Recent Advances in Multireference-Based Perturbation Theory

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Received February 28, 2003

Accurate *ab initio* computational chemistry has evolved dramatically. In particular, the development of multireference-based approaches has opened up a completely new area, and has had a profound impact on the potential of theoretical chemistry. Multireference-based perturbation theory (MRPT) is an extension of the closed-shell single reference Moller-Plesset method, and has been successfully applied to many chemical and spectroscopic problems. MRPT has established itself as an efficient technique for treating nondynamical and dynamical correlations. Usually, a complete active space self-consistent field (CASSCF) wave function is chosen as a reference function of MRPT. However, CASSCF often generates too many configurations, and the size of the active space can outgrow the capacity of the present technology. Many attempts have been proposed to reduce the dimension of CASSCF and to widen the range of applications of MRPT. This review focuses on our recent development in MRPT.

Key Words : Multireference-based perturbation theory, MRMP, MC-QSPT, QCAS, SPS-SCF

Introduction

Single reference many-body perturbation theory and coupled cluster theory are effective in describing dynamical correlation, but fail badly in dealing with (quasi-)degenerate nondynamical correlation. Truncated configuration interaction (CI) can handle nondynamical correlation well, but configuration expansion in multireference CI is quite lengthy and is not an optimal approach. Multireference techniques can handle nondynamical correlation well. Once the state-specific nondynamical correlation is removed, the rest is primarily composed of dynamical pair correlation and individual pair correlation, and can be described even by second-order perturbation theory. This is the basic idea of the multireference-based perturbation theory (MRPT).

Multireference Moller-Plesset (MRMP)[1-4] and quasi-degenerate perturbation theory (MC-QDPT)[5,6] have been successfully applied to many chemical and spectroscopic problems, and this approach has established itself as an efficient method for treating nondynamical and dynamical correlation effects. MRMP can handle any state, regardless of charge, spin, or symmetry, with surprisingly high and consistent accuracy. However, MRMP has a sharp limit to the number of configurations of the reference complete active space (CAS) SCF wave function.[7-9] To avoid this problem, many approaches have been proposed. We have developed perturbation theory (PT) based on the quasi-complete active space (QCAS) SCF wave function.[10,11] QCAS is defined as the product space of CAS spanned by the determinants or configuration state functions (CSFs). Although QCAS works quite well, QCAS requires physically sound judgment and intuition in the choice of subspace. More flexible reference functions are required. A second-order PT starting with *general* multiconfiguration (MC) SCF wave functions[12] has been developed. The general MCSCF functions are wave functions optimized in an active space spanned by an arbitrary set of Slater determinants or CSFs. The approach can dramatically reduce the dimension of the reference function. Recently, a very efficient string product space (SPS) SCF/PT has been proposed, where the total space is defined as a product of α and β string spaces.

This review will focus on our recent development in multireference-based perturbation theory.

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Multireference Møller-Plesset Perturbation Method

Our basic problem is to find approximations to some low-lying solutions of the exact Schrödinger equation,

$$H\Psi = E\Psi . \tag{1}$$

H is the Hamiltonian and it is decomposed into two parts, a zeroth-order Hamiltonian H_0 and a perturbation V,

$$H = H_0 + V . \tag{2}$$

We assume that a complete set of orthonormal eigenfunctions $\{\Psi_i^{(0)}\}$ and corresponding eigenvalues is available,

$$H_0\Psi_i^{(0)} = E_i^{(0)}\Psi_i^{(0)} . \tag{3}$$

Then the state wave function Ψ_I is expanded in terms of basis functions $\Psi_k^{(0)}$ as

$$\Psi_I = \sum_k C_{Ik}\Psi_k^{(0)} . \tag{4}$$

Some of the basis functions define an active space P, and the remaining part of Hilbert space is called the orthogonal space $Q = 1 - P$. The active space is spanned by the basis functions that have a filled core and the remaining active electrons distributed over a set of active orbitals. The

orthogonal complete space incorporates all other possible basis functions that are characterized by having at least one vacancy in a core orbital. The state wave function in an active space is written as

$$\Psi_I^{(0)} = \sum_k C_k \Phi_k , \tag{5}$$

where the sum runs over the active space basis functions $\{\Phi_i\}$ and C_k are the coefficients of just the active space basis functions. It is convenient to use intermediate normalization, *i.e.*

$$\langle \Psi_I^{(0)} | \Psi_I^{(0)} \rangle = \langle \Psi_I^{(0)} | \Psi_I \rangle = 1 . \tag{6}$$

