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Line-integral formulas for exchange and correlation potentials separately

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Formal *separate* expressions for the exact exchange and correlation potentials v_x and v_c are extracted from the formal line-integral expression of Holas and March for the whole exact exchange-correlation potential. Relations for the components of v_c are extracted for each order in the electron-electron repulsion coupling constant, through use of the coupling-constant expansion of Görling and Levy for the external potential. The resultant expressions for v_c and v_x are separately path independent. The difference between v_x and the Harbola-Sahni approximation to it, v_x^{HS}, is identified as arising from a first-order contribution to the kinetic-energy density tensor. It is shown that this small correction to v_x^{HS}, which we express in terms of perturbation theory, would be precisely *zero* if the Kohn-Sham determinant were identical to the Hartree-Fock determinant for the same density. In other words, v_x^{HS} would equal v_x if the optimized effective potential determinant were the same as the Hartree-Fock determinant. This same property is shared by the Slater potential. [S1050-2947(97)06503-7]

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I. INTRODUCTION

Recently, Holas and March [1] have derived a formal line-integral expression for the exact density-functional exchange-correlation potential $v_{xc}([n];\vec{r})$. For the purpose of its separation into the exchange and correlation contributions, we shall here formulate the Holas-March [1] expression as a function of the electron-electron repulsion coupling constant λ, in order to develop relations which are associated with each order in λ. The first-order one yields a formal expression for the exact exchange potential, $v_x([n];\vec{r})=\delta E_x[n]/\delta n(\vec{r})$. This exchange expression identifies the correction to the Harbola-Sahni [2] approximation to v_x. We shall show that this correction, which is small in atoms, is zero if the Hartree-Fock single determinant, for the given density, were exactly the same as the Kohn-Sham single determinant for the same density. These determinants are known to be generally quite close in atoms [3].

Higher-order terms in λ yield formal expressions for the corresponding parts of the exact correlation potential, $v_c([n];\vec{r})=\delta E_c[n]/\delta n(\vec{r})$. It is especially important to have knowledge of a separate exact expression for v_c when one employs an approximation to v_x which does not include line integrals or if one attaches an approximation for v_c to an exact optimized effective potential (OEP) calculation or to a Hartree-Fock calculation. Consequently, an explicit formal expression for v_c is presented here.

II. DERIVATION OF SEPARATE EXPRESSIONS FOR v_x AND v_c

In accordance with the constrained-search approach, define $\Psi_{[n]}^{\lambda}$ as that antisymmetric wave function which yields the density n and minimizes $\langle T+\lambda \hat{V}_{ee}\rangle$.

Here, for an N-electron system in atomic units,

$$\hat{T}=\sum_{i=1}^{N} -\frac{1}{2}\nabla_i^2$$

and

$$\hat{V}_{ee}=\sum_{i=1}^{N-1}\sum_{j=i+1}^{N}|\vec{r}_i-\vec{r}_j|^{-1}.$$

The exchange energy associated with $\Psi_{[n]}^{\lambda}$ is

$$E_x^{\lambda}[n]\equiv\langle\Psi_{[n]}^{0}|\lambda\hat{V}_{ee}|\Psi_{[n]}^{0}\rangle-\lambda\int\int\frac{n(\vec{r}_1)n(\vec{r}_2)}{|\vec{r}_1-\vec{r}_2|}d^3r_1d^3r_2 =\lambda E_x[n], \tag{1}$$

while the corresponding correlation energy is

$$E_c^{\lambda}[n]=\langle\Psi_{[n]}^{\lambda}|\hat{T}+\lambda\hat{V}_{ee}|\Psi_{[n]}^{\lambda}\rangle-\langle\Psi_{[n]}^{0}|\hat{T}+\lambda\hat{V}_{ee}|\Psi_{[n]}^{0}\rangle. \tag{2}$$

Next, define v_{xc}^{λ} through

$$v_{xc}^{\lambda}([n];\vec{r})=v_x^{\lambda}([n];\vec{r})+v_c^{\lambda}([n];\vec{r}), \tag{3}$$

where $v_x^{\lambda}([n];\vec{r})=\delta E_x^{\lambda}[n]/\delta n(\vec{r})$ and $v_c^{\lambda}([n];\vec{r})=\delta E_c^{\lambda}[n]/\delta n(\vec{r})$. From Eq. (1), observe that

$$v_x^{\lambda}([n];\vec{r})=\lambda v_x([n];\vec{r}) \tag{4}$$

and from Görling and Levy [4,5], note that

$$v_c^{\lambda}([n];\vec{r})=\lambda^2 v_{c,2}([n];\vec{r})+\lambda^3 v_{c,3}([n];\vec{r})+\cdots. \tag{5}$$

The essence of the development which follows depends on the fact that v_c^{λ} commences in *second order*, while v_x^{λ} commences in *first order*.

