Efficient implementation of relativistic and non-relativistic quasidegenerate perturbation theory with general multiconfigurational reference functions

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Abstract

An efficient computational scheme for using the relativistic and non-relativistic quasidegenerate perturbation theory with general multiconfigurational reference functions is implemented. The scheme is based on the matrix element between the reference and the zero- to two-electron ionized determinants. Comparison with a previous scheme based on diagrams is made using the excitation spectra of $[PtCl_4]^{2-}$, CH_3I, and H_2CO as examples, and the efficiency of the scheme is illustrated.
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1. Introduction

Multireference perturbation theory (MRPT) has now become a basic tool for studying the electronic structures and chemical reactions of molecules. Today, we can use MRPT through many quantum chemistry program packages. An advantage of MRPT compared with other multireference methods, such as MR configuration interaction (CI) and MR coupled cluster (CC) methods, is the feasibility for relatively large active spaces and basis sets; neither a long CI vector nor CC amplitude is necessary. Another advantage is its efficiency as there are no large-scale diagonalization or linear-equation problems. For MRPT to take advantage of these features, an efficient computational scheme is essential.

We have proposed an MRPT, which we call quasidegenerate perturbation theory with multiconfigurational reference functions (MC-QDPT) [1], and extended it to general MC reference spaces [2,3]. This MC-QDPT with general MC reference functions (GMC-QDPT) has been implemented using a scheme based on Goldstone diagrams. In this Letter, we present a more efficient scheme based on matrix elements between the reference and ionized determinants.

There have been several computational schemes for MRPTs. Andersson et al. used the internally contracted configuration (ICC) scheme for their complete active space (CAS) PT [4]. Hirao utilized bonded functions to realize his MR Møller–Plesset PT [5]. Celani and Werner derived matrix elements formulas involving ICC for their general MRPT2 [6]. These three examples are all based on spin-adapted configuration state functions. Kozlowski and Davidson employed a determinant-based algorithm [7]. The scheme to be presented here is an intermediate scheme between those of Celani–Werner and Kozlowski–Davidson. Our scheme uses spinor/spin-orbital based determinants and matrix elements to be a common scheme to the relativistic and non-relativistic MRPTs.

2. Method

Let $|\mu\rangle$ and $E_\mu^{(0)}$ be general multiconfigurational reference functions and their zeroth-order energies:

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

(GCS stands for *general configuration space*), respectively. Here $a_p^\dagger$ and a_p are the creation and annihilation operators for an electron in spin-orbital (or spinor) p, respectively, and the orbital energies ε_p are defined by

$$\varepsilon_p = h_{pp} + \sum_{rs} D_{rs}^{\text{ave}}[(pp|rs) - (ps|rp)],$$

where D_{rs}^{ave} is the averaged one-particle density matrix. The effective Hamiltonian up to the second-order $H_{\text{eff}}^{(0-2)}$ of GMC-QDPT [2,3] is given by

$$\left(H_{\text{eff}}^{(0-2)}\right)_{\mu\nu} = E_\mu^{\text{GCS-CI}}\delta_{\mu\nu} + \frac{1}{2}\left\{\sum_{I \notin \text{GCS}} \frac{\langle\mu|H|I\rangle\langle I|H|\nu\rangle}{E_\nu^{(0)} - E_I^{(0)}} + \sum_{I \notin \text{GCS}} \frac{\langle\mu|H|I\rangle\langle I|H|\nu\rangle}{E_\mu^{(0)} - E_I^{(0)}}\right\}, \quad (1)$$

where I is a determinant outside the GCS.

We define the corresponding CAS (CCAS) as a CAS constructed from the same active electrons and orbitals, that is, the minimal CAS that includes the reference GCS. The summation over I in Eq. (1) can be divided into summations over determinants outside CCAS and over determinants outside the GCS but inside CCAS, and then the former term in the curly brackets of Eq. (1) can be written as

$$\left(H_{\text{eff}}^{(2)}\right)_{\mu\nu} = \sum_{I \notin \text{CCAS}} \frac{\langle\mu|H|I\rangle\langle I|H|\nu\rangle}{E_\nu^{(0)} - E_I^{(0)}} + \sum_{I \in \text{CCAS} \wedge I \notin \text{GCS}} \frac{\langle\mu|H|I\rangle\langle I|H|\nu\rangle}{E_\nu^{(0)} - E_I^{(0)}}. \quad (2)$$

(The latter term can be simply obtained by taking the Hermite conjugate of $\left(H_{\text{eff}}^{(2)}\right)_{\mu\nu}$). The first term in Eq. (2) represents external excitations, while the second term represents internal excitations [2].