We also assume that $\Psi_I^{(0)}$ is diagonal in P space.

$$\langle \Psi_I^{(0)} | H | \Psi_J^{(0)} \rangle = \delta_{IJ} (E_I^{(0)} + E_I^{(1)}) , \tag{7}$$

with

$$E_I^{(0)} = \langle \Psi_I^{(0)} | H_0 | \Psi_I^{(0)} \rangle , \tag{8}$$

$$E_I^{(0)} = \langle \Psi_I^{(0)} | V | \Psi_I^{(0)} \rangle . \tag{9}$$

The state-specific Rayleigh-Schrödinger PT based on the unperturbed eigenvalue equation

$$H_0 \Psi_I^{(0)} = E_I^{(0)} \Psi_I^{(0)} \tag{10}$$

leads to the first few $E_I^{(k)}$ as

$$E_I^{(2)} = \langle \Psi_I^{(0)} | VRV | \Psi_I^{(0)} \rangle , \tag{11}$$

$$E_I^{(3)} = \langle \Psi_I^{(0)} | VR(V - E_I^{(1)}) RV | \Psi_I^{(0)} \rangle . \tag{12}$$

$$\begin{aligned} E_I^{(4)} = {} & \langle \Psi_I^{(0)} | VR(V - E_I^{(1)}) R(V - E_I^{(1)}) RV | \Psi_I^{(0)} \rangle \\ & - E_I^{(2)} [\langle \Psi_I^{(0)} | VR^2 V | \Psi_I^{(0)} \rangle + \langle \Psi_I^{(0)} | VRH_0 SH_0 RV | \Psi_I^{(0)} \rangle] \\ & \text{. etc.} \end{aligned} \tag{13}$$

R and S are the resolvent operators

$$R = Q/(E_I^{(0)} - H_0) , \tag{14}$$

$$S = P'/(E_I^{(0)} - H_0) . \tag{15}$$

where $P' = P - |\Psi_I^{(0)}\rangle\langle\Psi_I^{(0)}|$.

$E_I^{(0)}$ is given in terms of orbital energies as

$$E_I^{(0)} = \sum_k D_{kk} \varepsilon_k , \tag{16}$$

and the orbital energies are defined as

$$\varepsilon_i = \langle \varphi_i | F | \varphi_i \rangle \tag{17}$$

with

$$F_{ij} = h_{ij} + \sum_{kl} D_{kl} \left[(ij|kl) - \frac{1}{2} (ik|lj) \right] , \tag{18}$$

where D_{ij} is the one-electron density matrix. The MCSCF orbitals are resolved to make the F_{ij} matrix as diagonal as possible. This zeroth-order Hamiltonian is closely analogous to the closed-shell Fock operator. The definition of an active space, the choices of active orbitals and the specification of the zeroth-order Hamiltonian completely determine the perturbation approximation.

When a CASSCF[7-9] wave function is used as the reference, the zeroth plus first order energy $E_I^{(0)} + E_I^{(1)}$ is equal to the CASSCF energy. The lowest non-trivial order is therefore the second order. Let the reference function $|\Psi_\alpha^{(0)}\rangle$ be a CASSCF wave function,

$$|\alpha\rangle = \sum_A C_A |A\rangle . \tag{19}$$

The energy up to the second order is given by

$$E_\alpha^{(0+2)} = E_\alpha^{\mathrm{CAS}} + \sum_I \frac{\langle \alpha | V | I \rangle \langle I | V | \alpha \rangle}{E_\alpha^{(0)} - E_I^{(0)}} \tag{20}$$

where $\{|I\rangle\}$ is the set of all singly and doubly excited configurations from the reference configurations in CAS. This is our multireference Moller-Plesset (MRMP) method.[1-4]

We have also proposed a multistate multireference perturbation theory, the quasidegenerate perturbation theory with MCSCF reference functions (MC-QDPT).[5,6]

The Perturbation Theory Based on QCAS-SCF and MCSCF Wave Functions

CASSCF[7-9] can handle the near-degeneracy problem in a balanced way and therefore can treat chemical reactions and excited states. Once the active space is chosen, the wave function is completely specified. It is size-consistent and the wave function is invariant to transformations among active orbitals. Although CASSCF does not include dynamical correlation, it provides a good starting point for such studies. However, CASSCF often generates too many configurations with the number of active orbitals and active electrons.