We now observe that Eq. (2.29) of Holas and March [1] can be viewed as an expression for v_{xc}^{λ} with $\lambda=1$. In other words, we view λ as simply determining the square of the charge on the electron. It follows that Eq. (2.29), for all $\lambda\geqslant 0$, becomes

$$v_{xc}^{\lambda}([n];\vec{r}_0)=-\int_{\infty}^{\vec{r}_0}d\vec{r}\cdot\vec{f}_{xc}([u^{\lambda},n,\rho^0,\rho^{\lambda},\Gamma^{\lambda}];\vec{r}), \tag{6}$$

where, using a slightly different notation than in Ref. [1] for simplicity of exposition,

$$\vec{f}_{xc}([u^{\lambda},n,\rho^{0},\rho^{\lambda},\Gamma^{\lambda}];\vec{r})=\Big\{\vec{z}([\rho^{0}];\vec{r})-\vec{z}([\rho^{\lambda}];\vec{r})+\int d^{3}r'[\vec{\nabla}u^{\lambda}(\vec{r},\vec{r}\,')][n(\vec{r})n(\vec{r}\,')-2\Gamma^{\lambda}(\vec{r},\vec{r}\,')]\Big\}n^{-1}(\vec{r}). \qquad (7)$$

In expressions (6) and (7),

$$u^{\lambda}(\vec{r},\vec{r}\,')=\lambda|\vec{r}-\vec{r}\,'|^{-1}, \qquad (8)$$

$\Gamma^{\lambda}_{[n]}(\vec{r},\vec{r}\,')$ is the diagonal part of the second-order density matrix of $\Psi^{\lambda}_{[n]}$, and $\rho^{\lambda}_{[n]}(\vec{r},\vec{r}\,')$ is its first-order density matrix. Here,

$$\rho^{\lambda}_{[n]}(\vec{r},\vec{r}\,')=N\int\cdots\int\Psi^{\lambda}_{[n]}(\vec{r}\sigma,\vec{x}_{2},\ldots,\vec{x}_{N})\Psi^{\lambda *}_{[n]}(\vec{r}\,'\sigma,\vec{x}_{2},\ldots,\vec{x}_{N})d\sigma d\vec{x}_{2}\cdots d\vec{x}_{N}$$

and

$$\Gamma^{\lambda}_{[n]}(\vec{r},\vec{r}\,')=\frac{N(N-1)}{2}\int\cdots\int\Psi^{\lambda}_{[n]}(\vec{r}\sigma,\vec{r}\,'\sigma',\vec{x}_{3},\ldots\vec{x}_{N})\Psi^{\lambda *}_{[n]}(\vec{r}\sigma,\vec{r}\,'\sigma',\vec{x}_{3},\ldots,\vec{x}_{N})d\sigma d\sigma' d\vec{x}_{2}\cdots d\vec{x}_{N}.$$

Hence $\rho^{0}_{[n]}(\vec{r},\vec{r}\,')$ is the first-order density matrix of the noninteracting (Kohn-Sham) [6] single determinant $\Psi^{0}_{[n]}$. Further, the vector field $\vec{z}$ is now given in terms of ρ^{λ}. In other words,

$$z_{\alpha}([\rho^{\lambda}];\vec{r})=2\sum_{\beta}\frac{\partial}{\partial r_{\beta}}t_{\alpha\beta}([\rho^{\lambda}];\vec{r}), \qquad (9)$$

with

$$t_{\alpha\beta}([\rho^{\lambda}];\vec{r})=\frac{1}{4}\left(\frac{\partial^{2}}{\partial r'_{\alpha}\partial r''_{\beta}}+\frac{\partial^{2}}{\partial r'_{\beta}\partial r''_{\alpha}}\right)\rho^{\lambda}(\vec{r}\,',\vec{r}\,'')\bigg|_{\vec{r}\,'=\vec{r}\,''=\vec{r}}. \qquad (10)$$

