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Influence of a quasi-molecular mechanism of recombination on the formation of hydrogen in the early Universe

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ABSTRACT

In the framework of a quasi-molecular approach, the formation of hydrogen atom in the pre-recombination period of evolution of the Universe is analysed quantitatively. Calculations in an adiabatic multilevel representation enable estimates of probabilities of radiative transitions. The quasi-molecular mechanism of recombination allows the formation of hydrogen molecular ion, H_2^+ , in its ground state. The probability of this process is comparable with the probability of the creation of atomic hydrogen. The participation of a second proton in the recombination increases the binding energy of an electron and decreases the rate of recombination of hydrogen.

Key words: atomic processes - cosmic background radiation - early Universe.

1 INTRODUCTION

Cosmological recombination was responsible for the formation of neutral hydrogen and helium atoms in the early Universe. For an electron and a proton, the cosmological recombination was first studied by Zel'dovich, Kurt & Syunyaev (1968) and slightly later by Peebles (1968). Despite substantial progress achieved after these pioneering works, there remain problems in understanding how the details of recombination affect the cosmological parameters. The present level of study of the problems can be found in review of Kurt & Shakhvorostova (2014) and in references therein.

To explore the influence on the cosmological parameters, Liu et al. (2019) and Chiang & Slosar (2018) varied physical and phenomenological parameters in a standard code to compute the recombination history of the Universe. They found that a cosmological parameter, the Hubble constant, is robust against perturbations of recombination history, unless non-standard physics modifies the atomic constants during the recombination epoch.

In our recent paper (Kereselidze, Noselidze & Ogilvie 2019b), a quasi-molecular mechanism of recombination (QMR) was suggested and applied to treat the formation of atomic hydrogen in the early Universe. According to this QMR, in the pre-recombination period of evolution of the Universe (a redshift $z \gtrsim 2000$), when the temperature and density of protons were higher than those of subsequently, the recombination of an electron and a proton occurred in the presence of the nearest neighbouring proton, which participated in the process. An electron and two protons were considered to constitute quasimolecule H_2^+ temporarily formed during a collision.

According to the QMR, a free electron emits a photon and creates H_2^+ in a highly excited state. Free–bound radiative transitions occur at distances between protons greater than the radius of the hydrogen atom in a highly excited state. If H_2^+ is formed in a repulsive state, the system rapidly dissociates into an excited hydrogen atom and a proton. The duration of dissociation is defined by the collision period, which is about 10^{-11} s for highly excited states and decreases to 10^{-14} s for the lowest states. From an excited state, H descends to the state with principal quantum number n = 2. A radiative decay from state 2^2 P involving one photon or from state 2^2 S involving two photons then yields the hydrogen atom in its ground state.

If a quasi-molecule is formed in an attractive state, which can bind the colliding particles, a direct formation of the hydrogen atom is impossible. In this case, radiative transitions lead to a cascade downwards to low-lying attractive or repulsive quasi-molecular states. The QMR thus leads to a radiative transition of two types: free–bound with a direct formation of the hydrogen atom in the highly excited state, and free–bound with subsequent intermediate bound– bound quasi-molecular transitions that end with the formation of H.

The main conclusion made by Kereselidze et al. (2019b) was that the radiative transition of an electron to an excited attractive state of H_2^+ affects the probability of recombination; the QMR should hence be included in a calculation of the cosmological recombination radiation.

As an electron is much lighter than a proton, the velocity of an electron substantially exceeds the velocity of a proton in the quasimolecule. This fact allows us to treat H_2^+ on a basis of an adiabatic representation. In this approximation, all characteristics of H_2^+ , such as the electron binding energy, dipole strengths, quasi-molecular energy terms, and profiles of spectral lines, depend upon the distance *R* between protons. According to the QMR, a free electron emits a photon and creates

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The purpose of this paper is to describe quantitatively the nonstandard QMR. For this purpose, we implemented the appropriate calculations and answer this question: Is the QMR significant for a complete study of the cosmological recombination problem? The treatment is performed in an adiabatic multilevel representation.

The paper is organized as follows: After stating our objective, we analyse the behaviour of the energy terms of H_2^+ in Section 2, and evaluate radiative transition probabilities in Section 3. Using the obtained equations, we perform the appropriate calculations in Section 4, before a conclusion in Section 5. Unless otherwise indicated, atomic units ($e = m_e = \hbar = 1$) are used throughout the paper.

