

# Benchmarking the AK13 Exchange Functional: Ionization Potentials and Electron Affinities

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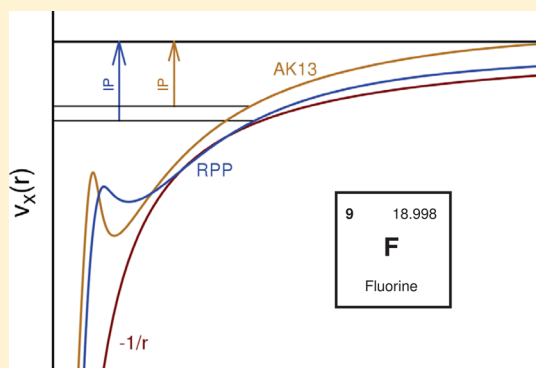
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## Supporting Information

**ABSTRACT:** We perform benchmark calculations for the ionization potential and electronic affinity of atoms and small molecules using several semilocal exchange-correlation functionals of density-functional theory with improved asymptotic behavior. We are particularly interested in a new generalized-gradient approximation for exchange [Armiento and Kümmel, *Phys. Rev. Lett.* **2013**, *111*, 036402] that provides an energy functional whose functional derivative yields a potential with better decay behavior. We find that it yields energies that are worse than traditional energy functionals and potentials that are less accurate than functionals that model directly the exchange-correlation potential. However, we find that this functional offers a excellent balance between the quality of the energy and of the potential and is therefore a good compromise for applications that require at the same time reasonable energies and good potentials.



## 1. INTRODUCTION

It is well-known that the usefulness of any density functional theory (DFT) depends mainly on the accuracy of the approximations to the elusive exchange-correlation (xc) functional. This is the quantity that describes all complicated many-body effects and that has, therefore, to be approximated in any practical use of the theory. Many such approximations have appeared in the literature. In fact, more than 300 xc functionals have been put forward over the past 50 years. However, and in spite of all the remarkable progresses done in this field, no functional is fully satisfying, and in fact, different functionals are often used in different situations.

In this paper, we will be concerned by explicit density functionals that yield xc potentials with good asymptotic behavior for finite systems. It is true that most functionals are derived with the xc energy in mind, yielding potentials that decay exponentially to zero instead of having the correct  $-1/r$  behavior. However, the correct asymptotics are of paramount importance in several physical situations. For example, potentials with the incorrect exponential asymptotics do not possess Rydberg states and often do not bind extra electrons. Moreover, in this case, the potential is shifted up leading to eigenvalues of the highest occupied molecular orbital (HOMO) that are too high. As this value should be equal to minus the ionization potential of the system in DFT, it leads to systems with too small ionization potentials. This, in turn, has catastrophic consequences when studying, for example, the interaction of molecules with strong laser fields.

Probably the first density functional with the correct asymptotics was put forward by van Leeuwen and Baerends in 1994<sup>1</sup> (LB94). The recipe was very simple and consisted in writing an explicit functional for the potential in the same form as the famous 1988 exchange functional of Becke<sup>2</sup> (B88)

$$v_{xc,\sigma}^{\text{LB94}} = \alpha v_{x,\sigma}^{\text{LDA}} + v_{c,\sigma}^{\text{LDA}} - n_{\sigma}^{1/3} \frac{\beta x_{\sigma}^2}{1 + 3\beta x_{\sigma} \sinh^{-1}(x_{\sigma})} \quad (1)$$

where  $n_{\sigma}$  is the (spin-dependent) electronic density,  $x_{\sigma} = |\nabla n_{\sigma}|/n_{\sigma}^{4/3}$  is the reduced, dimensionless gradient,  $\alpha = 1$ , and  $\beta = 0.05$  is an empirical parameter fitted to the beryllium atom. Finally,  $v_{x,\sigma}^{\text{LDA}}$  and  $v_{c,\sigma}^{\text{LDA}}$  are respectively the exchange and correlation parts of the local density approximation (LDA) of Perdew and Wang<sup>3</sup> (PW). Note that with respect to the B88 exchange energy functional,<sup>2</sup> there is a 3 in the denominator instead of a 6 in order to accommodate for the different asymptotics of the potential.