To reduce the CAS dimension, we have proposed the quasi-complete active space (QCAS) SCF method.[10,11] QCAS is an attempt to extend the method to widen the range of applications. QCAS is defined as a product of complete active spaces. Let us divide the active electrons and orbital sets into N subsets and fix the number of active electrons, m_i, and orbitals, n_i, in each subset.

$$m_{act} = \sum_i^N m_i , \quad n_{act} = \sum_i^N n_i \tag{21}$$

where m_{act} and n_{act} denote the number of active electrons and active orbitals, respectively. We define the QCAS as the product space of CAS spanned by the determinants or CSF

$$\begin{aligned} QCAS(\{m_i\},\{n_i\}) = {} & CAS(m_1,n_1) \times CAS(m_2,n_2) \\ & \times \cdots \times CAS(m_N,n_N) \end{aligned} \tag{22}$$

Each active space is defined by a fixed number of active electrons and active orbitals. Solution of the CI eigenvalue

problem involves the σ_I vector, which is given by

$$\sigma_I = \sum_J H_{IJ} C_J$$

$$= \sum_J \left\{ \sum_{ij} h_{ij} \langle I|E_{ij}|J\rangle + \frac{1}{2} \sum_{ijkl} (ij|kl) \langle I|E_{ij}E_{kl} - \delta_{jk}E_{il}|J\rangle \right\} C_J \tag{23}$$

Here, I and E_{ij} are the CI basis functions and the group generators. We adopt Slater determinants rather than CSF and split a determinant into α and β strings of each group

$$|I\rangle = |I_\alpha^1 \cdots I_\alpha^N, I_\beta^1 \cdots I_\beta^N\rangle = |I_\alpha^1\rangle \cdots |I_\alpha^N\rangle |I_\beta^1\rangle \cdots |I_\beta^N\rangle \tag{24}$$

Then we can decompose the one-body α and β coupling constants into the coupling constants for the strings of the groups as

$$\langle I|E_{ij}|J\rangle = \langle I|E_{ij}^\alpha|J\rangle + \langle I|E_{ij}^\beta|J\rangle$$

$$= \begin{cases} \langle I_\alpha^G|E_{ij}^\alpha|J_\alpha^G\rangle \prod_{H\neq G} \delta_{I_\beta^H J_\beta^H} \prod_H \delta_{I_\alpha^H J_\alpha^H} + \langle I_\beta^G|E_{ij}^\alpha|J_\beta^G\rangle \prod_H \delta_{I_\alpha^H J_\alpha^H} \prod_{H\neq G} \delta_{I_\beta^H J_\beta^H} & (i,j \in G) \\ 0 & (otherwise) \end{cases} \tag{25}$$

Thus, the σ-vector and the one- and two-particle density matrices are expressed by the coupling constants for the strings of the groups.

The dimension of QCAS is much smaller than that of CAS constructed from the same set of electrons and orbitals. Let us consider CAS(16e, 16o), where16 electrons are distributed among 16 orbitals. CAS(16e, 16o) is spanned by the 165 636 900 determinants (with $M = 0$). If we divide the active electrons and orbitals into five groups: (4e, 4o) + (4e, 4o) + (4e, 4o) + (2e, 2o) + (2e, 2o), the dimension of QCAS is reduced to 746 496. Using QCAS as a reference function in the perturbation theory, we may therefore extend active electrons and orbitals beyond the limit of CAS. QCASSCF/PT works quite well. However, it is not always possible to select an appropriate QCAS, depending on the molecular systems of interest. QCAS requires physically sound judgment and intuition in the choice of subspace.