2 BEHAVIOUR OF QUASI-MOLECULAR ENERGY TERMS

For our purpose, it is important to know the behaviour of the energy terms of H_2^+ at large distances *R* between protons. More precisely, for the QMR the existence of energy terms that are attractive is crucial, so that, accordingly, the colliding particles can bind during a period greater than a collision interval.

At large *R*, the energy terms of H_2^+ are representable as (Bates & Reid 1968)

$$U_{n_1,n_2,|m|}^{g,\mathfrak{u}}(R) = -\frac{1}{2n^2} + \frac{3n(n_1 - n_2)}{2R^2} + O(R^{-3}) \mp \Delta_{n_1,n_2,|m|}(R).$$
(1)

Here, the first three terms define the long-range interaction between the hydrogen atom and proton; the last term describes the exponentially small exchange interaction between the particles and is defined as (Komarov, Ponomarev & Slavyanov 1976)

$$\Delta_{n_1 n_2 |m|}(R) = \frac{(-1)^{|m|}}{n^3 n_2! (n_2 + |m|)!} \left(\frac{2R}{n}\right)^{n - n_1 + n_2} \cdot e^{-\frac{R}{n} - n} \left(1 + O(R^{-1})\right).$$
(2)

In equations (1) and (2), n_1 , n_2 , and m are the parabolic quantum numbers that specify electron states in the separate hydrogen atom; the total quantum number n is related to n_1 , n_2 , and m with equation $n = n_1 + n_2 + |m| + 1$. Quasi-molecular energy terms $U_{n_1,n_2,|m|}^{g,u}(R)$ are distinguished by parity, which is even (*gerade*) or odd (*ungerade*). As is clear from equation (1), the energy term is attractive at large Rif $n_2 > n_1$. Among the terms with $n_1 = n_2$ and m = 0, the g term is attractive and the u term is repulsive.

We proceed to investigate the behaviour of the energy terms of H_2^+ in the entire region of internuclear distances *R*. To avoid cumbersome calculations and at the same time to maintain generality, we restrict the treatment to the lowest 30 quasi-molecular terms with m = 0 (σ terms). These terms correlate with the levels of the hydrogen atom with n = 1, 2, 3, 4, and 5 at $R = \infty$. The behaviour of the energy terms is depicted in Fig. 1.

The quasi-molecular terms are specified with quantum numbers n_0 and l_0 that, together with m, characterize an electron in the *united* atom (R = 0). Parabolic quantum numbers n_1 and n_2 are related to quantum numbers n_0 , l_0 , and m according to the molecular-orbital correlation rules $n_1 = n_0 - l_0 - 1$ and $n_2 = (l_0 - |m|)/2$ for g orbitals and $n_2 = (l_0 - |m| - 1)/2$ for u orbitals (Bates & Reid 1968; Kereselidze 1987).

3 RADIATIVE TRANSITION PROBABILITIES

In this section, we evaluate the probabilities for radiative transitions involved in the QMR. Fig. 1 shows that, among the states under



Figure 1. σ energy terms of H₂⁺ as functions of distance *R* between protons, with blue curves for attractive terms and red curves for repulsive terms. Thin arrows indicate radiative transitions between attractive quasi-molecular states; $a_0 = \hbar^2/m_e e^2 = 0.529 \times 10^{-8}$ cm is the first Bohr radius of hydrogen and $\varepsilon_0 = m_e e^4/\hbar^2 = 27.21$ eV. Energy terms (6f σ_u , 5p σ_u), (5f σ_u , 3s σ_g), and (3p σ_u , 2s σ_g) are so close that they are indistinguishable in the figure.

consideration, the attractive ones are

- 1s, 3d, 4f, 5g, 6h, 4d, 7i, 8j,
- 6g, 7h, 9k, 10l, 8i, 9j, 7g,

(3)

Table 1. Equilibrium distances, R_0 , and energies of the lowest 16 electronic states of H_2^+ at $R = R_0$; parabolic quantum numbers n_1 and n_2 and parity of state are shown within parentheses.