To arrive at our first desired result, in Eqs. (6) and (7) employ relations (3)–(5) and (8), together with

$$\Gamma^{\lambda}_{[n]}=\Gamma^{0}_{[n]}+\lambda\Gamma^{c}_{1,[n]}+\lambda^{2}\Gamma^{c}_{2,[n]}+\cdots \qquad (11)$$

and

$$\rho^{\lambda}_{[n]}=\rho^{0}_{[n]}+\lambda\rho^{c}_{1,[n]}+\lambda^{2}\rho^{c}_{2,[n]}+\cdots. \qquad (12)$$

Couple the linear terms in λ to obtain

$$v_{x}([n];\vec{r}_{0})=-\int_{\infty}^{\vec{r}_{0}}d\vec{r}\cdot\vec{f}_{x}, \qquad (13)$$

where

$$\vec{f}_{x}=\Big\{\int d^{3}r'[\vec{\nabla}(|\vec{r}-\vec{r}\,'|^{-1})][n(\vec{r})n(\vec{r}\,')-2\Gamma^{0}(\vec{r},\vec{r}\,')]-\vec{z}([\rho^{c}_{1}];\vec{r})\Big\}n^{-1}(\vec{r}) \qquad (14a)$$

or

$$v_{x}([n];\vec{r}_{0})=v_{x}^{\mathrm{HS}}([n];\vec{r}_{0})+\int_{\infty}^{\vec{r}_{0}}d\vec{r}\cdot\vec{z}([\rho^{c}_{1}];\vec{r})n^{-1}(\vec{r}). \qquad (14b)$$

The existence of $\vec{z}([\rho^{c}_{1}];\vec{r})$ is responsible for the difference between the exact v_{x} and v_{x}^{HS} the Harbola-Sahni approximation to v_{x}. Hence

$$g([n];\vec{r}_{0})=\int_{\infty}^{\vec{r}_{0}}d\vec{r}\cdot\vec{z}([\rho^{c}_{1}];\vec{r})n^{-1}(\vec{r}) \qquad (15)$$

is the correction to the Harbola-Sahni expression. Since Eq. (14) represents an exact expression for v_{x}, its value does not vary with the particular path chosen for the integration, while v_{x}^{HS} and its correction in Eq. (15), taken separately, may, depending upon the situation, vary with the integration path.

To determine v_{x}^{HS} one requires knowledge of the off-diagonal elements, as a functional of its diagonal density $n(\vec{r})$, of the noninteracting first-order density matrix $\rho^{0}_{[n]}$ in order to construct $\Gamma^{0}_{[n]}$. While this information is available [7,8] to all orders in a perturbation theory based on a one-body potential $v_{s}(\vec{r})$, we have not, to date, been able to sum up the resultant infinite series except in the limit when $v_{s}(\vec{r})$ varies slowly in space [7,8]. In Eq. (12), the term in $\rho^{\lambda}(\vec{r},\vec{r}\,')$, which is of order 1 in λ, is required to calculate the kinetic tensor correction to v_{x}^{HS}. This term, as already noted, suffices, at least in principle, to eliminate any path dependence from the resultant exchange-only potential in density-functional theory.

For the purpose of helping to approximate them, terms in higher orders of λ can be coupled. For instance, for the correlation potential, the coupling of second-order terms gives

$$v_{c,2}([n];\vec{r}_{0})=-\int_{\infty}^{\vec{r}_{0}}d\vec{r}\cdot\vec{f}_{c,2}, \qquad (16)$$

where

$$\vec{f}_{c,2}=-2\left\{\int d^3r'[\vec{\nabla}|\vec{r}-\vec{r}'|^{-1}]\Gamma_1^c(\vec{r},\vec{r}') + \vec{z}([\rho_2^c];\vec{r})\right\}n^{-1}(\vec{r}). \tag{17}$$

[Note that $v_{c,2}$ is [4,5] the functional derivative of $\lim_{\gamma\to\infty}E_c[n_\gamma]$, where $n_\gamma(x,y,z)=\gamma^3 n(\gamma x,\gamma y,\gamma z)$.] For this reason, $\int n(\vec{r})\vec{r}\cdot\vec{\nabla}v_{c,2}([n];\vec{r})d^3r=0$.