Later, in 2000, the LB94 potential was generalized by introducing a second empirical parameter.<sup>4</sup> The parameters  $\alpha = 1.19$  and  $\beta = 0.01$  were then fitted to reproduce the excitation energies and the dipole polarizabilities of small molecules. It turns out that this LB $\alpha$  potential not only improves the magnitude of the static hyperpolarizabilities but also modifies the relative frequency dependence with respect to the LDA and the original LB94 results.

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These functionals are often used in time-dependent simulations where ionization plays an important role. However, one has to keep in mind that modeling directly the potential leads to a series of problems. In fact, it can be proved that in general these potentials are not functional derivatives of any energy functional and therefore violate serious constraints such as the zero-force theorem.<sup>5,6</sup> As a consequence, we do not have access to the total energy so we cannot, for example, calculate structural properties or cohesive energies. This problem is also present in *all* other functionals that model or approximate directly the potential.

The next episode in our story involves the so-called meta-GGAs, that is, functionals that depend locally not only on the density and its gradient but also on its Laplacian and on the kinetic energy density  $\tau_\sigma$ . In 2006, Becke and Johnson<sup>7</sup> noted that the difference between the exact-exchange (EXX) potential and the Slater potential,  $\Delta v_{x,\sigma} = v_{x,\sigma}^{\text{EXX}} - v_{x,\sigma}^{\text{Slater}}$ , is characterized by a step-like structure in multishell atoms, and that this structure can be modeled by the ratio  $\tau_\sigma/n_\sigma$ . They thus proposed this very simple approximation for the exchange potential (that we will refer to as BJ).

$$v_{x,\sigma}^{\text{BJ}} = v_{x,\sigma}^{\text{Slater}} + \frac{1}{\pi} \sqrt{\frac{5}{12}} \sqrt{\frac{2\tau_\sigma}{n_\sigma}} \quad (2)$$

that fulfils the following conditions: (i) it is invariant with respect to unitary orbital transformations; (ii) it has the step-like structure characteristic of  $\Delta v_{x,\sigma}$  in multishell atoms; (iii) it has the exact homogeneous electron gas limit; (iv) it is exact for any hydrogenic atom. As this functional models directly the potential, it suffers from the same drawbacks as the LB94 functional. Moreover, asymptotically it approaches a constant whose value depends on the eigenvalue of the highest occupied orbital, and it is not gauge invariant. Because of the high computational cost of its evaluation, the Slater potential appearing in eq 2 is sometimes<sup>8,9</sup> replaced by the Becke–Roussel (BR) form,<sup>10</sup> as suggested by Becke and Johnson. We will follow this recipe in this paper.

In 2010, Räsänen, Pittalis, and Proetto (RPP) proposed a modification of BJ designed to correct some of its deficiencies.<sup>8,11</sup> The modified potential can be written as

$$v_{x,\sigma}^{\text{RPP}} = v_{x,\sigma}^{\text{Slater}} + \frac{1}{\pi} \sqrt{\frac{5}{12}} \sqrt{\frac{D_\sigma}{n_\sigma}} \quad (3)$$

where the quantity

$$D_\sigma = 2\tau_\sigma - \frac{1}{4} \frac{[\nabla n_\sigma]^2}{n_\sigma} - \frac{\mathbf{j}_\sigma^2}{n_\sigma} \quad (4)$$

introduces a dependency in the spin-dependent paramagnetic current density  $\mathbf{j}_\sigma$ . Contrary to the Becke–Johnson potential, this potential is gauge-invariant, is exact for any single-orbital system, and approaches zero asymptotically. Finally, we note that these improvements are achieved without compromising the accuracy of the functional.<sup>12</sup>

