Supporting Information (SI)

Comprehending the Quadruple Bonding Conundrum in C_2 from Excited State Potential Energy Curves

Ishita Bhattacharjee, Debashree Ghosh*, Ankan Paul*

School of Chemical Sciences, Indian Association for the Cultivation of Science, Kolkata 700 032, India

Corresponding Author Email: pcdg@iacs.res.in, rcap@iacs.res.in

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S1. COMPUTATIONAL DETAILS

All the Hartree Fock (HF)[1], complete active space self-consistent field (CASSCF)[2] and Restricted active space self-consistent field (RASSCF)[2] computations have been done using MOLPRO[3] quantum mechanical package. The wavefunctions for the CASSCF computations are considered using full configuration interactions of ‘m’ electrons in ‘n’ orbitals and they may be denoted as CAS(m,n). For all the systems mentioned in the manuscript, we have taken full valence CAS i.e. (8,8), (10,8), (10,10), (4,8), (8,8) and (8,8) CAS for C_2, N_2, acetylene, Be_2, CN^+ and BN respectively. We have used cc-PVQZ[4] basis set for all the aforementioned computations. We have carried out RASSCF computations for C_2 and Be_2. In case of C_2, we have restricted the occupation number of each of the π-orbitals to 1.0 in order to avoid any bonding from the π system and henceforth carried out RASSCF computations for the σ system using (4,4) CAS. Similarly, for Be_2, we restricted the occupation number of each of the π-orbitals to 0.0 and performed RASSCF calculations using (4,4) CAS. The potential energy curves (PECs) are obtained by scanning the CASSCF energy values along the X-Y bond distance (X, Y: the atoms constituting the above-mentioned diatomic systems). In order to include effects of dynamic correlation, we have performed MRCI computations using the CASSCF orbitals for C_2, BN and CN^+. All the PECs obtained from CASSCF and RASSCF computations are plotted using GNUPLOT[5] program.

The PECs obtained from the state specific CASSCF computations for C_2, N_2 and acetylene for all the spin states included a lot of avoided crossings. So, in order to smoothen out the curves, we have taken into account two-state averaged PECs for all the spin states (apart from the spin states where the PECs are completely dissociative, since only one configuration state function is possible for such spin states i.e., nonet for C_2, CN^+ and BN and septet for N_2 and acetylene). However, in case of the quintet state of C_2, even the two-state averaging is not sufficient for a smooth PEC. So, for this particular state we have obtained the PEC corresponding to four-state average CASSCF energy values.

S2. POTENTIAL ENERGY CURVES (PECs) AND ENERGETICS

I. PECs of Four Spin States of Acetylene

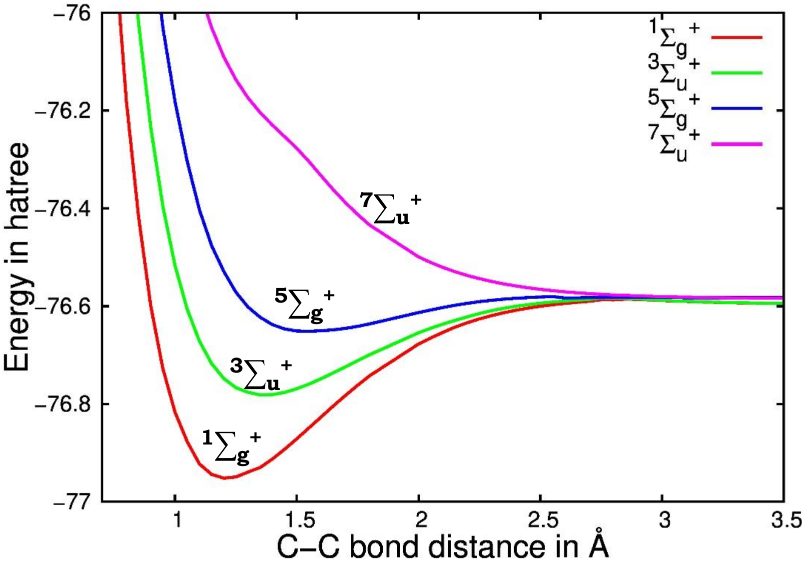


Figure S1. PECs corresponding to the four spin states in acetylene.