The *whole* correlation component v_c^λ of v_{xc}^λ is obtained by subtracting expression (13) from expression (6). At $\lambda=1$, this gives

$$v_c([n];\vec{r}_0)=-\int_\infty^{\vec{r}_0} d\vec{r}\cdot\vec{f}_c, \tag{18}$$

where

$$\vec{f}_c=\vec{z}([\rho^0+\rho_1^c-\rho^1];\vec{r})n^{-1}(\vec{r}) + 2\left[\int d^3\vec{r}'[\vec{\nabla}|\vec{r}-\vec{r}'|^{-1}][\Gamma^0(\vec{r},\vec{r}')-\Gamma^1(\vec{r},\vec{r})]\right]n^{-1}(\vec{r}) \tag{19}$$

and where $\vec{z}[\rho^0+\rho_1^c-\rho^1]=\vec{z}[\rho^0]+\vec{z}[p_1^c]-\vec{z}[\rho^1]$. In expression (19), ρ^1 and Γ^1 refer to the density matrices at full charge, $\lambda=1$. [Observe that since both v_x and v_c are exact, it follows that the right-hand sides are path independent in both expressions (13) and (18).]

III. REQUIREMENTS FOR ρ^λ AND Γ^λ

We here list several requirements for approximating ρ^λ and Γ^λ. First, path independence is certainly a requisite with either expression (13) or (18). Next, constraints immediately follow from the fact that the density of ρ^λ and Γ^λ is n and therefore independent of λ. Consequently, in expression (19), $\int d^3r'[\Gamma^0(\vec{r},\vec{r}')-\Gamma^1(\vec{r},\vec{r}')]=0$, and, in expressions (11) and (12), we note that $\rho_i^c(\vec{r},\vec{r})=0$ and $\int\Gamma_i^c(\vec{r},\vec{r}')d^3r'=0$.

We now observe that previous work [5] on the behavior of the kinetic energy at very small λ, which utilizes the fact that $\rho^0(\vec{r},\vec{r}')$ is that first-order density matrix which minimizes the kinetic energy at fixed n, dictates that $-\frac{1}{2}\int\nabla^2\rho_{1,\,[n]}^c(\vec{r},\vec{r}')d^3r=0$ (or $\int d^3r\Sigma_\beta t_{\beta\beta}([\rho_{1,\,[n]}^c];\vec{r})=0$). Further, the fact [5] that $\lim_{\gamma\to\infty}E_c[n_\gamma]>-\infty$ implies, by the Ghosh-Parr relation [9], that $\int\nabla^2\rho_{2,[n]}^c(\vec{r},\vec{r}')=\int\int\Gamma_{1,[n]}^c(\vec{r},\vec{r}')|\vec{r}-\vec{r}'|^{-1}d^3r\,d^3r'$. Moreover, the required uniform scaling property for g in Eq. (15) is [9,10]

$$g([n_\gamma];\vec{r}_0)=\gamma g([n];\gamma\vec{r}_0),$$

and [9–12] g also satisfies $\int d^3r\,n(\vec{r})\vec{r}\cdot\vec{\nabla}g([n];\vec{r})=0$.

It should prove useful to study $\rho_{[n]}^\lambda(\vec{r},\vec{r}')$ in terms of its natural orbital expansion [13], which is

$$\rho^\lambda(\vec{r},\vec{r}')=\sum_i d_i^\lambda\chi_i^{\lambda*}(\vec{r}')\chi_i^\lambda(\vec{r}), \tag{20}$$

where the d_i^λ are the occupation numbers and the χ_i^λ are the natural orbitals. In Eq. (20),

$$d_i^\lambda=1+\lambda d_{i,1}+\cdots,\quad i\leqslant N,$$

$$d_i^\lambda=\lambda d_{i,1}+\cdots,\quad i>N,$$

and for $i\leqslant N$, $\chi_i(\vec{r})=\varphi_i(\vec{r})+\lambda L_{i,1}(\vec{r})+\cdots$, where the φ_i are the occupied Kohn-Sham orbitals of n.