Recently, Armiento and Kümmel<sup>13</sup> gave a step forward and derived an expression for the *energy functional* that is semilocal in the density and at the same time leads to a potential that exhibits all of the interesting properties of BJ. The basic ingredients are the asymptotic limits of the potential for a finite system, for a semi-infinite bulk system, the gradient expansion for small  $x_\sigma$ , and the requirement that the functional is well-behaved for all  $x_\sigma$ . The resulting functional has the standard

form of a standard exchange generalized gradient approximation (GGA) functional

$$\epsilon_x^{\text{AK13}} = \sum_{\sigma=\uparrow,\downarrow} \epsilon_x^{\text{LDA}}(n_\sigma) F_x^{\text{AK13}}(x_\sigma) \quad (5)$$

where  $\epsilon_x^{\text{LDA}}(n_\sigma) = -A_x n_\sigma^{4/3}$  is the exchange energy density with  $A_x = (3/8)(3/\pi)^{1/3} 4^{2/3}$ , and

$$F_x^{\text{AK13}} = 1 + B_1 s \log(1 + s) + B_2 s \log(1 + \log(1 + s)) \quad (6)$$

The variable  $s_\sigma = x_\sigma/2(6\pi^2)^{1/3}$ , and the constants  $B_1 = 3 \mu_{\text{GE}}/5 + 8\pi/15$  and  $B_2 = \mu_{\text{GE}} - B_1$  with  $\mu_{\text{GE}} = 10/81$ . These constants are *not* empirical, as they are determined from the theoretical requirements. As in the case of the BJ potential, the AK13 potential asymptotically approaches a constant whose value depends on the eigenvalue of the highest occupied orbital. Note that due to the third term of eq 6 the AK13 potential actually has a leading  $\log(r)/r$  asymptotic behavior for finite systems (see Supporting Information of ref 13).

The purpose of this article is to provide a fairly extensive benchmark of these functionals. In particular, we are interested in finding out if the AK13 functional holds its promise of yielding, at the same time, accurate energies and potentials, and how it compares to more traditional approaches.

Of course, there are many other approaches in DFT that yield functionals with the correct asymptotics. First of all, there are orbital functionals such as the EXX<sup>14,15</sup> or the self-interaction corrected LDA of Perdew and Zunger.<sup>16</sup> There are also some hybrid functionals based on the Coulomb attenuated method, such as the tuned-CAM-B3LYP,<sup>17</sup> or some long-range corrected hybrid functionals.<sup>18</sup> Finally there are also several techniques to obtain Kohn–Sham potentials with the correct  $-1/r$  decay behavior from xc functionals with the incorrect asymptotics.<sup>19–22</sup> These functionals are, however, not explicit density functionals and go far beyond the scope of this benchmark.

## 2. METHODOLOGY

Our objective is to benchmark the new AK13 functional against other explicit density functionals that have the correct asymptotic behavior for finite systems for atoms and small molecules. In the former case, we decided to look at all atoms up to Kr, as for larger atoms relativistic corrections start becoming of crucial importance. For molecules, we used the well-known G2/97 molecule set.<sup>23,24</sup> The set contains 119 neutral systems and 29 radicals, 35 nonhydrogen systems, 22 hydrocarbons, 47 substituted hydrocarbons, and 15 inorganic hydrides. We will be particularly interested in the functionals LB94, LB $\alpha$ , BJ, RPP, and AK13. These will be compared to the more conventional LDA in the parametrization of Perdew–Wang<sup>3</sup> (PW) and the Perdew–Burke–Erzerhof<sup>25</sup> (PBE) GGA. In the case of the exchange functionals BJ, RPP, we combined them with the PW correlation<sup>3</sup> and replaced the Slater potential with the Becke–Roussel meta-GGA.<sup>10</sup> We will therefore denote them as BRBJ-PW and BRRPP-PW hereafter. For AK13, we combined it with both the PW and the PBE correlation functionals.

We wish to test both the quality of the energy (for the functionals that allow it) and the potential. We chose, therefore, to benchmark ionization potentials (IPs) and electron affinities (EAs) for two reasons: (i) there is considerable experimental and theoretical studies of these quantities; (ii) within DFT, IPs

and EAs can be calculated in two different and independent ways (that should yield the same value for the exact xc functional, of course). The first involves calculating the energy difference between systems with plus or minus one electron and the neutral system—this allows to measure the quality of the energy functional. The second looks at the eigenenergy of the HOMO of the neutral system that in DFT is equal to minus the ionization potential<sup>26</sup> (assuming an asymptotically vanishing potential). Of course, the EA can be obtained by looking at the IP of the negatively charged system. This method allows us to measure the quality of the potential.