| State | R_0, a_0 | $U(R_0),\varepsilon_0$ | State | R_0, a_0 | $U(R_0), \varepsilon_0$ |
|-----------------------|------------|------------------------|-----------------------|------------|-------------------------|
| $1s(00_{g})$ | 2.00 | -0.6026 | $2p(00_{\rm u})$ | 12.546 | - 0.500 061 |
| 3d (01 _g) | 8.83 | -0.1750 | $4f(01_{u})$ | 20.92 | -0.1307 |
| $5g(02_{g})$ | 23.90 | -0.0782 | $6h(02_{\rm u})$ | 40.52 | -0.0606 |
| 4d (11g) | 17.85 | -0.0588 | 7i (03g) | 47.36 | -0.0436 |
| $6g(12_{g})$ | 33.64 | -0.0379 | 8j (03 _u) | 68.17 | -0.0352 |
| $7h(12_{u})$ | 56.09 | -0.0326 | 9k (04g) | 79.23 | -0.0276 |
| 8i (13 _g) | 59.68 | -0.0255 | $101(04_{\rm u})$ | 103.94 | -0.0230 |
| 9j (13 _u) | 84.55 | -0.0218 | 7g (22 _g) | 49.31 | -0.0207 |

whereas the repulsive states are

4s, 5p, 8h, 6d, 7f, 5s, 6p.

In equations (3) and (4), a symbol σ is omitted and states are arranged in order of increasing energy at large *R*; the subscripts g and u are also omitted because the parity of a state is uniquely defined with quantum number l_0 .

Adjusting a harmonic oscillator potential to the attractive energy term, one can readily show that each potential well depicted in Fig. 1 contains not less than 10 vibrational levels. For attractive states, the equilibrium distances, R_0 , are presented in Table 1, with the corresponding energy minima.

The lifetime of H_2^+ in an excited electronic state, about 10^{-9} to 10^{-7} s, is much greater than the duration of a collision. Being formed in an excited repulsive state, H_2^+ dissociates immediately to proton and hydrogen atom (direct channel to produce H in an excited state), but if H_2^+ is formed in an excited attractive state, there is a possibility to descend to a lower lying quasi-molecular state (repulsive or attractive) with a subsequent dissociation or cascade down. This effect constitutes an indirect channel of producing H in an excited state.

In our treatment, we assume that H_2^+ is created at a large distance between protons in excited σ electronic states (thick arrow in Fig. 1). There are five repulsive states – 5s, 6d, 8h, 7f, and 6p (not shown in Fig. 1) – that correlate with states of the hydrogen atom with n =5 at $R = \infty$. In these states, H_2^+ rapidly dissociates into hydrogen atom and proton. As for attractive states, being in states 7g and 8i the quasi-molecules rapidly relax to the lowest vibrational level and then descend to lower lying states according to the Franck–Condon principle (vertical transitions). Transitions from remaining attractive states 9j, 10l, and 9k are inhibited by the extremely small Franck– Condon factors (their minima are located too far from the minima of lower lying attractive states).

Taking into account that dipole transitions are allowed only between states of opposite parity, the problem reduces to the treatment of the following transitions:

$$\begin{cases} 7g\\ 8i \end{cases} \to \{6f, 5p, 5f, 4p, 3p, 2p \end{cases}$$
 (5)

for the direct channel and

for the indirect channel.

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3.1 Formation of the hydrogen atom

The total probability of the various processes is a sum of the probabilities of the separate processes just as the duration of consecutive processes is a sum of the separate periods. Taking that effect into account and following equation (5), one can write for the probability per unit time of a direct formation of atomic hydrogen in the ground state from quasi-molecular states 7g and 8i that

 $W_{\rm dir} = \Omega(7g)W_{\rm dir}(7g) + \Omega(8i)W_{\rm dir}(8i),$

in which

(4)

$$W_{\rm dir}(i) = \rho(i \to 2p) + \left[\rho^{-1}(i \to 6f) + W_{\infty}^{-1}(6f)\right]^{-1} \\ + \left[\rho^{-1}(i \to 5p) + W_{\infty}^{-1}(5p)\right]^{-1} \\ + \left[\rho^{-1}(i \to 5f) + W_{\infty}^{-1}(5f)\right]^{-1} \\ + \left[\rho^{-1}(i \to 4p) + W_{\infty}^{-1}(4p)\right]^{-1} \\ + \left[\rho^{-1}(i \to 3p) + W_{\infty}^{-1}(3p)\right]^{-1}.$$
(7)

Here, $\Omega(i)$ is the probability that H_2^+ is created in the state $|i\rangle$; $\rho(i \rightarrow j)$ is the probability per unit time of transition from $|i\rangle$ to $|j\rangle$ quasi-molecular state; $W_{\infty}(i)$ is the probability per unit time of a cascade downward to the ground state of H after the dissociation of H_2^+ .

