

CHARGE EXCHANGE COLLISIONS INVOLVING MULTIELECTRON ATOMS (LITHIUM AND SODIUM)

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Summary

The cross section for forming both ground state and excited state hydrogen atoms by charge exchange between protons and lithium or sodium atoms is calculated. These calculations are performed using the Brinkman-Kramers approximation along with a multiplicative correction factor; the target lithium and sodium atoms are first described by simple "effective- Z " wavefunctions, and then the lithium case is treated more accurately both by including the inner electrons and by using a more accurate numerical lithium wavefunction.

The results are in satisfactory agreement with the experiments of Il'in *et al.* (Both theory and experiment pertain to incident proton energies of around 10–100 keV.)

I. INTRODUCTION

The charge exchange collision has been a subject of some interest over the past 15 years, stimulated by an interest in producing beams of excited neutral particles for injection into plasma devices such as ALICE, PHOENIX, and OGRA II, which are described in articles by Futch *et al.* (1966), Bernstein *et al.* (1966), and Artemenkov *et al.* (1966).

The method of production is to inject fast protons into a neutral gas, resulting in excited neutral atoms formed by charge exchange. An essential parameter for this process is the charge exchange cross section which, as is well known, is difficult to calculate exactly. In the present case this will not be attempted, but rather several stages of approximation will be considered and the results compared with the experimental results of Il'in *et al.* (1965).

The problem is usually formulated in one of two ways, one being the impact-parameter method as described by Wu and Ohmura (1962), and the other, the wave treatment as given by Mott and Massey (1965); a Born approximation is then generally applied in either case. (In the present work we will employ the wave treatment.) In either of the methods used there are two points to consider. Firstly the change in momentum of the exchanged electron must be fully described, allowing for the change in the centre of mass of the two heavy particle systems. The second point concerns the choice of interaction potential for the collision.

There has been considerable controversy over the appropriate interaction potential to be used in treating this collision in Born approximation. The usual Born treatment leads to a matrix element $\langle \psi_i | V | \psi_f \rangle$, where ψ_i and ψ_f are the initial and final wavefunctions of the electron and V is the interaction potential. The ψ_i, ψ_f are

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taken as products of the bound state wavefunction of the electron and a plane wave representing the momentum between the colliding systems. It is in the choice of V that the trouble arises.

The original Brinkman-Kramers (BK) assumption is that the interaction V should consist wholly of the interaction between the electron and the incoming proton since it is unlikely that the repulsive nucleus-nucleus interaction should influence the transfer of an electron from one nucleus to the other.

It is well known that the cross sections calculated in this BK approximation are too large particularly at resonance (~ 25 keV) but also at high energy. The nucleus-nucleus term was therefore included by Bates and Dalgarno (1952) and Jackson and Schiff (1953) to obtain much better results. However, in the Jackson-Schiff paper an added note by Wick suggests that the nucleus-nucleus contribution should be less by an order of m/M than the value of the electron-nucleus term. Also Jackson (1956) has shown that for the proton-hydrogen charge exchange a term in the second Born approximation cancels most of the nucleus-nucleus term if it is included in the first Born approximation.

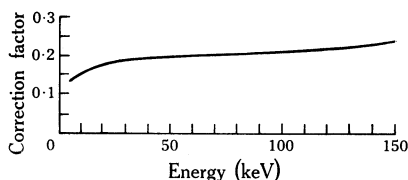


Fig. 1.—Average correction factor evaluated using hydrogen and helium.

More recently Bates (1958) and Bassel and Gerjouy (1960) have independently sought to account for the lack of orthogonality between the initial and final wavefunctions (a feature of exchange collisions). In both cases the resulting effective interaction potentials contained a term resembling the nucleus-nucleus term of Bates and Dalgarno and of Jackson and Schiff. So although it may be shown that the nucleus-nucleus term should contribute only an order m/M (e.g. May 1964*a*), when lack of orthogonality is included the Jackson-Schiff-type term is justified.

Therefore it appears to be necessary to use the nuclear term or the more complex interaction of Bates or Bassel and Gerjouy. However, Jackson and Schiff (1953) have observed for hydrogen that although the BK cross sections are too large for the reaction $H^+ + H \rightarrow H(nl) + H^+$, the ratios of the BK cross sections for different n agree quite well with those obtained using more exact formulae. That is, for hydrogen the BK cross sections may be used and multiplied by a correction factor (energy dependent but independent of n) to obtain the cross sections for hydrogen.