As noted in the previous section, the BJ and AK13 potentials go asymptotically to a finite constant. This constant redefines the zero of orbital energy and therefore needs to be taken into account when computing the IPs and EAs from orbital eigenvalues. Following the same procedure as in a previous work,<sup>12</sup> we have systematically shifted the BJ and AK13 potentials in our calculations so that they go asymptotically to zero. At this point, we should note that the asymptotic limit of the AK13 potential also implies a redefinition of the zero of the exchange energy density. Indeed, if we write the shifted AK13 exchange potential, that is, the potential that goes asymptotically to zero, as

$$v_{x,\sigma}^{0,AK13}(\mathbf{r}) = v_{x,\sigma}^{AK13}(\mathbf{r}) - C_{\sigma} \quad (7)$$

where  $C_{\sigma}$  is the asymptotic limit of the unshifted potential  $v_{x,\sigma}^{AK13}(\mathbf{r})$ , then the exchange energy density should be shifted by exactly the same amount

$$\varepsilon_x^{0,AK13}(\mathbf{r}) = \varepsilon_x^{AK13}(\mathbf{r}) - C_{\sigma} \quad (8)$$

in order to obtain eq 7 when taking the functional derivative with respect to the density of the corresponding exchange energy:

$$E_x^{0,AK13} = \sum_{\sigma=\uparrow,\downarrow} \int d\mathbf{r} n_{\sigma}(\mathbf{r}) \varepsilon_x^{0,AK13}(n_{\sigma}(\mathbf{r})) \quad (9)$$

Unfortunately, we found that the IPs and EAs obtained from energy differences using  $E_x^{0,AK13}$  are highly inaccurate, with average relative errors much larger than 100%, most likely because this redefinition of the zero of the exchange energy density was not taken into account when designing the functional. Therefore, the results presented here use the unshifted exchange energy  $E_x^{AK13}$ .

All the functionals benchmarked in this article were implemented in Libxc, a library of xc functionals.<sup>27</sup> For the atomic calculations we used the code APE,<sup>28</sup> while for molecules we used a modified version of NWChem.<sup>29</sup> In the later case, we used a Dunning aug-cc-pTZP Gaussian basis set. Note that the introduction of polarization functions is important, as it allows for a more accurately representation of the tail of the atomic orbitals.

Finally, we would like to comment on the numerical problems we encountered when implementing the AK13 functional. There are two standard ways to obtain the xc potential for a GGA energy functional. The first uses the formula

$$v_{xc,\sigma} = \frac{\partial E_{xc}^{GGA}}{\partial n_{\sigma}} - \nabla \frac{\partial E_{xc}^{GGA}}{\partial \nabla n_{\sigma}} \quad (10)$$

with the divergence in the second term calculated numerically. The second evaluates this divergence analytically:

$$\nabla \frac{\partial E_{xc}^{GGA}}{\partial \nabla n_{\sigma}} = \sum_{\sigma'} \frac{\partial^2 E_{xc}^{GGA}}{\partial \nabla n_{\sigma} \partial n_{\sigma'}} \nabla n_{\sigma'} + \frac{\partial^2 E_{xc}^{GGA}}{\partial \nabla n_{\sigma} \partial \nabla n_{\sigma'}} \nabla^2 n_{\sigma'} \quad (11)$$

Both formulas are equivalent from the theoretical point of view, but their numerical behavior is quite different. In fact, eq 10 turns out to be more stable and is therefore preferred in most codes. We had no problems implementing it in NWChem. However, the term  $\partial E_{xc}^{AK13} / \partial \nabla n_{\sigma}$  diverges linearly in the asymptotic region. This behavior should be canceled exactly by the divergence, but in practice, this leads to spurious numerical noise. We witnessed this both in APE<sup>28</sup> and in the real-space code OCTOPUS.<sup>30,31</sup> In APE, the problem could be circumvented by using eq 11 (probably due to the fine, precise logarithmic grid), but we were unable to find a solution in OCTOPUS. Unfortunately, this numerical problem can seriously complicate the use of AK13 in grid or plane-wave based approaches.