We now find an explicit expression for ρ_i^c in Eqs. (15) and (19), in terms of Kohn-Sham orbitals. For simplicity of notation, let us assume that everything is real and now expand $\Psi_{[n]}^\lambda$ as $\Psi_{[n]}^\lambda=\Psi_{[n]}^0+\lambda\Psi_{1,[n]}+\lambda^2\Psi_{2,[n]}+\cdots$, where $\rho_{1,[n]}^c$ in Eq. (12) is the transition first-order density matrix of $\Psi_{[n]}^0\Psi_{1,[n]}+\Psi_{1,[n]}\Psi_{[n]}^0$ etc. From previous studies [4], we know that $\Psi_{1,[n]}$, the first-order wave function, is given by

$$\Psi_{1,[n]}=-\sum_{k>0}\frac{\langle\Phi_k|\hat{V}_{ee}-\hat{V}_{xu}|\Phi_0\rangle}{E_k-E_0}\Phi_k, \tag{21}$$

where

$$\hat{V}_{XU}=\sum_{i=1}^N v_x([n];\vec{r}_i)+\sum_{i=1}^N\int\frac{n(\vec{r})}{|\vec{r}_i-\vec{r}|}d^3r.$$

Also, the Φ_k are the single-determinant eigenstates of that noninteracting Kohn-Sham Hamiltonian for which $\Phi_0=\Psi_{[n]}^0$ is the ground-state single determinant. The E's are sums of Kohn-Sham orbital energies. It follows that

$$\rho_{1,[n]}^c(\vec{r},\vec{r}')=-\sum_{k>0}\frac{\langle\Phi_k|\hat{V}_{ee}-\hat{V}_{xu}|\Phi_0\rangle}{(E_k-E_0)}\times[\gamma_{k,0}(\vec{r},\vec{r}')+\gamma_{k,0}(\vec{r}',\vec{r})], \tag{22}$$

where

$$\gamma_{k,0}(\vec{r}|\vec{r}')=N\int\cdots\int\Phi_k(\vec{r}\sigma,x_2,\ldots,x_N)\Phi_0(\vec{r}'\sigma,x_2,\ldots,x_N)d\sigma dx_2\cdots dx_N.$$

Now, let Φ_0 be the energy minimizing OEP single determinant [14,15] for some Hamiltonian

$$\hat{H}=\hat{T}+\hat{V}_{ee}+\sum_{i=1}^{N} v(\vec{r}_i) \tag{23}$$

and, in expression (22), add $\hat{T}+\Sigma_{i=1}^{N}v(\vec{r}_i)$ to $\hat{V}_{ee}$ and subtract $\hat{T}+\Sigma_i v(\vec{r}_i)$ from $-\hat{V}_{xu}$. We obtain

$$\rho^{c}_{1,[n]}(\vec{r},\vec{r}\,')=-\sum_{k>0}\frac{\langle\Phi_k|\hat{H}|\Phi_0\rangle}{(E_k-E_0)}[\gamma_{k,0}(\vec{r},\vec{r}\,')+\gamma_{k,0}(\vec{r}\,',\vec{r})], \tag{24}$$

where, in Eq. (24), each Φ_k pertains to a singly excited determinant with respect to Φ_0, because otherwise $\gamma_{k,0}$ vanishes. Next, *if* Φ_0 is simultaneously the Hartree-Fock determinant of the $\hat{H}$ in Eqs. (23) and (24), then $\rho^{c}_{1,[n]}(\vec{r},\vec{r}\,')$ would vanish, because, by Brillouin's theorem, $\langle\Phi_k|\hat{H}|\Phi_0\rangle=0$, for all $k>0$. Consequently, v_x^{HS} would equal v_x *if* Φ_0 were a Hartree-Fock determinant. (Of course, it should be noted that we observe that the Slater exchange potential [16] would also equal v_x if Φ_0 were a Hartree-Fock determinant, because the Slater potential [or [17] averaged Fock approximation (AFA)] is invariant to a unitary transformation among the orbitals of which it is composed. However, the Slater potential does not satisfy the Levy-Perdew viral relation [12] while v_x^{HS} does [2]. Incidentally, it has recently been shown by Kleinman [17] that the Slater potential may be obtained as a partial functional derivative of the Hartree-Fock exchange expression.)