This situation has been investigated by Mapleton (1962) for helium using both BK and corrected potentials and he has found a similar situation, namely, that the ratios between BK cross sections are preserved. In particular by choosing the "average correction factor" given in Figure 1 both the hydrogen and helium cross sections fit to within 12% over the range of energies used by Mapleton. These values for the hydrogen cross section compare well with the experimental values of Gilbody and Ryding (1966).

We will therefore make the simple assumption that the situation described above for hydrogen and helium remains satisfactory for the case of lithium and sodium. The BK approximation will therefore be used to calculate cross sections of charge exchange for protons on lithium and sodium gas targets. The same average correction factor of Figure 1 will be used for these cases. The results of this will then be compared with the experimental results of Il'in *et al.* (1965) to determine (1) if the correction factor is satisfactory, and (2) if the ratios between excited states are still predicted by the BK approximation.

II. CROSS SECTION FORMULA

We consider now the charge exchange reaction in which a proton of speed v passes a complex atom M_B of N electrons and captures the j th electron. The distance between the nuclei is t and between the centres of mass of the two initial and final systems is ρ and σ respectively.

The initial and final wavefunctions are

$$\begin{aligned}\psi_1 &= \phi_{M_B}(\dots \mathbf{r}_i \dots) \exp(i\mathbf{k}_0 \cdot \rho) \exp(-iE_0 t/\hbar), \\ \psi_f &= \phi_{M_B}^*(\dots \mathbf{r}_i (i \neq j) \dots) \exp(i\mathbf{k}_f \cdot \sigma) \exp(-iE_n t/\hbar),\end{aligned}$$

and the interaction potential in the prior case is

$$V = e^2 \sum_i |\mathbf{t} + \mathbf{r}_i|^{-1}.$$

For the type of reaction considered here the wavefunction of a complex atom may be replaced by a product of single-particle wavefunctions. (Mapleton (1962) has verified the validity of this for helium by using both post and prior interactions.)

The situation then reduces to a form dealt with by May (1964b) and May and Lodge (1965) and yields

$$\sigma_n^e = \frac{(\text{con})^2}{(2\pi p)^2} \iint d\mathbf{k}'_x d\mathbf{k}'_y |\langle \phi_H(\mathbf{t}) t^{-1} \exp(i\mathbf{K}_1 \cdot \mathbf{t}) \rangle \langle \phi_{M_{Bj}}(\mathbf{r}_j) \exp(i\mathbf{K}_2 \cdot \mathbf{r}_j) \rangle|^2, \quad (1)$$

where

$$\mathbf{K}_1 = (k'_x, k'_y, (2a_0)^{-1} \{p + (Z_B^2/n_B^2 - 1/n^2)/p\}),$$

$$\mathbf{K}_2 = (k'_x, k'_y, (2a_0)^{-1} \{p - (Z_B^2/n_B^2 - 1/n^2)/p\}),$$

$$\text{con} = \left| \prod_{i \neq j} \langle \phi_{M_{Bi}}(\mathbf{r}_i) \phi_{M_{Bi}}^*(\mathbf{r}_i) \rangle \right|,$$

$-Z_B^2/2n_B^2$ is the potential energy of the j th electron, a_0 is the radius of the Bohr orbit, and $p = \hbar v/e^2$ (kinetic energy = $25p^2$ keV). In the above $\phi_{M_{Bi}}(\mathbf{r}_i)$ denotes the orbital wave function of the i th electron after the j th electron has been removed.

Clearly when the j th electron is an outer electron the orbits are not greatly disturbed and so $(\text{con})^2 \sim 1$. But when an inner electron is removed this may not be so. However, since this unusual type of wavefunction is not known and since it is expected that the effect will not be large, we take $(\text{con})^2 = 1$, observing that it is at least an upper limit. This general form will now be used to evaluate the cross sections where both inner and outer electrons are involved.

III. PARTICULAR CASES

Initially the two exchange media (lithium and sodium) will be treated using simple effective- Z hydrogenic wavefunctions in which only the outer electron is included. Then lithium will be treated more accurately firstly by including the inner electrons in the effective- Z treatment and lastly by using accurate wavefunctions derived by Roothaan, Sachs, and Weiss (1960).