The figure depicts that the septet state is completely dissociative, indicating the fact that the acetylene does contain three bonds.

II. Ground State PEC for Be_2 as Obtained from RASSCF Computations

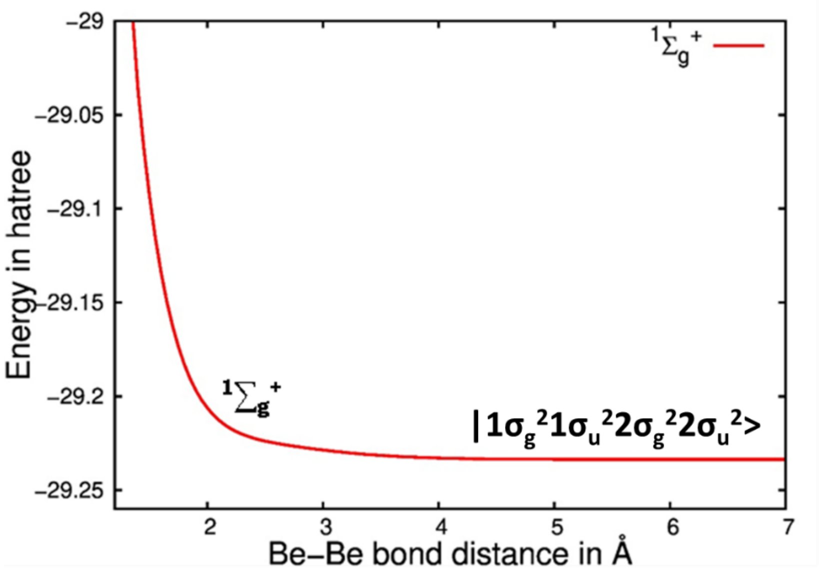


Figure S2. PEC corresponding to the RASSCF computation for the singlet spin state of Be_2 along with the dominant CSF of that state.

This curve is consistent with the PEC obtained by Piris et. al., when they conducted CASSCF computations on Be_2.[6] The curve is a dissociative one depicting a no bond situation in the ground state of Be_2. Also, the dominant CSF of the $^{1}\sum_{g}^{+}$ state of Be_2 indicates a bond order of 0.0.

III. PECs for Five Spin States of C_2 as Obtained from MRCI Computations

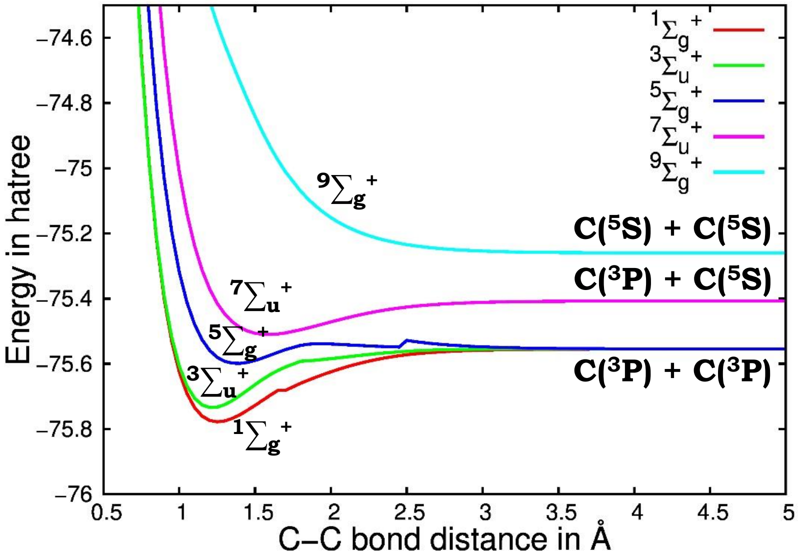


Figure S3. PECs corresponding to the MRCI computation for the five spin states of C_2.

The PECs obtained from the MRCI computations for the five spin states of C_2 follow similar trends as obtained from the CASSCF computations. Here also singlet, triplet, quintet and septet states exhibit distinct minima whereas the nonet state is a dissociative one.