The internal term is computed through matrix operations for the Hamiltonian matrix

$$\left(H_{\text{internal}}^{(2)}\right)_{\mu\nu} = \mathbf{v}^\dagger(\mu) \cdot \mathbf{w}(\nu)$$

with

$$v_I(\mu) = \sum_{A \in \text{GCS}} \langle I|H|A\rangle C_A^\mu,$$

$$w_I(\nu) = \sum_{B \in \text{GCS}} \langle I|H|B\rangle C_B^\nu \Big/ \left(E_\nu^{(0)} - E_I^{(0)}\right).$$

The intermediate determinants I are constructed by exciting one or two electron(s) from the reference determinants within the active orbital (spinor) space. In general, the computational time for the internal term is small compared with that for the external term.

The external term has been computed with a diagrammatic scheme in the previous implementation [2,3]. Here, we present another computational scheme. The external term is expressed by

$$\left(H_{\text{external}}^{(2)}\right)_{\mu\nu} = \sum_{XB^M} \frac{\langle\mu|HE_X|B^M\rangle\langle B^M|E_X^\dagger H|\nu\rangle}{E_\nu^{(0)} - E_{XB^M}^{(0)}},$$

where $|B^M\rangle$ are (ionized) determinants composed from M active spin-orbitals, E_X are operators that make holes in core spin-orbitals and/or electrons in virtual spin-orbitals, and $E_{XB^M}^{(0)}$ are zeroth-order energies of $E_X|B^M\rangle$. Possible combinations of E_X and $|B^M\rangle$ are as follows:

$$\{E^{ef}|B^{N-2}\rangle\}, \quad (I)$$

$$\{E^e|B^{N-1}\rangle, E_i^{ef}|B^{N-1}\rangle\}, \quad (II)$$

$$\{E_i^e|B^N\rangle, E_{ij}^{ef}|B^N\rangle\}, \quad (III)$$

$$\{E_i|B^{N+1}\rangle, E_{ij}^e|B^{N+1}\rangle\}, \quad (IV)$$

$$\{E_{ij}|B^{N+2}\rangle\}, \quad (V)$$

where e and f are external spinor/spin-orbital labels, i and j are core spinor/spin-orbital labels, and N is the number of active electrons. The matrix elements for these combinations are given through the normal ordering as

$$\langle\mu|HE^{ef}|B^{N-2}\rangle = \frac{1}{2}\sum_{pr}\sum_A (pe\|rf)C_A^{\mu*}\langle A|E^{pr}|B^{N-2}\rangle,$$

$$\langle\mu|HE^e|B^{N-1}\rangle = \sum_p\sum_A f_{pe}^{\text{core}}C_A^{\mu*}\langle A|E^p|B^{N-1}\rangle + \frac{1}{2}\sum_{prs}\sum_A (pe\|rs)C_A^{\mu*}\langle A|E_s^{pr}|B^{N-1}\rangle,$$

$$\langle\mu|HE_i^{ef}|B^{N-1}\rangle = \sum_p\sum_A (pe\|if)C_A^{\mu*}\langle A|E^p|B^{N-1}\rangle,$$

$$\langle\mu|HE_i^e|B^N\rangle = \sum_A f_{ie}^{\text{core}}C_A^{\mu*}\langle A|B^N\rangle + \sum_{pq}\sum_A (pq\|ie)C_A^{\mu*}\langle A|E_q^p|B^N\rangle,$$

$$\langle\mu|HE_{ij}^{ef}|B^N\rangle = \sum_A (ie\|jf)C_A^{\mu*}\langle A|B^N\rangle,$$