(a) *Effective- Z Cases*

The formula for the cross section (1) may be rewritten in terms of the functions g and f given by May and Lodge (1965):

$$\sigma_{n_2}^e = \frac{1}{(2\pi p)^2} \iint dk'_x dk'_y |g(\mathbf{K}_1) f_{MB}(\mathbf{K}_2)|^2, \quad (2)$$

$$\mathbf{K}_1 = (k'_x, k'_y, (2a_0)^{-1}\{p + (Z_1^2/n_1^2 - 1/n_2^2)/p\}),$$

and

$$\mathbf{K}_2 = (k'_x, k'_y, (2a_0)^{-1}\{p - (Z_1^2/n_1^2 - 1/n_2^2)/p\}),$$

which give

$$a_0^2 K_1^2 + 1/n_2^2 = a_0^2 K_2^2 + Z_1^2/n_1^2 = a_0^2(k_x'^2 + k_y'^2) + Z_1^2\beta,$$

$$\beta = (4p^2 Z_1^2)^{-1}\{p^4 + 2p^2(Z_1^2/n_1^2 + 1/n_2^2) + (Z_1^2/n_1^2 - 1/n_2^2)^2\},$$

$$g_H(\mathbf{K}_1) = \int \phi_H(\mathbf{r}) r^{-1} \exp(i\mathbf{K}_1 \cdot \mathbf{r}) d\mathbf{r}, \quad f_{MB}(\mathbf{K}_2) = \int \phi_{MB}(\mathbf{r}) \exp(i\mathbf{K}_2 \cdot \mathbf{r}) d\mathbf{r},$$

and

$$\sum_{lm} |g_H(\mathbf{K}_1)|^2 = (2^4 \pi a_0 / n_2^3) (a_0^2 K_1^2 + 1/n_2^2)^{-2}.$$

The second term in the integral (2) involves the wavefunction of the atom M_B which may be a complex atom. However, for this case a simple hydrogenic effective- Z wavefunction will be used. The type of wavefunction we use is actually quite restricted. In the above the K_1 dependence of $\Sigma |g|^2$ is in terms of the function $a_0^2 K_1^2 + 1/n_2^2$, which was shown to be equal to a similar term in K_2 . This equality came originally from energy considerations, but the term $a_0^2 K_2^2 + Z_1^2/n_1^2$, which will occur in $\Sigma |f(K_2)|^2$, comes from the wavefunction. This means that, for a simple result, a single effective Z must be chosen for both energy and wavefunction. When this is done the result reduces to

$$\sigma_{n_2}^e = \pi a_0^2 (p^2 n_2^3 Z_{\text{eff}}^5)^{-1} F(n_1, l_1, \beta),$$

as given by May and Lodge (1965) in which the quantum number m of the initial state is averaged over, and the quantum numbers l_2, m_2 of the final state are summed over. This type of situation has also been investigated by Nikolaev (1967), who has described the electron by a different effective Z for energy and for wavefunction. The resultant expression is more complex in this situation and of course still requires the wavefunction to be hydrogenic. Bearing this in mind and considering the simple result obtained in Section III(b) below, in which a much more flexible wavefunction

is allowed, we take the view that if the one-parameter restriction is relaxed then it is no more difficult (with a computer) to use an accurate wavefunction (parameterized in the manner of Roothaan, Sachs, and Weiss 1960) than it is to use a two-parameter description. Thus in the following a single effective Z will be used.

In the cases of interest the initial atom is in the 1S, 2S, or 3S state and for these the F functions are

$$\begin{aligned} n = 1, \quad F_{1s} &= \frac{2^8}{5\beta^5}, \\ n = 2, \quad F_{2s} &= \frac{2^5}{5\beta^5} \left(1 - \frac{5}{6\beta} + \frac{5}{28\beta^2} \right), \\ n = 3, \quad F_{3s} &= \frac{2^8}{135\beta^5} \left(1 - \frac{80}{81\beta} + \frac{1760}{5103\beta^2} - \frac{320}{6561\beta^3} + \frac{1280}{531441\beta^4} \right). \end{aligned}$$

These formulae were used to obtain cross sections for $n_2 = 1, \dots, 5$ and also the limit highly excited form $\lim_{n_2 \rightarrow \infty} n_2^3 \sigma_{n_2}^e$. Only the total and highly excited cross sections will be presented here.