IV. PECs of Five Spin States of CN^+ as obtained from MRCI Computations

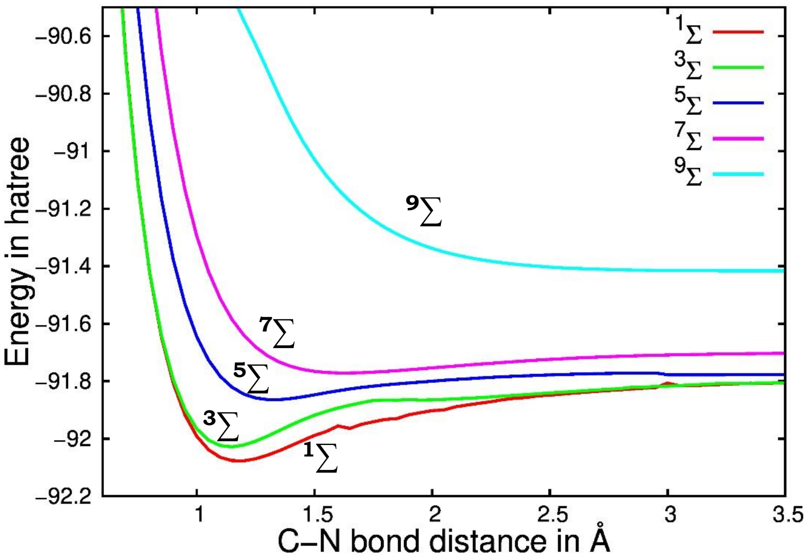


Figure S4. PECs corresponding to the MRCI computation for the five spin states of CN^+.

V. PECs of Five Spin States of BN as obtained from MRCI Computation

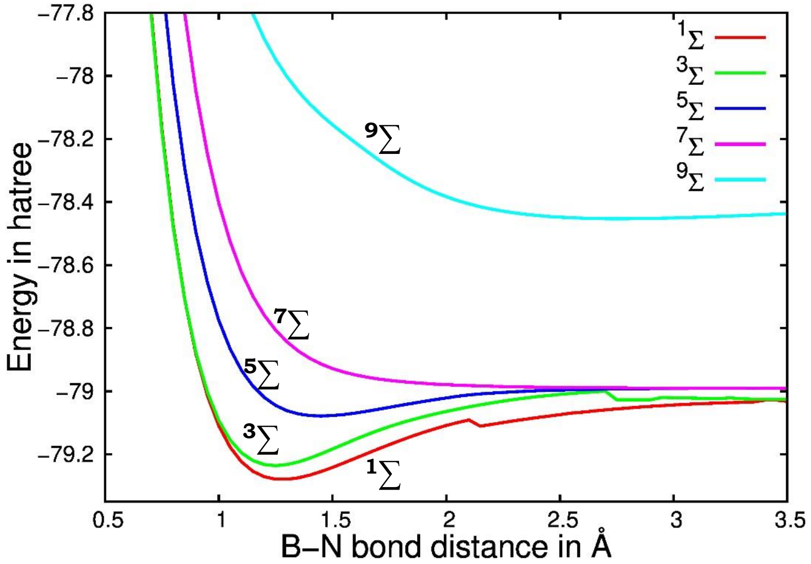


Figure S5. PECs corresponding to the MRCI computation for the five spin states of BN.

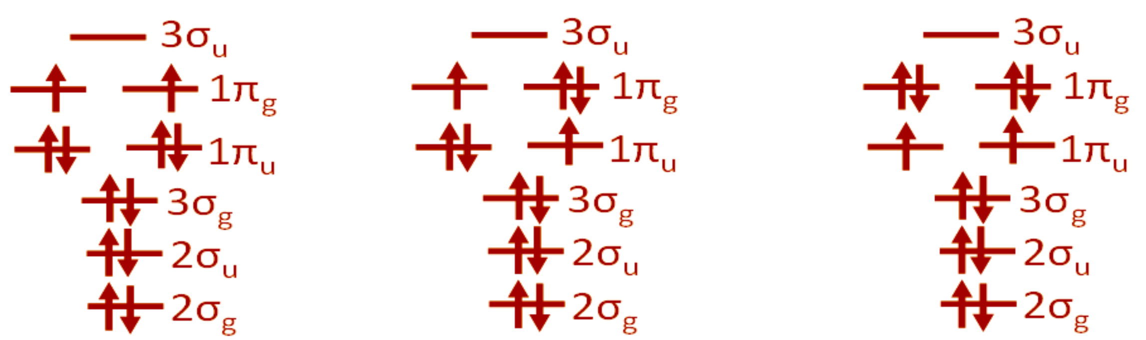
S3. ENERGETICS FOR THE HIGH SPIN STATES OF C_2