$$\langle\mu|HE_i|B^{N+1}\rangle = -\sum_q\sum_A f_{iq}^{\text{core}}C_A^{\mu*}\langle A|E_q|B^{N+1}\rangle - \frac{1}{2}\sum_{qrs}\sum_A (iq\|rs)C_A^{\mu*}\langle A|E_{qs}^r|B^{N+1}\rangle,$$

$$\langle\mu|HE_{ij}^e|B^{N+1}\rangle = -\sum_q\sum_A (iq\|je)C_A^{\mu*}\langle A|E_q|B^{N+1}\rangle,$$

and

$$\langle\mu|HE_{ij}|B^{N+2}\rangle = \frac{1}{2}\sum_{qs}\sum_A (iq\|js)C_A^{\mu*}\langle A|E_{qs}|B^{N+2}\rangle,$$

where f_{pq}^{core} is the core Fock matrix, $(pq\|rs)$ are antisymmetrized two-electron integrals $((pq\|rs) = (pq|rs) - (ps|rq))$, and $E_{qs\dots}^{pr\dots}$ are operators defined by

$$E_{qs\dots u}^{pr\dots t} = a_p^\dagger a_r^\dagger \dots a_t^\dagger a_u \dots a_s a_q.$$

A simplification can be obtained if we adopt $E_{ij}^{ef}|\nu\rangle$ instead of $E_{ij}^{ef}|B^N\rangle$ in (III):

$$\langle\mu|HE_{ij}^{ef}|\nu\rangle = (ie\|jf)\langle\mu|\nu\rangle = (ie\|jf)\delta_{\mu\nu}.$$

In this case, the contribution of $E_{ij}^{ef}|\nu\rangle$ to the effective Hamiltonian matrix becomes the second-order Møller–Plesset formula for the diagonal elements and zero for the off-diag-

onal elements. We use this simplified form in the applications in the next section.

We have used spin-orbital-based determinants and coupling coefficients. In the non-relativistic case, the spin symmetry is only considered to treat integrals in the molecular (spatial) orbital basis.

3. Applications

We applied the present computational scheme to some molecular systems and measured CPU times (on a 3.4 GHz Pentium 4 processor) to illustrate its performance. We calculated the excitation energies of $[PtCl_4]^{2-}$ and CH_3I with four-component relativistic GMC-QDPT and the excitation energies of H_2CO with non-relativistic GMC-QDPT. The spinors were determined with the Dirac–Hartree–Fock (DHF) method in the relativistic cases and the orbitals were determined by the multiconfiguration self-consistent field method in the non-relativistic case. The emphasis in the discussions is placed mainly on the efficiency of the schemes rather than the computed excitation energies themselves.

3.1. d–d Excitation energies of $[PtCl_4]^{2-}$

The target states of our first example, $[PtCl_4]^{2-}$, were the 12 excited states due to d–d single excitations, as well as the ground state. The reference space was a multireference singles (MRS) type space constructed from 20 electrons and 26 spinors. The determinants that spanned the reference space were generated from 41 parent configurations (DHF configuration and single excitation configurations constructed from 20 occupied and the two lowest unoccupied spinors) and selected according to their weight in the reference functions. Only the determinants whose weights

were greater than 10^{-8} (i.e. $|C_I| > 10^{-4}$) were selected. The basis sets used were Dyall's VDZ set [8] for Pt and the cc-pVDZ-DK set of Patterson et al. [9] for Cl.

The computed excitation energies are summarized in Table 1. The two-component time-dependent density functional theory (TDDFT) results of Wang and Ziegler [10] and experimental values of Patterson et al. [11] are also listed for comparison. The assignment was done similarly to that provided by Wang and Ziegler [10]. The GMC-QDPT computed values for $1E_g$ (2.18 eV), $1B_{2g}$ (2.42 eV), $1B_{1g}$ (2.55 eV) [or $2E_g$ (2.60 eV)], $3E_g$ (2.92 eV), $2A_{2g}$ (3.23 eV), and $4E_g$ (3.76 eV) were in good agreement with the peak values of band 1–6 (2.12, 2.24, 2.57, 2.97, 3.23, and 3.67 eV, respectively). The values of the approximate reference weight [2], which is a measure of the quality of the reference wave functions, are also listed in Table 1. The close values of the weight mean the qualities of the reference wave functions were well balanced.

