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Letter

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Generalized Optimized Effective Potential for Orbital Functionals and Self-Consistent Calculation of Random Phase Approximations

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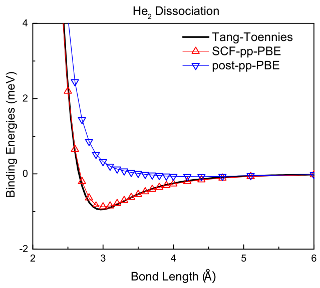
Abstract

A new self-consistent procedure for calculating the total energy with an orbital-dependent density functional approximation (DFA), the generalized optimized effective potential (GOEP), is developed in the present work. The GOEP is a non-local Hermitian potential that delivers the sets of occupied and virtual orbitals and minimizes the total energy. The GOEP optimization leads to the same minimum as does the orbital optimization. The GOEP method is promising as an effective optimization approach for orbital-dependent functionals, as demonstrated for the self-consistent calculations of the random phase approximation (RPA) to the correlation functionals in the particle-hole (ph) and particle-particle (pp) channels. The results show that the accuracy in describing the weakly interacting van der Waals systems is significantly improved in the self-consistent calculations. In particular, the important single excitations contribution in non-self-consistent RPA calculations can be captured self-consistently through the GOEP optimization, leading to orbital renormalization, without using the single excitations in the energy functional.

Graphical TOC Entry



Density functional theory (DFT)[1–5] has achieved much success in electronic structure theory. It has been widely implemented in modern quantum chemistry softwares and has made significant impacts in many fields. However, challenges remain for the DFT in describing van der Waals interaction,[6] strongly correlated systems,[7] systems having features of fractional charges and fractional spins because of the delocalization and static correlation errors.[8] In general, the accuracy of the functionals can be improved by introducing the orbital dependence into the exchange-correlation energy expression.[9] Hybrid functionals such as B3LYP[10–13] are the simplest type of orbital functionals depending on the occupied orbitals through the one-electron density matrix. For such functionals, self-consistent calculations are carried normally by solving the generalized Kohn-Sham (GKS) equations. Virtual orbitals can be used in the correlation energy functionals as in the second order Møller-Plesset (MP2),[14] double hybrid (DH) functionals,[15–20] and random-phase approximations (RPA).[21–32] Orbital dependent functionals can also be more complicated because of the lack of invariance with respect to unitary rotations, such as the self-interaction correction (SIC)[33] and Koopmans-compliant (KC) functionals.[34]

The calculations with functionals depending on virtual orbitals are usually performed in a post-SCF procedure, which will lead to non-variational total energies and unrelaxed orbitals.[18] A self-consistent field (SCF) calculation is desired for higher accuracy. The optimized effective potential (OEP)[35–39] and orbital optimization (OO)[40] are widely used for SCF calculations. For the OEP, it can provide accurate local exchange-correlation potentials and has been used extensively for functionals of occupied orbitals, such the exact exchange and hybrid functionals. However, the ground state energies are not improved for functionals depending on virtual orbitals.[41–43] The reason for this failure is that the orbitals are only optimized in the space of v-representable densities by a local potential, the OEP, rather than the whole space. In contrast, the orbitals from OO are optimized in the whole space. Both MP2 and DH functionals have been self-consistently calculated with OO.[44,45] But no OO has been developed for the RPA functionals.

Here we developed a new optimization method, the generalized optimized effective potential (GOEP) method to achieve the SCF calculations for general orbital-dependent functionals. The GOEP is a non-local potential in space,

$$v_s^{\mathrm{GOEP}}(\mathbf{r},\mathbf{r}') = \sum_{pq} \langle \mathbf{r}|\phi_p\rangle (v_s^{\mathrm{GOEP}})_{pq} \langle \phi_q|\mathbf{r}'\rangle + h.c. \tag{1}$$