Table ST1: Dissociation energies of the four spin states of C_2 based on CASSCF computations

Spin Multiplicity	**Equilibrium bond distance (Å)**	**Dissociation Energy (D_e) kcal/mol**
$^1\Sigma_g^+$	1.25	143.2
$^3\Sigma_u^+$	1.20	116.0
$^5\Sigma_g^+$	1.40	104.5
$^7\Sigma_u^+$	1.60	57.4

S4. A SHORT NOTE ON LIMITATIONS OF OUR METHODOLOGY

One of the pertinent questions that may arise regarding our approach in determining the number of bonds through analysis of CASSCF/RASSCF based PECs and the corresponding wavefunctions with their formal bond orders is how universal is this methodology. Whether it can be used to determine the number of bonds in diatomic systems with $^3\Sigma_g^-$ ground state, like O_2 and B_2?



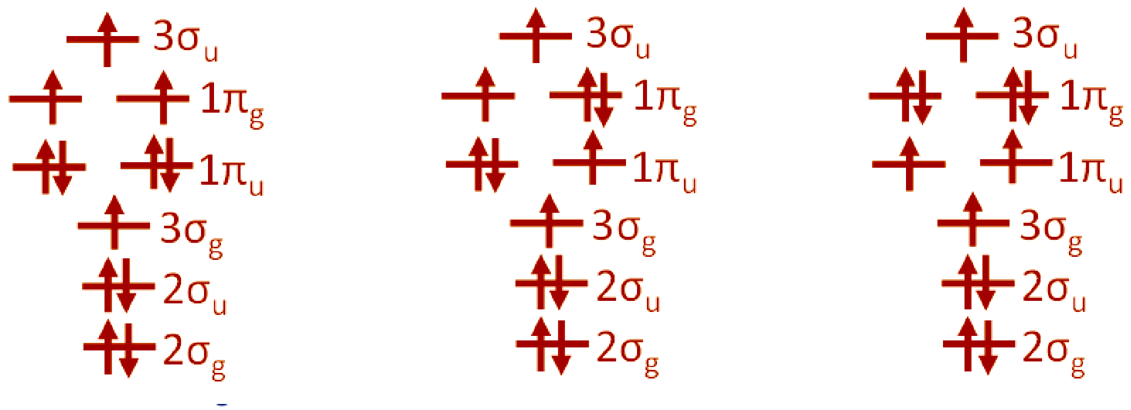
(a) $^3\Sigma_g^-$
σ B.O.=1.0; π B.O.=1.0
Ground state
PEC with a minimum

(b) $^3\Sigma_u^+$
σ bond intact; σ B.O.= 1.0
π bond broken; π B.O.= 0.0
A PEC with minimum is expected

(c) $^3\Sigma_g^-$
σ bond intact; σ B.O.= 1.0
π B.O.= -1.0
But since σ bond is stronger than π bond, a minimum is expected

Figure S6. Different relevant triplet sigma states of O_2. (a) represents the ground state of O_2; (b) represents sigma states obtained by excitation of an electron from a π bonding orbital to the corresponding antibonding orbital and (d) two electron excitation, one each form one of the π bonding orbitals to its corresponding orbital.

It turns out the same strategy also works for O_2 and B_2 in determining accurately the number of bonds from their PECs, albeit with some justifiable modifications due to the distinct differences in the ground state spin symmetry (See Figure S8 and Figure S9).



(a) $^5\Sigma_u^-$
π bond intact; π B.O.= 1.0
σ bond broken; σ B.O.= 0.0
A PEC with minimum is expected

(b) $^5\Sigma_g^+$
π bond broken; π B.O.= 0.0
σ bond broken; σ B.O.= 0.0
A dissociative curve expected

(c) $^5\Sigma_u^-$
π B.O.=-1.0
σ B.O.= 0.0
A dissociative curve expected

Figure S7. Different relevant quintet states of O_2 as obtained from one electron excitation from a σ orbital to the corresponding antibonding orbital with respect to the triplet states shown in Figure S6.