Table 2 shows the CPU times for the diagrammatic and the present matrix-element schemes. The notations zero- to three-body mean the CPU times for zero- to three-body terms in the diagrammatic scheme. The symbol $E_i^e|B^N\rangle$, for example, means the CPU time for the terms involving $E_i^e|B^N\rangle$ in the matrix-element scheme. The word *internal* means the term involving active-to-active excitations, which is common to the diagrammatic and matrix-element schemes. There is no one-to-one correspondence between the terms of the diagrammatic and matrix-element schemes except for the internal term; hence, there is also no one-to-one correspondence in CPU times. However, we can divide the CPU time according to the integral types processed: all-internal $(ij\|kl)$, one-external $(ei\|jk)$, and two-external $(ei\|fj)$ integrals $(i,j,k,l$: internal (core and active) spinor labels; e,f: external spinor labels). Table 2 also shows the CPU times according to this division.

Table 1
d–d Excitation energies of $[PtCl_4]^{2-}$ (eV)

State	GCS-CI	GMC-QDPT	Ref. weight[a] (%)	TDDFT[b]	Band[c]	Expt.[c]
$2A_{1g}$	1.88	2.03	76.2	2.30		
$1A_{2g}$	1.96	2.13	76.3	2.34	1	2.06–2.14 (peak value: 2.12)
$1E_g$	1.99	2.18	76.4	2.38		
$1B_{2g}$	2.08	2.42	76.7	2.49	2	2.16–2.29 (2.24)
$1B_{1g}$	2.38	2.55	76.2	2.59	3	2.42–2.60 (2.57)
$2E_g$	2.40	2.60	76.4	2.69		
$3A_{1g}$	2.92	2.78	75.6	2.98	4	2.84–3.05 (2.97)
$3E_g$	2.98	2.92	75.9	3.03		
$2A_{2g}$	3.39	3.23	75.7	3.19	5	3.08–3.33 (3.23)
$2B_{2g}$	3.29	3.42	76.1	3.43		
$4E_g$	3.74	3.76	75.9	3.50		
$2B_{1g}$	3.74	3.94	76.4	3.53	6	3.41–3.91 (3.67)
$5E_g$	–	–	–	3.53		
$3B_{2g}$	–	–	–	3.71		
$3B_{1g}$	–	–	–	3.74	7	4.09– (4.53)

[a] The reference weight of the ground state was 76.6%.
[b] Ref. [10].
[c] Ref. [11].

Table 2
CPU times for the $[PtCl_4]^{2-}$ calculations (s)

Diagrammatic scheme		Present scheme	
All internal integral term		All internal integral term	
Internal	10	Internal	10
1 External integral terms		1 External integral terms	
0-Body	199	$E_i^e\|B^N\rangle$	143
1-Body	2162	$E^e\|B^{N-1}\rangle$	58
2-Body	6241	$E_i\|B^{N+1}\rangle$	6
3-Body	9955	$E_{ij}^e\|B^{N+1}\rangle$	107
		$E_{ij}\|B^{N+2}\rangle$	1
Subtotal	18557	Subtotal	315
2 External integral terms		2 External integral terms	
0-Body	0	$E_{ij}^{ef}\|v\rangle$	0
1-Body	2128	$E_i^{ef}\|B^{N-1}\rangle$	2610
2-Body	1839	$E^{ef}\|B^{N-2}\rangle$	866
Subtotal	3967	Subtotal	3476
Total time	22534	Total time	3801

Because the CPU times for the internal term were small and common to both schemes, we focus on the CPU times for one- and two-external integral terms. The CPU times for the one-external terms were quite different. The CPU times for the diagrammatic and matrix-element schemes were 18557 and 315 s, respectively. The present matrix-element scheme was 58.9 times faster than the diagrammatic scheme. On the other hand, the CPU times for the two-external integral terms were not so different, being 3967 and 3476 s for the diagrammatic and matrix-element schemes, respectively. Mainly because of the difference in one-external integral terms, the total CPU time of the matrix-element scheme was 5.93 times smaller than that of the diagrammatic scheme.