Following equation (6), one can write for the probability of an indirect formation of atomic hydrogen in the ground state from quasimolecular states 7g and 8i that

$$W_{\text{indir}} = \Omega(7\text{g})W_{\text{indir}}(7\text{g}) + \Omega(8\text{i})W_{\text{indir}}(8\text{i}),$$

in which

$$W_{\text{indir}}(\mathbf{i}) = \left[\rho^{-1}(\mathbf{i} \to 7\mathbf{h}) + \rho^{-1}(7\mathbf{h} \to 7\mathbf{i}) + \rho^{-1}(7\mathbf{i} \to 2\mathbf{p})\right]^{-1} + \left[\rho^{-1}(\mathbf{i} \to 7\mathbf{h}) + \rho^{-1}(7\mathbf{h} \to 7\mathbf{i}) + \rho^{-1}(7\mathbf{i} \to 6\mathbf{h}) + \rho^{-1}(6\mathbf{h} \to 5\mathbf{g}) + \rho^{-1}(5\mathbf{g} \to 2\mathbf{p})\right]^{-1} + \left[\rho^{-1}(\mathbf{i} \to 7\mathbf{h}) + \rho^{-1}(7\mathbf{h} \to 7\mathbf{i}) + \rho^{-1}(7\mathbf{i} \to 6\mathbf{h}) + \rho^{-1}(6\mathbf{h} \to 5\mathbf{g}) + \rho^{-1}(5\mathbf{g} \to 4\mathbf{f}) + \rho^{-1}(4\mathbf{f} \to 3\mathbf{d}) + \rho^{-1}(3\mathbf{d} \to 2\mathbf{p})\right]^{-1}.$$
(8)

A sum of (7) and (8) defines the complete probability of the formation of atomic hydrogen in the ground state. In the above equations, non-adiabatic transitions between quasi-molecular states are entirely ignored.

3.2 Formation of H₂⁺ in the ground state

Repulsive energy term 2p of H_2^+ has a minimum at $R = 12.546a_0$ (Landau & Lifshitz 1977). This minimum, which is due to van der Waals forces, is much shallower than that of ground-state term 1s (see Table 1). Adjusting a harmonic-oscillator potential to the numerical data, one can find that the potential well contains one vibrational level. Adjusting the Morse potential (Morse 1929) to the numerical data leads, notably, to the same result. Hence, hereafter 2p might be considered as an attractive state.

The existence of a bound state with equilibrium distance near $R_0 = 2.0a_0$ leads to a possibility of the formation of H_2^+ in the ground state. The complete probability per unit time of a transition from states 7g and 8i to the ground state of H_2^+ is

$$W_{\rm mol} = \Omega(7g)W_{\rm H_2^+}(7g) + \Omega(8i)W_{\rm H_2^+}(8i),$$

$$\begin{split} W_{\mathrm{H}_{2}^{+}}(\mathbf{i}) &= \left\{ \left[\rho(\mathbf{i} \to 2\mathbf{p}) + \left(\rho^{-1}(\mathbf{i} \to 7\mathbf{h}) + \rho^{-1}(7\mathbf{h} \to 7\mathbf{i}) \right. \\ &+ \rho^{-1}(7\mathbf{i} \to 2\mathbf{p}) \right)^{-1} + \left(\rho^{-1}(\mathbf{i} \to 7\mathbf{h}) + \rho^{-1}(7\mathbf{h} \to 7\mathbf{i}) \right. \\ &+ \rho^{-1}(7\mathbf{i} \to 6\mathbf{h}) + \rho^{-1}(6\mathbf{h} \to 5\mathbf{g}) + \rho^{-1}(5\mathbf{g} \to 2\mathbf{p}) \right)^{-1} \\ &+ \left(\rho^{-1}(\mathbf{i} \to 7\mathbf{h}) + \rho^{-1}(7\mathbf{h} \to 7\mathbf{i}) + \rho^{-1}(7\mathbf{i} \to 6\mathbf{h}) \right. \\ &+ \rho^{-1}(6\mathbf{h} \to 5\mathbf{g}) + \rho^{-1}(5\mathbf{g} \to 4\mathbf{f}) + \rho^{-1}(4\mathbf{f} \to 3\mathbf{d}) \\ &+ \rho^{-1}(3\mathbf{d} \to 2\mathbf{p}) \right)^{-1} \right]^{-1} + \rho^{-1}(2\mathbf{p} \to 1\mathbf{s}) \bigg\}^{-1}. \end{split}$$