Since the Φ_k in Eq. (22) are singly excited determinants, it can be shown that it follows that

$$\rho^{c}_{1,[n]}(\vec{r},\vec{r}\,')=-\sum_{\ell>N}\sum_{i=1}^{N}\frac{\langle\varphi_\ell|\hat{v}_x^{\mathrm{HF}}-v_x|\varphi_i\rangle}{(\varepsilon_\ell-\varepsilon_i)}\times[\varphi_\ell(\vec{r}\,')\varphi_i(\vec{r})+\varphi_\ell(\vec{r})\varphi_i(\vec{r}\,')], \tag{25}$$

where the φ's are Kohn-Sham orbitals, the ε's are the corresponding orbital energies, and $\hat{v}^{\mathrm{HF}}$ is the familiar nonlocal Fock potential, except that it is composed of Kohn-Sham orbitals.

Consider $\hat{H}_\lambda=\hat{T}+\lambda\hat{V}_{ee}+\Sigma_{i=1}^{N}v_\lambda([n];\vec{r}_i)$, where v_λ is such that n, the Hartree-Fock density of $\hat{H}_\lambda$, is constrained to be independent of λ. Then it can be shown through a perturbation analysis of Eq. (22) in Ref. [27] that the $\rho^{c}_{1,[n]}$ in Eqs. (22) and (25), of the present paper, is the difference, to first order in λ, between the Hartree-Fock $\rho^{\lambda}(\vec{r},\vec{r}\,')$ of $\hat{H}_\lambda$ and the Hartree-Fock (or Kohn-Sham) $\rho^{0}(\vec{r},\vec{r}\,')$ of $\hat{H}_0$. Note that $\rho^{0}(\vec{r},\vec{r}\,')$ consists of Kohn-Sham orbitals. Hence, the Harbola-Sahni exchange potential v_x^{HS} would equal the exact exchange potential v_x if $\partial\rho^{\lambda}/\partial\lambda|_{\lambda=0}=0$, where ρ^{λ} is the Hartree-Fock $\rho^{\lambda}(\vec{r},\vec{r}\,')$.

Finally, in calculations, perhaps one can approximate v_x in Eq. (25) for use in the z in Eq. (14). Approximations for the v_x in Eq. (25) might include v_x^{HS} itself, the potentials of Krieger, Li, and Iafrate [18,19] or, even, the Slater potential [20].

IV. CLOSING REMARKS CONCERNING THE CORRELATION POTENTIAL

As implied in the Introduction, knowledge of a *separate* formal exact expression for v_c is important when one wishes to focus upon an approximation for v_c independently, and one employs the exact OEP for v_x, or if one wishes to employ one of the highly encouraging approximations for v_x as presented, or discussed, for instance, in the works in Refs. [2] and [17–22].

In expressions (18) and (19), one would model the correlating second-order density matrix (nondiagonal as well as diagonal elements) as a functional of the density to determine an approximate v_c as a functional of the density (the component ρ_1^c can be extracted through coordinate scaling [5]). The accuracy of this modeled correlating second-order density matrix would be tested by first forming the corresponding correlation energy functional with it through that coupling-constant formula obtained [5,23] by combining the adiabatic connection formula [24,25] with coordinate scaling [5] and then by taking the functional derivative of this correlation functional. For the modeled correlating second-order density matrix to be accurate, the resultant functional derivative would have to agree closely with the approximation for v_c which is obtained through expressions (18) and (19).

Finally, the constraints in Secs. III and IV of van Leeuwen and Baerends [26] should be tested on an approximation to $v_c([n];\vec{r})$, which is obtained through expressions (18) and (19). Also, one could generate an approximation to E_c by performing a functional integration with the approximate $v_c([n];\vec{r})$ by utilizing one of the paths of van Leeuwen and Baerends [26]. As a necessary requisite for accuracy, the resultant approximation to E_c would have to agree closely with that approximation to E_c which is obtained through the coupling-constant formula described in the previous paragraph. The present work concerns line integrals for obtaining an approximation to v_c, while Ref. (26) concerns line integrals for obtaining an approximation to E_c from an approximation to v_c.

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