3.2. Excitation energies of CH_3I

The target excited states of CH_3I were the lowest five states (1E, 2E, 3E, $1A_2$, and $2A_1$), which come mainly from n (iodine $5p\pi$) to σ^* (CH antibonding) single excitations. The 3E state roughly corresponds to the singlet n–σ^* state in the non-relativistic case, whereas the other roughly correspond to the triplet n–σ^* states. The basis set used was Dyall's VTZ set for I [12] and the cc-pVTZ-DK set for C and H [9]. Two reference spaces of MRSD- and MRS-type were used, which were constructed from 12 electrons and 20 spinors, and 12 electrons and 36 spinors, respectively. Apart from the basis sets, the computational conditions were the same as those in Ref. [3].

The computed excitation energies are summarized in Table 3. The excitation energies at the GMC-QDPT level were a little larger than those in a previous paper [3] because of the difference in the basis sets. However, overall,

Table 3
Vertical excitation energies of CH_3I (eV)

State	MRSD reference space			MRS reference space			Expt.
	GCS-CI	GMC-QDPT	Ref. weight[a] (%)	GCS-CI	GMC-QDPT	Ref. weight[a] (%)	
1E	5.36	4.18	82.8	4.44	4.20	89.8	–
2E	5.51	4.35	83.2	4.62	4.36	89.7	4.13
$1A_2$	5.94	4.71	82.4	4.99	4.74	89.7	–
$2A_1$	6.03	4.78	82.6	5.12	4.81	89.5	4.75
3E	6.27	5.14	84.0	5.45	5.13	89.4	5.17

[a] The reference weight of the ground state was 91.0% (MRSD) and 90.7% (MRS).

Table 4
CPU times for the CH_3I calculations (s)

Diagrammatic scheme	MRSD	MRS	Present scheme	MRSD	MRS
All internal integral term			All internal integral term		
Internal	9	49	Internal	10	51
1 External integral terms			1 External integral terms		
0-Body	120	73	$E_i^e\|B^N\rangle$	78	77
1-Body	1125	688	$E^e\|B^{N-1}\rangle$	21	62
2-Body	3412	1334	$E_i\|B^{N+1}\rangle$	6	86
3-Body	4373	1287	$E_{ij}^e\|B^{N+1}\rangle$	99	109
			$E_{ij}\|B^{N+2}\rangle$	3	21
Subtotal	9030	3382	Subtotal	207	355
2 External integral terms			2 External integral terms		
0-Body	0	0	$E_{ij}^{ef}\|v\rangle$	0	0
1-Body	491	95	$E_i^{ef}\|B^{N-1}\rangle$	526	124
2-Body	453	104	$E^{ef}\|B^{N-2}\rangle$	97	23
Subtotal	944	199	Subtotal	623	147
Total time	9983	3630	Total time	840	553

the values were close to each other; the present values were larger than the previous ones by only 0.10 eV on average. Similar to the previous calculation, GMC-QDPT reproduced the experimental values well. The deviations were 0.22 (0.23), 0.03 (0.06), and 0.03 (0.04) eV for the 2E, 2A$_1$, and 3E states, respectively, in the case of the MRSD (MRS) reference space.

Table 4 shows the CPU times for each term. The tendency is similar to the [PtCl$_4$]$^{2-}$ case. The present scheme was much more efficient than the diagrammatic scheme for the one-external integral terms. The ratios of CPU times ($T_{Diagrammatic}/T_{Present}$) were 43.6 and 9.53 for MRSD and MRS reference spaces, respectively. On the other hand, for the two-external integral terms, the ratios were only 1.52 (MRSD) and 1.35 (MRS). As a result, the ratios of total CPU times were 11.88 and 6.56 for the MRSD and MRS reference spaces, respectively.

3.3. Excitation energies of H$_2$CO

The target states were the six lowest singlet excited states (1^{1}A$_2$, 1^{1}B$_2$, 1^{1}B$_1$, 2^{1}A$_1$, 2^{1}A$_2$, and 3^{1}A$_1$) and the ground state. The reference space used was almost the same as the largest one constructed from eight electrons and 24 spinors in a previous paper [2], but differs in the determinant selection according to the reference CI coefficients ($|C_I| > 10^{-4}$) in the present calculation. The basis set and geometry were the same as those in the previous paper. The seven target states were treated simultaneously, in contrast to the previous calculation, where states of the same symmetry were treated simultaneously.