where p and q are GOEP orbital indices. The orbitals $\{\phi_p\}$ are defined to be eigenvectors of the GOEP non-local Hamiltonian $h_s^{\mathrm{GOEP}} = t + v_s^{\mathrm{GOEP}}$. Thus unlike the local OEP method, the density matrix obtained from the GOEP is fully flexible because there is no restriction of the locality in real space of the potential within the GOEP. Note that the mapping of h_s^{GOEP} to the non-interacting density matrix, or the set of occupied and virtual orbitals is many-to-one. For example, within the occupied space, the diagonal elements ϵ_i of h_s^{GOEP} can vary arbitrarily as long as they are less than all the diagonal elements in the virtual space. Therefore, the eigenvalues of the GOEP do not have physical meanings. They only partition the space into occupied and virtual spaces during the optimization to ensure the occupied and virtual spaces will not cross. This many-to-one mapping does not pose any issue, because the unique non-interacting density matrix or the set of GOEP orbitals is what determines the total energy. We have proved that the optimization of an orbital functional with respect to the GOEP Hamiltonian is equivalent to OO (see Section 1 in SI[46]). Computationally, it is convenient to perform the GOEP in the eigenvector, or GOEP orbital space. Since all orbitals are determined uniquely by h_s^{GOEP}, a total energy orbital functional, E, is thus a functional of h_s^{GOEP}. The energy derivatives of GOEP off-diagonal elements can be expressed as the following,[46]

$$\frac{\partial E}{\partial (v_s^{\mathrm{GOEP}})_{pq}} = \frac{\langle \phi_q | \frac{\delta E}{\delta \phi_p^*}\rangle - \langle \left(\frac{\delta E}{\delta \phi_q}\right)^* |\phi_p\rangle}{\epsilon_p - \epsilon_q}. \tag{2}$$

We use the index $i/a/p$ to represent occupied/virtual/general orbitals. Notice that this expression assumes non-degenerate orbitals. Since the GOEP is Hermitian, $\partial E/\partial (v_s^{\mathrm{GOEP}})_{qp}$

will be the complex conjugate of $\partial E/\partial(v_s^{\mathrm{GOEP}})_{pq}$. At the stationary point, we have

$$\frac{\partial E}{\partial(v_s^{\mathrm{GOEP}})_{pq}} = 0. \tag{3}$$

The change in the GOEP, $\delta v_s^{\mathrm{GOEP}}$, is equivalent to the change in the Hamiltonian $\delta h_s^{\mathrm{GOEP}}$. For orbital functionals with invariance to unitary rotations within both occupied and virtual spaces, we only need to consider the variation of the $(h_s^{\mathrm{GOEP}})_{ia}$ block, because the variation of the $(h_s^{\mathrm{GOEP}})_{ij}$ and $(h_s^{\mathrm{GOEP}})_{ab}$ blocks only lead to unitary rotations within the occupied and virtual spaces. In this case, degeneracy within the occupied or virtual space in Eq. (2) does not matter because the denominator in Eq. (2), $\epsilon_a - \epsilon_i$, cannot be zero if the occupied and virtual spaces are not mixed.

Now we apply the GOEP method to the RPA for the correlation energy functional. The RPA can be developed in two channels: particle-hole (ph) channel leads to ph-RPA;[21–28] particle-particle (pp) and hole-hole (hh) channels lead to pp-RPA.[29,30] The ph-RPA is a fully non-local functional of density and can describe van der Waals interactions, crystalline solids, surface adsorption;[27] and furthermore the pp-RPA meets the flat-plane condition for systems with fractional charges and spins.[29] RPA calculations are usually performed in a post-SCF fashion. Despite the correct dissociation limit of diatomic systems with ph-RPA, the lack of SCF will lead to problems in the intermediate distance.[47] Although RPA has been self-consistently calculated with the local OEP, the binding energy curves are not improved compared to those from post-SCF calculations.[41,42] In this work, we aim to explore the SCF calculations of RPA correlation functionals in both the ph-channel and the pp-channel with self-consistent calculations and without the local OEP restriction. The total energy expression is

$$E^{\mathrm{Total}} = E^{\mathrm{HF}}[\rho_s] + E_c^{\mathrm{RPA}}[\{\phi_p\}]. \tag{4}$$

where $\{\phi_p\}$ are the canonical orbitals of the GOEP and ρ_s is the reference density matrix consisting of the occupied GOEP orbitals,

$$\rho_s = \sum_i |\phi_i\rangle\langle\phi_i| \tag{5}$$

The total energy is calculated by combining the HF energy and RPA correlation energy, which are both evaluated with the GOEP orbitals. The RPA correlation energy can be formulated from the solution of the generalized eigenvalue problem (see SI Eq.(32,34)[46]). The ph-RPA correlation energy can be expressed as