The range of values of p was 0.5–2.5, that is, an energy range of 6 to 150 keV.

The effective Z for lithium was chosen to give the correct electron energy and, using values given by Slater (1960), yielded (1) inner electron $Z = 2.16$, and (2) outer electron $Z = 1.25$. The results for the effective Z for lithium when the inner electrons are included and when they are not are compared for the highly excited case in Figure 2. We see from this that for the lithium effective Z the inner electrons contribute a term equally important with the outer ones when $p \sim 1.6$, and when $p \sim 2.5$ the inner contribution is about five times as large as the outer. These results are compared with the experimental results of Il'in *et al.* (1965) in Figure 3. The correction factor used is the average factor given in Figure 1. The comparison with experiment for lithium is surprisingly good considering the crude effective- Z wavefunctions and the simple correction to the BK cross sections. Of more significance is the relationship between Figures 3(a) and 3(b), where we note that total cross sections and the highly excited cross sections are consistent, which indicates that the BK ratios are still yielding good predictions of the actual ratios as mentioned in the Introduction.

For sodium, again the electron energy (Slater 1960) was used to choose the effective Z . However, for sodium the full calculation with inner electrons included has not been done, so that the results are meaningful only at low energy. For these results we have used $Z = 1.85$ and p has been restricted to 1.7.

The results are compared with experimental values of Il'in *et al.* (1965) in Figure 4, again using the correction factor given in Figure 1. The total cross section (Fig. 4(a)) compares quite well but the highly excited cross section (Fig. 4(b)) does not compare so well. However, by altering the effective Z a better fit could undoubtedly be obtained. We see then that the BK approximation is now not giving such good ratios between cross sections as before, but is still quite good considering the crude wavefunction used for sodium. Also the calibration curve of Figure 1 calculated from hydrogen and helium cross sections is still apparently largely unchanged.

(b) *Accurate Lithium Case*

In the previous subsection the lithium wavefunction was set up using a crude effective- Z function. We now use a more accurate function given by Roothaan,

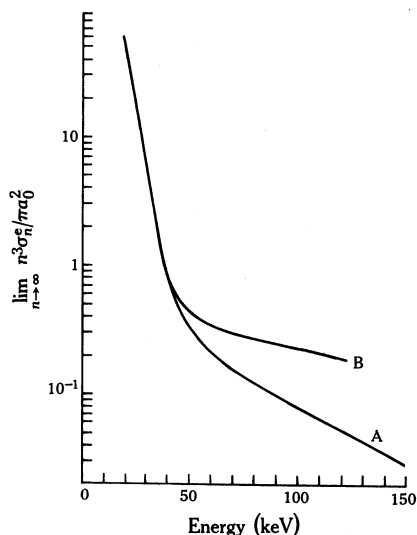


Fig. 2.—Highly excited charge exchange cross sections for lithium in the effective- Z approximation:

A, outer electron only;

B, both inner and outer electrons.

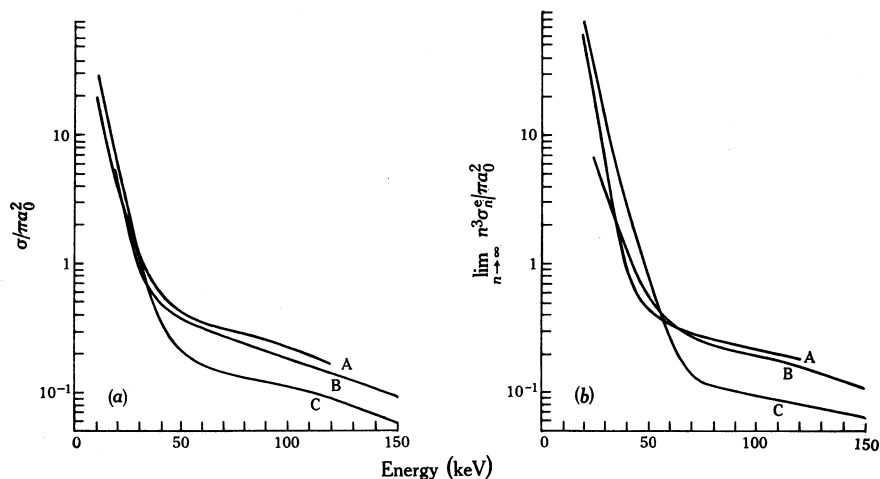


Fig. 3.—Total (a) and highly excited (b) charge exchange cross sections for lithium: A, experimental results of Il'in *et al.* (1965); B, results using the effective- Z wavefunction; C, results using the accurate wavefunction.