The excitation energies are listed in Table 5. The values for GMC-QDPT were similar to those of a previous paper [2], as expected from the similar computational conditions, although the values were slightly smaller than the previous values (by −0.11 eV on average). The 1^{1}A$_2$ (4.00 eV), 1^{1}B$_1$ (9.34 eV), and 3^{1}A$_1$ (10.48 eV) excitation energies were close to the available experimental values (4.07, 9.00, and 10.70 eV, respectively).

Table 6 shows the CPU times for this calculation. The tendency is different from that of [PtCl$_4$]$^{2-}$ and CH$_3$I. For one-external integral terms, the present scheme (1247 s) was 2.7 times more efficient than the diagrammatic scheme (3344 s). Similarly, for the two-external integral terms, the ratio was 4.0 (1430 s/356 s). The present scheme

Table 6
CPU times for the H$_2$CO calculations (s)

Diagrammatic scheme		Present scheme	
All internal integral term		All internal integral term	
Internal	91	Internal	91
1 External integral terms		1 External integral terms	
0-Body	17	$E_i^e\|B^N\rangle$	102
1-Body	152	$E^e\|B^{N-1}\rangle$	327
2-Body	787	$E_i\|B^{N+1}\rangle$	720
3-Body	2388	$E_{ij}^e\|B^{N+1}\rangle$	55
		$E_{ij}\|B^{N+2}\rangle$	43
Subtotal	3344	Subtotal	1247
2 External integral terms		2 External integral terms	
0-Body	0	$E_{ij}^{ef}\|v\rangle$	0
1-Body	137	$E_i^{ef}\|B^{N-1}\rangle$	169
2-Body	1293	$E^{ef}\|B^{N-2}\rangle$	187
Subtotal	1430	Subtotal	356
Total time	4865	Total time	1694

was 2.9 times more efficient than the diagrammatic scheme in total CPU time. This difference in tendency was not due to the difference between the relativistic and non-relativistic treatments, but mainly due to the difference in the number of core spin-orbitals (or spinors) that were correlated in the perturbation calculations. There were 20 core spinors included in the perturbation calculations in both the [PtCl$_4$]$^{2-}$ and CH$_3$I cases, whereas, in the H$_2$CO case, there were only two core spin-orbitals included. This difference affected the ratio of the time for one- and two-external integral terms, thus giving the difference in tendency.

For these three examples, the present scheme was more efficient than the diagrammatic scheme. However, we do not claim that it is always the case. There were few but some instances where the diagrammatic scheme was more efficient. The I$_2$ molecule reported in Ref. [3] was such an instance (e.g. 1070 s (present) and 788 s (diagrammatic) at $R = R_e$).

4. Concluding remarks

An efficient computational scheme for GMC-QDPT has been implemented in the present Letter, which is based on the matrix element between the reference and ionized determinants. This scheme was tested on the excitation energies of [PtCl$_4$]$^{2-}$, CH$_3$I (for the relativistic GMC-QDPT) and H$_2$CO (for the non-relativistic GMC-QDPT) and compared with the previous diagrammatic scheme. The present scheme was about 3–12 times more efficient than the diagrammatic scheme for these molecules. These results indicate the effectiveness of the present scheme in both the relativistic and non-relativistic cases.

Table 5
Vertical excitation energies of H$_2$CO (eV)

State	Orbital picture	MC-SCF	GMC-QDPT	Ref. weight[a] (%)	Expt.
1^{1}A$_2$	$n \to \pi^*$	4.21	4.00	95.5	4.07
1^{1}B$_2$	$n \to 6a_1(\sigma^*)$	8.54	8.23	95.0	
1^{1}B$_1$	$5a_1(\sigma) \to \pi^*$	9.99	9.34	94.0	9.00
2^{1}A$_1$	$\pi \to \pi^*$; $n \to \sigma^*$	10.02	9.60	94.7	
2^{1}A$_2$	$1b_2(\sigma) \to \pi^*$	11.24	10.31	94.6	
3^{1}A$_1$	$n \to \sigma^*$; $\pi \to \pi^*$	11.00	10.48	94.1	10.70

[a] The reference weight of the ground state was 96.0%.

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