There is thus an additional channel – a molecular channel that leads to the formation of H_2^+ in its ground state. This statement becomes obvious when one takes into account that term 2p of H_2^+ with m = 1 has a deep minimum at $R = 7.93a_0$ (Bates & Reid 1968). The probability of a transition from this state to the ground state is hence substantial. An estimate of the contribution of π terms in the formation of H_2^+ in the ground state is a separate task, to be treated in forthcoming work.

3.3 Influence on the ionization energy

We seek to show how a participation of a second proton in a recombination alters the binding energy of an electron. At large R, the electron energy reads

$$\varepsilon_{n_1 n_2 |m|}(R) = \varepsilon_{n_1 n_2 |m|}(\infty) - \frac{1}{R} + O(R^{-2}),$$
 (10)

in which $\varepsilon_{n_1n_2|m|}(\infty) = -1/2n^2$ is the electron energy in the isolated hydrogen atom.

Inserting into equation (10) the average distance between protons during the pre-recombination period of evolution of the Universe, which might be assumed to be $\bar{R} = 2r_n$ (Kereselidze et al. 2019b) in which $r_n = 2n^2$ is the radius of the hydrogen atom in the excited state, we obtain that

$$\varepsilon_{n_1 n_2 |m|}(\bar{R}) = \varepsilon_{n_1 n_2 |m|}(\infty) - \frac{1}{4n^2}.$$
 (11)

Equation (11) shows that the participation of a second proton in the process increases the binding energy of an electron. We thus obtain that, in the perturbed hydrogen atom, a deviation of the ionization energy from its value in unperturbed H attains 50 per cent.

4 RESULTS OF CALCULATIONS

We proceed to calculate the probabilities involved in equations (7)–(9). The probability of bound–bound and bound-free radiative transitions in H_2^+ is defined as (Heitler 1954)

$$\rho(i \to f) = \frac{4w_{if}^3}{3c^3} \left| d_{if} \right|^2.$$
(12)

Here, w_{if} is the frequency of an emitted photon, *c* is the speed of light, and d_{if} is the transition matrix element defined with wavefunctions of H₂⁺.

In the adiabatic approximation, the wavefunctions of H_2^+ are representable as a product of two functions $\Psi = \chi \psi$, in which $\psi(\vec{r}, R)$ and $\chi(\vec{R})$ describe motion of an electron and protons, respectively. Inserting $\Psi = \chi \psi$ into the transition matrix element and accounting that ψ depends smoothly on *R*, we obtain that

$$d_{if}(R) = \left\langle \chi_f \middle| \chi_i \right\rangle \left\langle \psi_f \middle| z \left| \psi_i \right\rangle.$$
(13)

Table 2. Matrix elements of electric dipole strength at $R = R_0$ involving the lowest 10 electronic states of H₂⁺; R_0 is the equilibrium distance of the upper state.

| Transition | $\langle f z i\rangle, a_0$ | Transition | $\langle f z i\rangle, a_0$ |
|---------------------|-----------------------------|---------------------|-----------------------------|
| $7g \rightarrow 2p$ | - 0.003 | $8i \rightarrow 2p$ | 0.048 |
| $7g \rightarrow 7h$ | 3.031 | $8i \rightarrow 7h$ | 10.589 |
| $7h \rightarrow 7i$ | -1.130 | $7i \rightarrow 6h$ | 6.503 |
| $6h \rightarrow 5g$ | - 9.673 | $5g \rightarrow 4f$ | 3.004 |
| $4f \rightarrow 3d$ | 6.924 | $5g \rightarrow 2p$ | -0.287 |
| $3d \rightarrow 2p$ | 0.795 | $2p \rightarrow 1s$ | - 6.246 |

