62	4.61	5.02	4.63	4.65	4.65	–
2A <sub>1</sub>	5.44	4.67	4.71	5.13	4.68	4.75	4.69	4.75
3E	5.80	5.03	5.08	5.50	5.05	5.08	5.03	5.17

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