$$E_c^{\text{ph-RPA}} = \frac{1}{2}\left(\sum_{n>0}\omega_n^N - \mathrm{Tr}\mathbf{A}\right), \tag{6}$$

and that of the pp-RPA is

$$E_c^{\text{pp-RPA}} = \sum_n \omega_n^{N+2} - \mathrm{Tr}\mathbf{A}. \tag{7}$$

where ω_n are the neutral excitation energies, ω_n^{N+2} are two-electron addition energies and $\mathbf{A}$ represents matrices in the RPA eigenvalue equations.[25,29] Note that the non-canonical form of the generalized pp-RPA eigenvalue problem is used.[48] Because this expression is invariant with rotations as we have shown,[46] we can perform the optimization in the occupied-virtual space only. The ph-RPA can be derived within the framework of DFT via the adiabatic-connection fluctuation-dissipation (ACFD) theorem;[23,49–51] the pp-RPA can also be derived in the equivalence of ACFD in the pairing channel.[29] In all applications, a density functional approximation (DFA) is adopted as the reference DFA functional, the KS or GKS orbitals of which are used for constructing the RPA correlation energy.

It is important to realize that in the eigenvalue equations for either ph-RPA or pp-RPA, as shown in Section 2 of SI,[46] a DFA is used, explicitly through the KS or GKS Hamiltonians defined as the functional derivatives of the energy with respect to the density matrix. The use of DFA cannot be replaced with the GOEP because the GOEP does not provide meaningful orbital energies. The second-order functional derivatives of the DFA is also involved in the energy gradient for the GOEP calculations(see Section 3 in SI[46]). The full process of this optimization is as follow: (1) Carry out an SCF calculation with a certain DFA; (2) Build the RPA matrix and calculate the total energy perturbatively; (3) Calculate the gradient $\delta E/\delta h_s^{\mathrm{GOEP}}$ and update h_s^{GOEP} with the gradient information; (4) Diagonalize the Hamiltonian h_s^{GOEP} to obtain the canonical orbitals $\{\phi_p\}$; (5) Go to step 2 until both total energy and gradient converge.

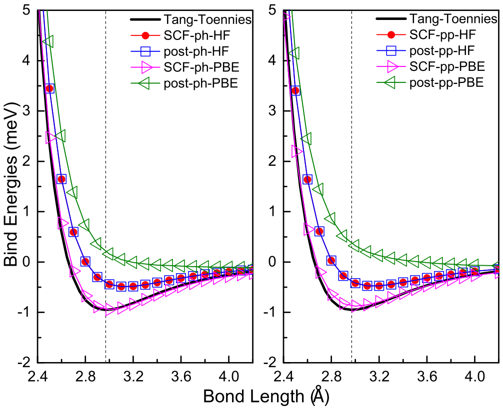


Figure 1: Binding energy curves for He_2 with both ph and pp-RPA. The reference curve is from Tang and Toennies.[52] The dash lines refer to the bonding distance. SCF-ph-HF stands for the ph-RPA with HF reference in a self-consistent procedure. Calculations are done in QM^{4}D.[53]

We first tested van der Waals systems. Figure 1 shows the binding energy curves with both ph and pp-RPA for He_2. The post-SCF results have the correct dissociation limit, however, at the intermediate distance it is underbinded. With the Hartree-Fock (HF) reference, the SCF calculation does not change from the post-SCF result. In contrast, both curves of SCF-ph-PBE and SCF-pp-PBE are improved significantly from the post-SCF results and in excellent agreement with the reference. This is a major difference from the SCF-RPA calculations carried out with the local OEP, where the converged total energies are not much changed from the post-SCF calculations,[42] highlighting the importance of full optimization with the GOEP.