### 3. RESULTS

We will start our discussion by looking at the IPs calculated through energy differences. A summary of the results can be found in Table 1, while tables including all our results can be

**Table 1. Mean Absolute Error (In Percentage) for the Ionization Potentials Calculated from Total Energy Differences<sup>a</sup>**

	LDA	PBE	AK13-PW	AK13-PBE
atoms	3.0	2.4	5.9	9.1
G2/97 (adiabatic)	2.3	2.5	4.7	7.5
G2/97 (vertical)	2.2	2.1	5.1	7.6

<sup>a</sup>As a reference, we used the experimental values taken from Ratzig and Smirnov<sup>32</sup> (for atoms) and from the NIST Chemistry WebBook<sup>33</sup> (for the G2/97 set).

found in the Supporting Information. It is clear that there is a price to pay when developing an exchange functional with the potential in mind: the error in the IPs calculated through energy differences is two times larger than with a standard LDA or GGA. Results are also quite consistent between atoms and small molecules, and between the adiabatic and vertical IPs for molecules. Finally, note that the AK13 functional seems to work best when paired with PW correlation.

The situation is of course completely different when we look at the IPs calculated from the eigenvalue of the HOMO orbital (see Table 2). As it is well-known, both the standard LDAs and GGAs yield too small IPs, as the xc potential is too shallow due to its wrong asymptotic behavior. The AK13 functional now yields much better results, with errors slightly larger than 10%, considerably better than the errors obtained with the BRBJ meta-GGA. The error is again smaller when one combines AK13 with PW correlation. However, the winner in this category is the van Leeuwen–Baerends potential, and in particular the generalized version LBa, that is better than even BRRPP-PW. With this functional one obtains consistently errors of the order of 5%, and this is the functional of choice when one wishes to obtain molecular properties connected to the ionization potentials.

A question that arises at this point is if the errors are due to the exchange functionals, or to the (lack of) cancellation of errors between the exchange and the PW correlation. We already saw that, for the AK13 functional, the results do change when going from the PW to the PBE correlation, but by a small

**Table 2. Mean Absolute Error (In Percentage) for the Ionization Potentials Calculated from the Highest Occupied Kohn–Sham Orbital<sup>a</sup>**

	LDA	PBE	AK13-PW	AK13-cPBE	LB94-PW	LB $\alpha$ -PW	BRBJ-PW	BRRPP-PW
atoms	39.4	40.7	11.2	13.9	6.6	5.2	20.5	5.8
G2/97	37.3	38.2	10.7	14.6	10.1	5.4	23.0	7.6

<sup>a</sup>As a reference, we used the experimental values taken from Ratzig and Smirnov<sup>32</sup> (for atoms) and from the NIST Chemistry WebBook<sup>33</sup> (for the G2/97 set).

amount. To shed further light on the subject we performed exchange only calculations for atoms and compared them to exact-exchange calculations of Engel and Vosko.<sup>34</sup> As expected, the results for the exchange only functionals given in Table 3

**Table 3. Mean Absolute Error (In Percentage) for the Ionization Potentials Calculated from the Highest Occupied Kohn–Sham Orbital for Atoms<sup>a</sup>**

xLDA	xPBE	AK13	xB94	xB $\alpha$	BRBJ	BRRPP
45.7	43.2	15.3	12.0	12.5	18.0	7.8

<sup>a</sup>As a reference we used results from Engel and Vosko.<sup>34</sup>

are absolutely consistent with Table 2, which proves that the main source of error is definitively the exchange. Note that the larger error of LB94 and LB $\alpha$  with respect to Table 2 are probably due to the fact that the separation between exchange and correlation in these functionals is somewhat arbitrary.

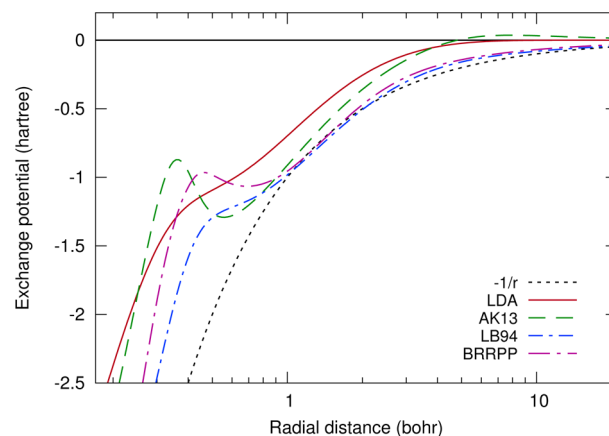
Finally, we turn our attention to EAs. These are in some sense more delicate than the IPs as the extra electron binds usually in states that are close to the continuum and that are therefore very sensitive both to the asymptotic behavior and to the shape of the potential close to the nuclei. A summary of our results for the EAs calculated from value of the HOMO of the anionic system can be found in Table 4.