Therefore, we have developed a second-order QDPT using a *general* multiconfiguration (MC) SCF wave function as a reference function (hereafter, GMC-QDPT).[12] The *general configuration space* (GCS) is defined by a space that is spanned by an arbitrary set of Slater determinants or CSFs. The orbitals are partitioned into three categories as in the ordinary MCSCF method: the core orbitals are doubly occupied and the virtual orbitals are unoccupied in all the determinants/CSFs, while the active orbitals may be occupied or unoccupied. The reference wave functions used in the perturbation calculations are determined by MCSCF as a variational space:

$$|\alpha\rangle = \sum_{A \in GCS} C_A(\alpha)|A\rangle . \tag{26}$$

The effective Hamiltonian up to the second order $H_{eff}^{(0-2)}$ of van Vleck perturbation theory with unitary normalization is given by

$$(H_{eff}^{(0-2)})_{AB} = H_{AB} + \frac{1}{2}[\langle \Phi_A^{(0)}|HR_BH|\Phi_B^{(0)}\rangle + \langle \Phi_A^{(0)}|HR_AH|\Phi_B^{(0)}\rangle] \tag{27}$$

with

$$R_A = \sum_{I \notin ref} |\Phi_I^{(0)}\rangle (E_A^{(0)} - E_I^{(0)})^{-1} \langle \Phi_I^{(0)}| , \tag{28}$$

where $\Phi_A^{(0)}(\Phi_B^{(0)})$ and $\Phi_I^{(0)}$ are reference wave functions and a function in the complement space (Q) of the reference space (P), respectively, and $E_B^{(0)}$ and $E_I^{(0)}$ are zeroth-order energies of functions $\Phi_B^{(0)}$ and $\Phi_I^{(0)}$.

Adopting (state-averaged) MCSCF wave functions α (β) as reference functions $\Phi_A^{(0)}(\Phi_B^{(0)})$, which define the P space, Eq. (27) becomes

$$(K_{eff}^{(0-2)})_{\alpha\beta} = E_\alpha^{MC-SCF} \delta_{\alpha\beta} + \frac{1}{2} \sum_{I \notin GCS} \left\{ \frac{\langle \alpha|H|I\rangle \langle I|H|\beta\rangle}{E_\beta^{(0)} - E_I^{(0)}} + (\alpha \leftrightarrow \beta) \right\} . \tag{29}$$

where I is a determinant/CSF outside the GCS. The notation $(\alpha \leftrightarrow \beta)$ means interchange α with β from the first term in curly brackets. The complementary eigenfunctions of the MCSCF Hamiltonian and the determinants/CSFs generated by exciting electrons out of the determinants/CSFs in GCS are orthogonal to the reference functions and define the Q space. The functions in the space complementary to the P space, however, do not appear in Eq. (29), because the interaction between the complementary functions and the reference functions is zero. We define here 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. (29) may be divided into summations over the determinants/CSFs outside CCAS and over the determinants/CSFs outside the GCS but inside CCAS:

$$\sum_{I \notin GCS} = \sum_{I \notin CCAS} + \sum_{I \notin CCAS \wedge \notin GCS} . \tag{30}$$

then the former second-order term may be written as

$$(K_{eff}^{(2)})_{\alpha\beta} = \sum_{I \notin CCAS} \frac{\langle \alpha|H|I\rangle \langle I|H|\beta\rangle}{E_\beta^{(0)} - E_I^{(0)}} + \sum_{I \notin CCAS \wedge I \notin GCS} \frac{\langle \alpha|H|I\rangle \langle I|H|\beta\rangle}{E_\beta^{(0)} - E_I^{(0)}} . \tag{31}$$

The first term in Eq. (31) represents external excitations, and the second term represents internal excitations. The external term is calculated by the diagrammatic method and the

internal term by the sum-over-states method.

The external term may be further written as

$$(H^{(2)}_{ext})_{\alpha\beta} = \sum_{A,B \in GCS} C_A(\alpha) C_B(\beta) (H^{(2)}_{ext})_{AB} \tag{32}$$

with

$$(H^{(2)}_{ext})_{AB} = \sum_{I \notin CCAS} \frac{\langle A|H|I\rangle\langle I|H|B\rangle}{E^{(0)}_B - E^{(0)}_I + (E^{(0)}_\beta - E^{(0)}_B)}, \tag{33}$$

where $(H^{(2)}_{ext})_{AB}$ is the effective Hamiltonian in the determinant/CSFs. Because the second-order diagrams do not depend on the denominator, the second-order effective Hamiltonian, Eq. (33) (hence, also Eq. (32)) is expressed by the same diagrams as in the conventional QDPT.