Sachs, and Weiss (1960) for lithium. This has already been done by Hiskes (1965), but in his calculation he failed to include the inner electrons, which are the major contributors above 40 keV.

Referring to equation (2) in Subsection (a), we have the expression for f

$$f_{MB}(\mathbf{K}_2) = \int \phi_{MB}(\mathbf{r}) \exp(i\mathbf{K}_2 \cdot \mathbf{r}) d\mathbf{r},$$

where $\phi_{MB}(\mathbf{r})$ is now a function defined by Roothaan, Sachs, and Weiss (1960) as

$$\phi_{MB}(\mathbf{r}) = (4\pi)^{-1} \sum \{ (2a_{0i} \zeta_i^{3/2} + (2/\sqrt{3})a_{1i} \zeta_i^{5/2} r) \exp(-\zeta_i r) \},$$

the constants ζ_i , a_{0i} , and a_{1i} being tabulated by them.

The energy of the electron involved is also needed for the term $(Z_B^2/n_B^2 - 1/n^2)$ which occurs in the expressions for $\mathbf{K}_1$ and $\mathbf{K}_2$. Roothaan, Sachs, and Weiss give a value for the difference in energy of a lithium atom with two and with three electrons, which yields this energy when the outer electron is captured. However, the situation in which there is one electron in the 1S level and one in the 2S level is not considered.

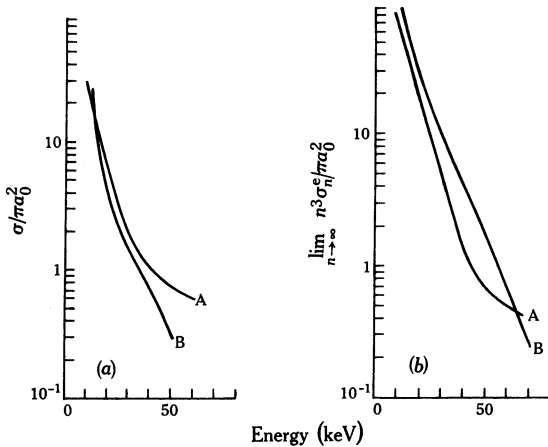


Fig. 4.—Total (a) and highly excited (b) charge exchange cross sections for sodium:

A, experimental results of Il'in *et al.* (1965);

B, effective- Z results with only outer electron included.

The energy for this was obtained from the wavelengths of Li^+ transitions given in Circular No. 467 of the United States National Bureau of Standards. In this regard we have two choices: the transitions $1S^2 \rightarrow 1S2S$, $J = 1$, and $1S^2 \rightarrow 1S2S$, $J = 0$. The resultant energies are not very different and, since the cross section is found to be insensitive to small changes in Z_B^2/n_B^2 (in this case), we take the average value, namely $Z_B^2/n_B^2 = 4.7$. The result for the cross section then reduces to

$$\sigma_{n_2}^e = \frac{2^6}{p^2 n_2^3 \beta^5} \int_0^1 y^4 dy \left| \sum_j \left(\frac{a_{0j}^*}{(1+c_j y)^2} + \frac{a_{1j}^* (\alpha_j - c_j) y - 1}{(1+c_j y)^3} \right) \right|^2 \pi a_0^2, \quad (3)$$

where

$$\beta = \frac{1}{4} p^4 + \frac{1}{4} p^{-2} (Z_B^2/n_B^2 - 1/n_2^2) + \frac{1}{2} (Z_B^2/n_B^2 + 1/n_2^2)^2,$$

$$c_j = (\zeta_j^2 - Z_B^2/n_B^2)/\beta, \quad \alpha_j = 4\zeta_j^2/\beta,$$

$$a_{0j}^* = 2a_{0j} \zeta_j^{5/2}, \quad a_{1j}^* = (2/\sqrt{3})a_{1j} \zeta_j^{5/2}.$$

The integral (3) could have been taken further analytically but it was judged to be simpler to proceed numerically from this point.