If we focus on O_2 the origin of the triplet ground state symmetry and the formal bond order of 2 in the framework of traditional MO theory originates from one σ bond and one π bond. The π bond is attributed to the four electrons in the bonding orbitals and two electrons in the antibonding orbitals (see Figure S6(a)). One can generate a higher spin state by breaking the bonding pair in the σ bonding orbital. It is obvious to disrupt the bonding arising from π orbitals one needs to excite a single electron from π to π* creating a configuration of the type $\pi_u^3\,\pi_g^{*3}$ instead of $\pi_u^4\,\pi_g^{*2}$ as that of in the ground state $^3\Sigma_g^-$. This would create a bond order of zero from π electrons. However, breaking the single π bond in O_2 would not create a higher spin state understandably as it leads to the $\pi_u^3\,\pi_g^{*3}$ configuration. This is obviously different from the molecules with singlet ground state $^1\Sigma_g^+$ that has π bonds (consider the case of N_2 or HC≡CH). Armed with this simple information one would expect to obtain $^3\Sigma_u^+$ with a minimum (conventional bond order=1 see Figure S6(b) and a $^5\Sigma_g^+$ with a dissociative curve (conventional bond order=0 see Figure S7(b)). Hence, according to our proposed strategy the PECs of these states should be examined using CASSCF and further studies with RASSCF if needed. The PECs of these states have been determined by previous thorough investigations by several groups.[7] It is found as expected the trend holds, i.e. $^3\Sigma_u^+$ with a well-defined minimum and the two lowest lying $^5\Sigma_g^+$ appearing to be dissociative in nature. This immediately falls in line with our proposed model. Even one may naively say that you can expect only two bonds in O_2 as breaking of the two bonds will lead to a dissociative state at the quintet stage and in case of C_2 you would get the totally dissociative state at the nonet stage due to the presence of quadruple bond in C_2. It must be remembered that for triplet ground state diatomic systems arising from $\pi_u^3\,\pi_g^{*3}$ and $\pi_u^4\,\pi_g^{*2}$ configurations moving the bonding electron to the antibonding electron would not create a sigma state with higher spin symmetry. If this may seem confusing one may tailor our strategy from a different viewpoint. Associated with these 2 configurations are low lying singlet $^1\Delta_g$ configuration (see Figure S8). From the lowest lying singlet state bonding pairs have to be broken to create high spin sigma states and the corresponding wavefunctions and their respective PECs have to be inspected to arrive at a proper conclusion regarding the number of bonds present in them. An adequately tailored strategy would yield two bonds for O_2.

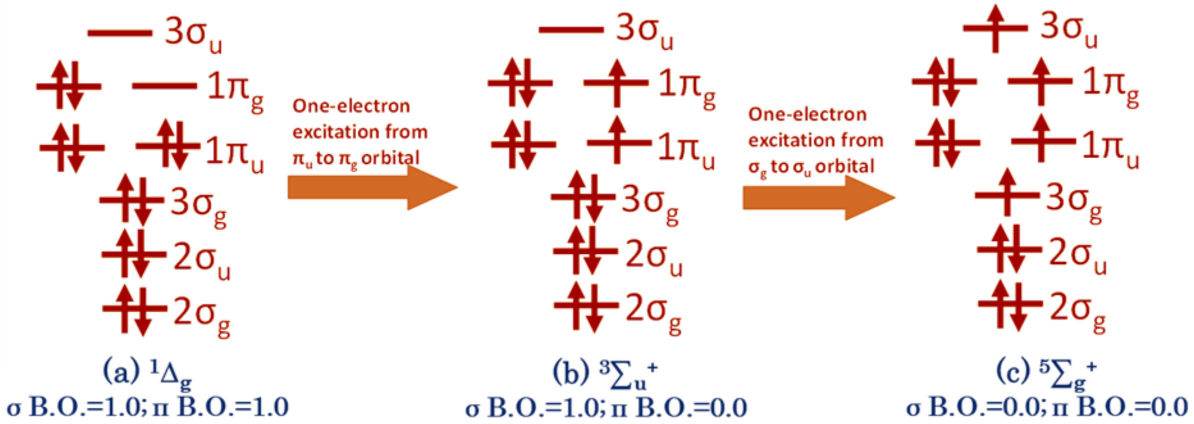


Figure S8. Breaking bonding pairs of electrons form lowest lying singlet state of O_2 to higher spin states.