Since the total energy contains several energy contributions, we decompose the total

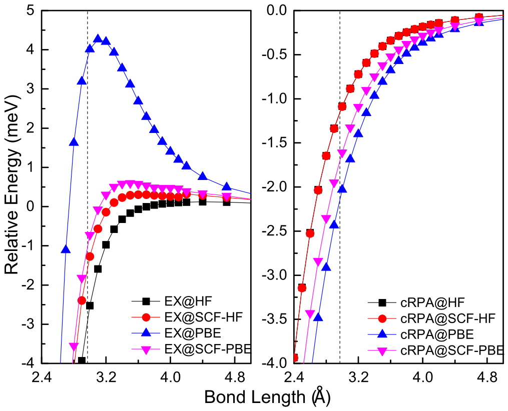


Figure 2: Decomposition of exchange and correlation energies from the SCF-ph-RPA and post-ph-RPA result. The dash line refers to the equilibrium bond length.

energy to investigate which part is improved in the GOEP calculation. In the following notations, E@F refers to the energy E evaluated with the canonical orbitals of the reference DFA functional F. And E@SCF-F refers to the energy E evaluated with the GOEP orbitals, where F is the DFA reference in the RPA functional. In this case, the total energy of a post-SCF calculation is further decomposed into

$$E^{\text{Total}} = E^{\text{T}}@F + E^{\text{ext}}@F + E^{J}@F + E^{\text{EX}}@F + E^{\text{RPA}}@F, \tag{8}$$

where E^{T}, E^{ext}, E^{J}, E^{EX}, E^{RPA} refer to the kinetic energy, external energy, Coulomb energy, exchange energy, and RPA correlation energy, respectively. In post-SCF RPA calculations, Ren and coworkers[54] shows that the exchange-correlation part is better described in a hybrid way with two sets of orbitals from HF and PBE[55] calculations,

$$E^{\text{xc}} = E^{\text{EX}}@\text{HF} + E^{\text{RPA}}@\text{PBE}. \tag{9}$$

To develop a clear understanding of the effects of full orbital optimization as in the GOEP, we analyzed the exchange and correlation energies with different methods and plotted the results in Figure 2. For post-SCF calculations, HF reference can provide better exchange energy, but the correlation energy has large error. PBE reference provides accurate correlation energy, however, the exchange energy has a 4 meV barrier in the intermediate range. The self-consistent calculation with HF reference does not change the binding energy as E^{EX}@SCF-HF and E^{RPA}@SCF-HF are almost the same with E^{EX}@HF and E^{RPA}@HF. But for the self-consistent calculation with PBE reference, E^{RPA}@SCF-PBE keeps the accuracy of E^{RPA}@PBE, while the exchange energy, E^{EX}@SCF-PBE, is corrected towards E^{EX}@HF. Therefore, the binding energy curve is significantly improved with the GOEP. The failure of the post-SCF RPA in the intermediate distance has been attributed to the neglect of the contribution from single excitations (SE).[54]

Whether there is a SE contribution to the RPA approximate correlation energy depends on the derivation. In the usual derivation of the ACFD theory, when the electron density is kept constant along the adiabatic connection, the singles contribution does not appear.[23,49,51,56] If the density is not kept constant along the adiabatic connection, then the singles contributes to the correlation energy.[56] With the commonly used post-SCF RPA scheme, most molecular systems are underbinded systematically. By adding the SE perturbatively, it has been shown that the SE contribution to the energy improves the result significantly.[54] However, in our GOEP calculations, the binding energy curves are improved greatly, without adding the SE contribution. We now analyze the SE within the GOEP. The SE contribution to the second-order correlation energy can be expressed as (see Section 4 in SI)[46,51,57]

$$E_c^{\mathrm{SE}} = \sum_i^{\mathrm{occ}} \sum_a^{\mathrm{vir}} \frac{|\langle \phi_i | f^{\mathrm{HF}} - h_s^{\mathrm{GOEP}} | \phi_a \rangle|^2}{\tilde{\epsilon}_i - \tilde{\epsilon}_a}. \tag{10}$$

where $\{\phi_i\}$ are the orbitals of the non-local GOEP Hamiltonian h_s^{GOEP}. The orbital energies, $\tilde{\epsilon}_i$ and $\tilde{\epsilon}_a$, are from the rotated GOEP orbitals that diagonalize the occupied and virtual subspaces of the reference KS or GKS Hamiltonian h_s from the DFA:

$$\begin{aligned} (h_s)_{ij} &= \delta_{ij}\tilde{\epsilon}_i; \\ (h_s)_{ab} &= \delta_{ab}\tilde{\epsilon}_a. \end{aligned} \tag{11}$$

Since $\{\phi_i\}$ are the eigenvectors of h_s^{GOEP}, so $\langle\phi_i|h_s^{\mathrm{GOEP}}|\phi_a\rangle$ will be zero. The only existing term on the numerator is thus the single-particle HF Fock operator, $|\langle\phi_i|f^{\mathrm{HF}}|\phi_a\rangle|^2$.