**Table 4. Mean Absolute Error (In Percentage) For the Electron Affinities Calculated from the Highest Occupied Kohn–Sham Orbital for Atoms<sup>a</sup>**

	LB94	LB $\alpha$	BRBJ-PW	BRRPP-PW
atoms	86.3 (24)	42.2 (23)	42.8 (5)	36.9 (19)
G2/97	81.5 (45)	32.3 (45)	60.8 (14)	39.5 (44)

<sup>a</sup>For the mean error, we only used systems that were bound in the calculations (number of bound systems between parentheses). As a reference, we used the experimental values taken from Ratzig and Smirnov<sup>32</sup> (for atoms) and from the NIST Chemistry WebBook<sup>33</sup> (for the G2/97 set).

The first thing to notice is the absence of many functionals from the list, as they were unable to bind an extra electron. It is well-known that standard LDAs and GGAs have many difficulties in this context due to the wrong asymptotics. However, it is rather surprising that also the AK13 failed to bind the anionic systems. To understand this behavior, we plot, in Figure 1, the AK13 spin-up potential for the F atom and compare it to the corresponding LDA, LB94, and BRRPP potentials. It is clear that in the asymptotic region, contrary to the LB94 and BRRPP potentials that follow closely the  $-1/r$  curve, the AK13 potential goes too quickly to zero, passing by a positive maximum. This is due to the third term of eq 6, which comes from the semi-infinite bulk used in the construction of the functional, and which is too dominating for a finite system.



**Figure 1.** (color online) Spin-up exchange potential for the F atom obtained with the LDA, AK13, LB94, and BRRPP functionals as a function of the radial distance. The  $-1/r$  curve is also plotted for comparison purposes.

Going back to Table 4, the van Leeuwen–Baerends functionals fare quite well, binding all anions, and yielding quite reasonable errors when compared with standard DFT approaches. Concerning the BRBJ-PW meta-GGA, some care has to be taken with our results. It is true that the error for the atoms is relatively small, but the truth (as can be seen in the complete tables in the Supporting Information) is that BRBJ-PW was only able to bind a handful of atoms and few molecules from the G2/97 set. Finally, we obtain good results with the BRRPP-PW meta-GGA. It is able to bind almost all anions with a reasonable error. From this discussion, it is clear that the LB $\alpha$  functional probably yields the best xc potentials for anions.

#### 4. CONCLUSIONS

Our main conclusion is that if one tries to design an energy functional that yields a Kohn–Sham potential with better asymptotic behavior there is clearly a price to pay. This is what happens with the AK13 functional. On the one hand, the potential is clearly better than with the standard LDA or GGA functionals but still considerably worse than the functionals for the potential (like van Leeuwen–Baerends or Becke–Johnson). The energy is, on the other hand, worse than for the standard functionals. Functionals like AK13 are however useful in situations where both the energy and the potential are important at the same time.

Clearly, a tantalizing question is if it is possible to design a semilocal functional yielding a potential with the correct asymptotics but keeping the quality and the precision of the standard energy functionals. We know that a standard GGA written in this way will yield the incorrect asymptotics for the exchange–correlation energy density. However, it is not even clear if such condition is of any practical importance to have a good total energy. In fact, and in contrast with, for example, the Becke 1988 exchange, many functionals have the incorrect



asymptotics for the energy density but yield good energies. This is the case, for example, for the famous local density approximation and the Perdew–Burke–Ernzerhof functional. In our opinion, there is still a lot of space to improve on the AK13, but further theoretical developments are clearly necessary.

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

Tables with the ionization potentials and electron affinities errors. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

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