A cautionary note:

Our investigations suggest that this approach is expected to be complicated when one encounters multiple avoided crossings in the PECs and the quintet states of O_2 may be considered as an example of such a tricky system. The three references mentioned above shows the lowest lying states of O_2 in its singlet, triplet and quintet spin states. The avoided crossings and the complicated nature of the PES including the different dissociated states are shown in Ref. 7 (a). We have applied the approach described in our paper to compute the number of bonds in O_2 to the PES described in the above references. We notice the bound state $^5\Sigma_u$ in Fig. 4 of Ref. 7 (b), while the next two degenerate dissociative states can be noticed from Fig. 1 in Ref. 7 (c). These two degenerate $^5\Sigma_g$ states occur due to excitation of π to π* orbitals thus, breaking the π bond. The configurations are given below. This indeed shows that there is a single π bond and a single σ bond in case of O_2 as expected from a simple MO theory description.

However, we would like to mention that due to the extensive avoided crossings and complicated dissociation pattern of O_2, the difficulties of applying our methodology can also be perceived clearly. This difficulty is not limited to O_2 molecule only, but will arise with all other complicated dissociation patterns in diatomics and is intrinsic to the method described by us.

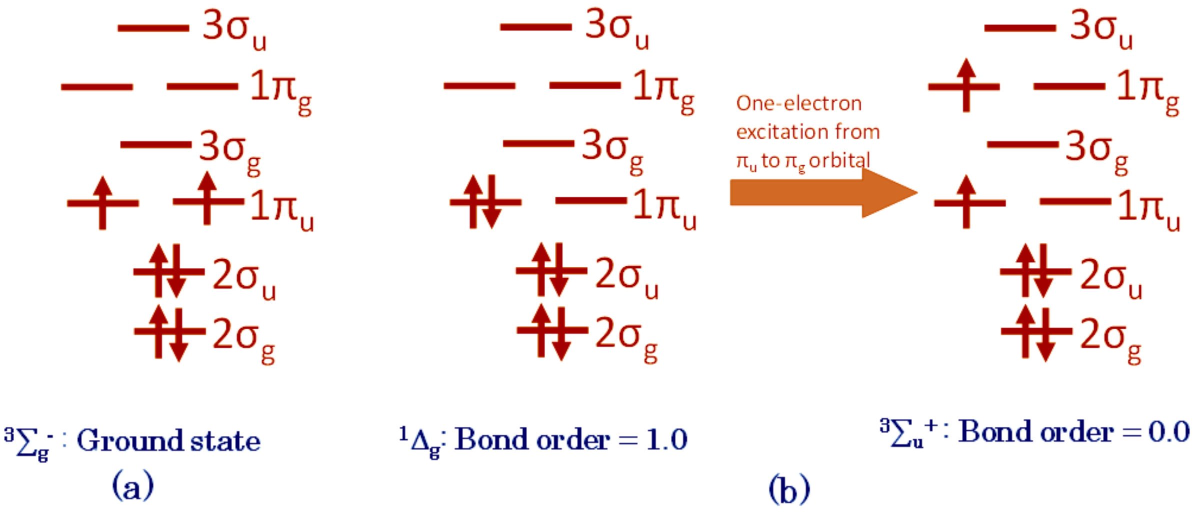


Figure S9. (a)Ground state of B_2 and (b)Breaking bonding pairs of electrons form lowest lying singlet state of B_2 to higher triplet state similar to O_2 (see Figure S8).

Metal dimers: Can this type of analysis be extended to transition metal dimers? At this stage the proposed methodology is in its nascent stage. Hence, extensive investigations with a slew of different many body techniques have to be used on several test case to determine if such methodology can be extended to transition metal dimers. In our approach we essentially state that a certain bonding pair is contributing a bond if it leaves it mark as a minimum on a PEC within the valence space. It must be noted that we are using only CASSCF and RASSCF with the active space only spanning the valence space of the dimer and then analysing the nature of the high spin sigma state PECs. For metal dimers even the valence space can be troublesome as has been pointed out by others due to the double shell effect.[8] Evidently, this would mean it would be premature to comment whether this approach can be extended to metal dimers at this stage.

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