The absolute values of the 2nd-order SE contribution were plotted with and without the SCF in Figure 3(c). At the intermediate range, the 2nd-order SE contribution from the PBE is -0.5 meV, while that from the GOEP is only -0.008 meV. Moreover, the 2nd-order SE contribution from the GOEP is almost 0 along all distances. A test set of atoms also shows a significant reduction of the 2nd-order SE with the GOEP (Table 1). This reduction is caused by the orbital renormalization. Since the HF energy is the predominant term in the total energy expression (Eq.(4)), the optimized orbitals within the GOEP bear great similarity to HF orbitals and the term $|\langle\phi_i|f^{\mathrm{HF}}|\phi_a\rangle|^2$ will approach zero. Therefore, at the stationary point, the effect of 2nd-order SE is mostly brought into the total energy. As a consequence, the optimal orbitals provide the much improved description for binding energy curves. A diagrammatic representation of this renormalization process is shown in Figure 3, from (a) to (b).

Table 1: Contribution of the 2nd-order SE for atoms with simple shell structures (Units: meV).

	H	He	Li	Be	Ne	Na	Mg	Ar
PBE	-0.5	-0.2	-19.5	-22.1	-22.4	-47.0	-54.5	-60.0
GOEP	0	-0.02	-0.1	-1.0	-3.9	-1.2	-2.9	-1.3

While the second-order SE was shown to be important for post-SCF calculations with a semilocal functional (e.g. PBE) as reference,[54,56] it will be ill-behaved for systems with small energy gaps, such as the dissociation limit because the gap of the molecule will approach zero. Thus higher order diagrams are required in this situation and the correction to the correlation energy is named renormalized SE (rSE).[54] However, in the SCF calculations with GOEP method, no ill behavior is found at the dissociation limit because the second-order SE is not included. It is absorbed into the total energy through the orbital renormalization in the self-consistent calculation. This is a key result from present SCF calculations of RPA functionals - we can have the RPA total energy functional with good accuracy and without

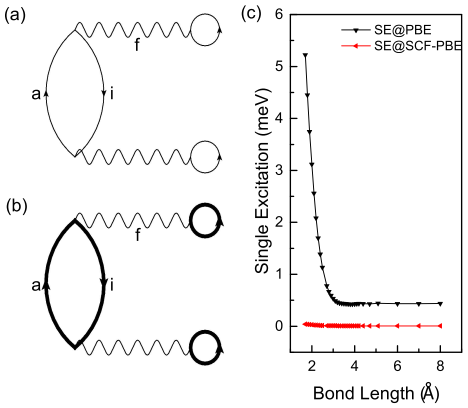


Figure 3: (a),(b) Goldstone diagrammatic representation of the 2nd-order SE contribution before and after the GOEP. (c) 2nd-order SE contribution comparison between post-SCF-RPA and SCF-RPA of He_2. Notice that the absolute value of the SE contribution is taken in (c).

the SE contribution, just as given in the derivation from ACFD with density being kept constant.

A more challenging case, Be_2, was also tested. The commonly used CCSD(T) method overbinds at the equilibrium region. And both ph and pp-RPA not only underbind, but show an unphysical local maximum beyond the binding region as well. Previous work suggested that this behavior may be caused by the lack of SCF in the calculation.[47] Moreover, this unphysical maximum was also observed in the SCF calculations with the local OEP method.[42] This now can be explained from Eq.10: orbitals from the local OEP are not fully optimized because of the local potential restriction, thus the 2nd-order SE correction is still required for RPA. Therefore, the SCF-RPA calculations with the GOEP is desirable for systems like Be_2 because of the orbital renormalization. The result shows that although the GOEP does not improve the binding length with the pp-RPA significantly, it completely eliminates the unphysical local maximum and corrects the binding energy(Figure 4). From the exchange energy decomposition, we notice that different from He_2, the barrier of E^{EX}@PBE curve emerges beyond the equilibrium bond length, which is exactly the region where the unphysical maximum (marked in the shaded area) occurs. The SCF calculation brings down this barrier so that the binding energy curve is corrected.