For internal terms, the diagrammatic approach may not be applied. Instead, matrix operations for the Hamiltonian matrix are used:

$$(H^{(2)}_{int})_{\alpha\beta} = \mathbf{v}^T(\alpha) \cdot \mathbf{w}(\beta) \tag{34}$$

with

$$\mathbf{v}_I(\alpha) = \sum_{A \in GCS} \langle I|H|A\rangle C_A(\alpha) \tag{35}$$

$$\mathbf{w}_I(\beta) = \sum_{B \in GCS} \langle I|H|B\rangle C_B(\beta)/(E^{(0)}_\beta - E^{(0)}_B) \tag{36}$$

The intermediate determinants/CSFs I are constructed by exciting one or two electrons from the reference determinants/CSFs within the active orbital space. In general, the number of I is not large, and thus they may be managed in computer memory.

In the present implementation, we used Slater determinants rather than CSFs. Let $\{I_\alpha\}$ and $\{I_\beta\}$ be sets of α and β strings appearing in the reference configurations, respectively. The reference space is defined by the β string sets for each α string, $\{I_\beta[I_\alpha]\}$, and equivalently the a string sets for each β string, $\{I_\alpha[I_\beta]\}$.

In the diagrammatic computation of the external terms, one-, two-, and three-body coupling coefficients are necessary. The one-body coupling coefficients are classified into two types.

$$\langle I_\alpha|E^\alpha_{pq}|J_\alpha\rangle\langle I_\beta|J_\beta\rangle \text{ and } \langle I_\alpha|J_\alpha\rangle\langle I_\beta|E^\beta_{pq}|J_\beta\rangle$$

the two-body coupling coefficients into three types.

$\langle I_\alpha|E^\alpha_{pq,rs}|J_\alpha\rangle\langle I_\beta|J_\beta\rangle$, $\langle I_\alpha|J_\alpha\rangle\langle I_\beta|E^\beta_{pq,rs}|J_\beta\rangle$, and

$\langle I_\alpha|E^\alpha_{pq}|J_\alpha\rangle\langle I_\beta|E^\beta_{rs}|J_\beta\rangle$,

and the three-body coupling coefficients into four types.

$\langle I_\alpha|E^\alpha_{pq,rs,tu}|J_\alpha\rangle\langle I_\beta|J_\beta\rangle$, $\langle I_\alpha|J_\alpha\rangle\langle I_\beta|E^\beta_{pq,rs,tu}|J_\beta\rangle$,

$\langle I_\alpha|E^\alpha_{pq,rs}|J_\alpha\rangle\langle I_\beta|E^\beta_{tu}|J_\beta\rangle$, and $\langle I_\alpha|E^\alpha_{pq}|J_\alpha\rangle\langle I_\beta|E^\beta_{rs,tu}|J_\beta\rangle$

with $J_\alpha \in \{I_\alpha\}$, $J_\beta \in \{I_\beta\}$, and

$$E^\alpha_{pq,rs,\ldots} = a^+_{p\alpha}a^-_{r\alpha}\cdots a_{s\alpha}a_{q\alpha}. \tag{37}$$

$$E^\beta_{pq,rs,\ldots} = a^-_{p\beta}a^-_{r\beta}\cdots a_{s\beta}a_{q\beta}. \tag{38}$$

Because string J_α (J_β) is determined by string I_α (I_β) and active orbital labels p and q, the one-body coupling coefficients for strings $\langle I_\alpha|E^\alpha_{pq}|J_\alpha\rangle$ ($\langle I_\beta|E^\beta_{pq}|J_\beta\rangle$) can be stored in the computer memory in the form $J_\alpha[I_\alpha;p,q]$ ($J_\beta[J_\beta;p,q]$). The perturbation calculation for three-body coupling coefficients, $\langle I_\alpha|E^\alpha_{pq,rs}|J_\alpha\rangle\langle I_\beta|E^\beta_{tu}|J_\beta\rangle$, for example, is performed as follows:

Loop over I_α
  Make all non-zero $\langle I_\alpha|E^\alpha_{pq,rs}|J_\alpha\rangle$ for I_α
   Loop over I_β [I_α]
    Loop over t and u
     If $J_\beta[I_\alpha;t,u] \neq 0$ and $J_\beta[I_\alpha;t,u] \in \{I_\beta[J_\alpha]\}$, then
     do 3-body PT calculations for $\langle I_\alpha|E^\alpha_{pq,rs}|J_\alpha\rangle\langle I_\beta|E^\beta_{tu}|J_\beta\rangle$
    End loop t and u
   End loop I_β [I_α]
  End loop I_α

The other terms can be computed similarly.