The results are given in Figure 3 and the BK cross sections (without correction factor) are presented in Table 1. In both cases the inner and outer electrons are included. From Figure 3 we see that the results are not as good as the effective- Z case. However, the trend is the same for both the highly excited case and the total cross sections, and thus we may say that the BK cross sections still give the correct ratios between states but the correction factor may not be appropriate for lithium, particularly in the region in which the inner electrons contribute.

It is apparent from the figures that crude effective- Z cross sections can approximate the results. This is not always the case. For lithium the largest cross section is for $n = 2$, and for this and all higher n cross sections there is reasonable agreement between effective- Z and Roothaan, Sachs, and Weiss cross sections. However, for

TABLE 1

BK CHARGE EXCHANGE CROSS SECTIONS FOR PROTON-LITHIUM COLLISION IN WHICH LITHIUM IS DESCRIBED BY A Roothaan, Sachs, and Weiss wavefunction

The correction factor of Figure 1 is not included. The table is for values of normalized velocity p against final states $n = 1(1)5$ and also the highly excited limit. The numbers in square brackets are the powers of 10 by which each value is to be multiplied: $6.74 [-1]$ means 6.74×10^{-1}

$p = \frac{\hbar v}{e^2}$	BK Cross Sections (πa_0^2 units)					
	$n = 1$	2	3	4	5	$\lim_{n \rightarrow \infty} n^3 \sigma_n^e$
0.7	6.74 [-1]	8.04 [+1]	4.69 [+1]	2.33 [+1]	1.27 [+1]	1.73 [+3]
0.9	6.33 [-1]	1.47 [+1]	9.62 [0]	5.19 [0]	2.96 [0]	4.44 [+2]
1.0	6.3 [-1]	5.96 [0]	3.98 [0]	2.18 [0]	1.25 [0]	1.91 [+2]
1.2	6.66 [-1]	9.45 [-1]	6.16 [-1]	3.38 [-1]	1.95 [-1]	3.02 [+1]
1.4	5.85 [-1]	1.76 [-1]	9.53 [-2]	5.06 [-1]	2.88 [-2]	4.37 [0]
1.7	5.84 [-1]	6.71 [-2]	2.06 [-2]	8.93 [-3]	4.64 [-3]	6.02 [-1]
2.0	4.31 [-1]	5.48 [-2]	1.62 [-2]	6.81 [-3]	3.48 [-3]	4.33 [-1]
2.5	1.26 [-1]	3.08 [-2]	9.34 [-3]	3.97 [-3]	2.04 [-3]	2.56 [-1]

the $n = 1$ cross section (not given) the effective- Z treatment grossly overestimates the Roothaan, Sachs, and Weiss wavefunction result. Thus it cannot always be assumed that a simple effective- Z result fitted to the electron energy will produce a satisfactory estimate of the cross section (nor could changing the effective Z to any other value help the fit).

IV. CONCLUSIONS

From the comparison between the present theoretical calculations and the experimental results of Π' in *et al.* (1965), we conclude the following.

- (1) At high incident proton energies the target's inner electrons must be included in the calculation.
- (2) When the inner electrons are included, the theoretical prediction as to the ratio between the cross section for producing highly excited hydrogen atoms and the total cross section is in agreement with experiment. (This extends to lithium and sodium targets the remarks made by Jackson and Schiff (1953) that the BK approximation predicts correct *ratios*.)

- (3) The present results for the total charge exchange cross section, and for the individual cross sections for particular final states, are also in agreement with experiment. This extends the conjectures of Nikolaev (1967) and tends to justify the use of the multiplicative correction factor for the individual cross sections.
- (4) With respect to the choice of wavefunction for the target atom, lithium exchange was evaluated both using a crude effective- Z wavefunction and a Roothaan, Sachs, and Weiss (1960) wavefunction. The result of this was that for exchange to excited states below the quasi-symmetric state the approximate results were badly in error, but for all other cases both the accurate and crude wavefunctions gave comparable results.

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