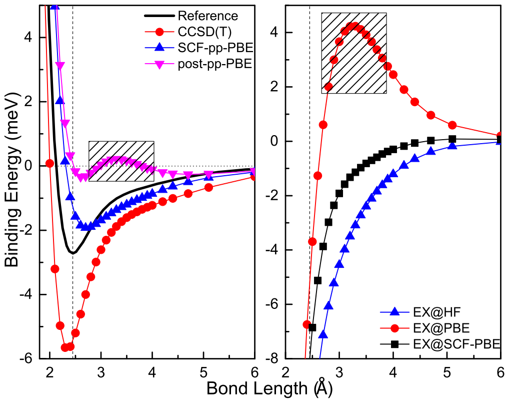


Figure 4: Left: binding energy curve of Be_2 with the pp-RPA. Right: relative exchange energy of different methods. The dash line refers to the equilibrium bond length. The reference is from.[58]

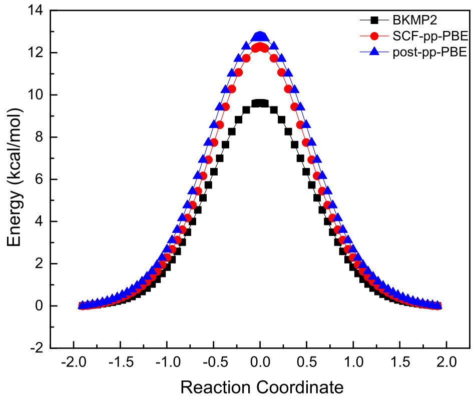


Figure 5: The potential energy surface of H + H_2 exchange reaction. The reference BKMP2 potential energy surface is from.[59]

We finally consider the H + H_2 exchange reaction with the GOEP SCF calculations, along with the post-SCF pp-RPA. The reaction energy curve is shown in Figure 5. The pp-RPA overestimates the reaction barrier by 4 kcal/mol. The SCF calculation brings down this barrier by 0.5 kcal/mol. And the reaction energy profile is closer to the reference with the SCF procedure. In addition, several bonded systems, such as He_2^+, H_2 and LiH, were tested. These systems do not show significant improvement with the SCF in comparison with the post-SCF results. In all cases, SE contributions are reduced with the SCF calculation. For these bonded systems, the error of the RPA originates mostly from the inherent error of the RPA functional itself. One explanation is that for bonded systems, the correlation energy is mainly contributed from double excitations.[57] It has been proved that the ph-RPA is equivalent to ring couple-cluster doubles (CCD)[24] and the pp-RPA is equivalent to ladder CCD.[30,60] Neither includes full diagrams of the doubles.

To summarize, we have developed a new optimization method, GOEP, to achieve SCF calculations for general orbital-dependent functionals. We applied the GOEP method to ph- and pp-RPA correlation energy functional. We have shown that for van der Waals systems, SCF is of great importance and the SCF-RPA using the GOEP performs well. It significantly improves the accuracy of the binding energy curves: the underbinded feature of He_2 is corrected and the unphysical local maximum of Be_2 is totally eliminated. The energy decomposition reveals that the exchange energy, E^{EX}@SCF-PBE, is much improved from E^{EX}@PBE. And the effect of 2nd-order SE contribution is brought into the total energy functional with the SCF calculation through the orbital renormalization, without using the single excitations in the energy functional. This is significant because the SE part of the functional can become singular for systems with zero or small gaps. Our results strongly support using the RPA correlation energy functional without the SE term in SCF calculations to achieve good accuracy and eliminate the possible singularity of the SE term. We conclude that the GOEP is a promising tool to achieve SCF calculation for orbital-dependent functionals.

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Supporting Information Available

The Supplementary Information is available at ... (to be edited by the editor.).

More introductions to the GOEP; The proof of unitary invariance of the RPA; The derivation of the gradient needed for the optimization; The derivation of the SE; Some additional results.

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