The one- and two-body coupling coefficients computed in the same manner are used for the CI-based calculation for the internal terms. The vectors $\mathbf{v}_I$ in Eq. (34) are computed as σ-vectors using strings.

A more efficient algorithm has been developed by using the α and β string spaces. Let us define the total space as a product of α and β string spaces. This method is called a string product space (SPS) SCF/PT method.[13] Taking advantage of the independence of the α and β string spaces, the computational efforts can be dramatically reduced. For example, the perturbation calculation for three-body coupling coefficients, $\langle I_\alpha|E^\alpha_{pq,rs}|J_\alpha\rangle\langle I_\beta|E^\beta_{tu}|J_\beta\rangle$, is simplified as follows:

Loop over I_α
  Make all non-zero $\langle I_\alpha|E^\alpha_{pq,rs}|J_\alpha\rangle$ for I_α
   Loop over I_β (=J_β)
    do 3-body PT calculations for $\langle I_\alpha|E^\alpha_{pq,rs}|J_\alpha\rangle\langle I_\beta|E^\beta_{tu}|J_\beta\rangle$
   End loop I_β
  End loop I_α

Compared with the diagrammatic algorithm, the present scheme does not require loops over t and u. Usually, the α and β string spaces are spanned by the singly and doubly excited configurations, respectively. Thus, the total SPS consists of configurations up to quadruple excitations. The dimension of the reference function can be drastically reduced. The dimensions of CAS(14e, 14o) and CAS(18e, 18o) are 11 778 624 and 2 363 904 400, respectively, while the corresponding dimensions of SPS(14e, 14o) and SPS(18e, 18o) are 241 081 and 1 898 884. Thus, we can handle PT based on the (18e, 18o) reference functions. A numerical illustration shows that SPS-PT can describe the double-bond breaking process and treat several potential energy curves simultaneously. The excited states are also calculated very accurately by SPS-PT.

Conclusion

The convergence of the dynamical correlation is rather slow, and the accurate representation of the dynamical correlation requires high levels of excitations in the many-electron wave function and high levels of polarization functions in a basis set. The situation is, however, quite different for nondynamical correlation. The nondynamical, near-degeneracy effect converges fairly smoothly with respect to both the one-electron basis function and the many-electron wave function. This implies that the near degeneracy problem can be handled quite well even in a moderate function space. This supports the use of QCASSCF or MCSCF instead of CASSCF as a reference function in MRPT calculations. The QCAS and MCSCF methods are apparently quite poor when compared with the CASSCF, but the deficiency is largely overcome when the dynamical correlation is considered at the level of MRPT.

MRPT can handle any state, regardless of charge, spin, or symmetry with surprisingly high and consistent accuracy, supporting our use of this method as our 'standard' for treating small to medium-sized molecules.

As is well known, *ab initio* computational effort depends heavily on the system, N. This dependence is of order N^4 for SCF and is of order N^5 and higher for MRPT. The steep nonlinear cost of the conventional correlated methods has no physical origin; it is an artifact caused mainly by the use of canonical orbitals. Canonical orbitals, although conceptually and computationally convenient, destroy the local character of dynamical correlation. The development of alternative formulations based on local quantities is both feasible and desirable. The steep scaling can be reduced using local electron correlation methods. There has been continuing interest in local MRPT[14] that uses the local character of the dynamical correlation. Research in this direction is now in progress.[15]

Acknowledgments. This research was supported in part by a grant-in-aid for Scientific Research in Specially Promoted Research "Simulations and Dynamics for Real Systems" from the Ministry of Education, Science, Culture, and Sports of Japan, and by a grant from the Genesis Research Institute.

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