In equation (13), $\langle \psi_f | z | \psi_i \rangle$ is the electric dipole moment matrix element; $\langle \chi_f | \chi_i \rangle$ is the vibrational overlap integral or the Franck– Condon factor. For a transition from a bound to antibound state χ_f should be replaced in $\langle \chi_f | \chi_i \rangle$ with the appropriate wavefunction Φ_f describing nuclear motion in a repulsive field. Explicit expressions for the Franck–Condon factor and overlap integral $\langle \Phi_f | \chi_i \rangle$ are presented in Appendix A.

We first calculate the ratio

$$\eta(i) = \frac{W_{\mathrm{H}_{2}^{+}}(i)}{W_{\mathrm{dir}}(i) + W_{\mathrm{indir}}(i)} \tag{14}$$

for i = 3d, 5g, 7i, 8i, and 7g. This ratio does not depend on $\Omega(i)$ and allows us to estimate relative contribution of the formation of H₂⁺ in its ground state in recombination.

In H₂⁺, the transition probabilities between two attractive states are values of the order of 10^{-10} – 10^{-14} (per atomic unit of time), whereas the transition probabilities from attractive to repulsive states 6f, 5p, 5f, 4p, and 3p are much smaller. Neglecting small terms, we thereby simplify $\eta(i)$. The appropriate expressions are presented in Appendix B.

Matrix elements of the electric dipole strength corresponding to the transitions involved in equations (B1)–(B4) are collected in Table 2. For the lowest four states, the data are taken from paper of Ramaker & Peek (1973); for the highly excited states, matrix elements are calculated with an algorithm developed by Devdariani et al. (2005), and employing asymptotic wavefunctions for H_2^+ (Kereselidze, Noselidze & Chibisov 2003).

Using equations (B1)–(B4), we calculated $\eta(i)$ and obtained that $\eta(3d) = 2.5 \times 10^{-5}$, $\eta(5g) = 5.1 \times 10^{-1}$, $\eta(7i) = 5.3 \times 10^{-1}$, and $\eta(7g) = \eta(8i) = 5.4 \times 10^{-1}$. This quantitative analysis thus revealed that, apart from $\eta(3d)$, which is a small value, all other $\eta(i)$ are values of order unity and are nearly equal. These obtained results clearly show that the formation of H₂⁺ in the ground state introduces an important contribution, together with formation of H(1S), to the recombination.

We proceed to calculate the probabilities of the initial free–bound transitions as a function of a redshift. In its general consideration, this task is complicated. A simplification becomes achievable on assuming that protons are located on the axis *z* and a colliding electron moves parallel to this axis. According to this approximation, one can calculate the transition probability using the two-Coulomb-centre wavefunctions corresponding to the continuous spectrum (Kereselidze, Noselidze & Devdariani 2019a) and discrete spectrum (Kereselidze et al. 2003); in the general case, the wavefunction of a colliding electron is a linear combination of the two-Coulomb-centre wavefunctions. The appropriate electric-dipole-strength matrix elements are derived in Appendix C. Equation (12) with these matrix elements allows us to estimate $\Omega(7g)$ and $\Omega(8i)$ at varied *z*. The results of calculations are depicted in Fig. 2.



Figure 2. Probabilities $\Omega(i)$ as functions of a redshift *z*; red curves – influence of a neighbouring proton is neglected ($R = \infty$ in equation C5); blue curves – influence of a neighbouring proton is taken into account ($R < \infty$ in equation C5). Curves 1 and 2 correspond to probabilities $\Omega(7g)$ and $\Omega(8i)$, respectively.



Figure 3. Ratios $\tau(i)$ as functions of redshift *z*; red curve – $\tau(7g)$ and blue curve – $\tau(8i)$.

Fig. 2 shows that the free–bound transition probabilities with and without inclusion of the corrections, arising because of the existence of a second proton, coincide completely for z < 2000, and differ negligibly for 2000 < z < 3000 but differ perceptibly for 3000 < z < 5000. The transition probability $\Omega(8i)$ into the state with parabolic quantum numbers $n_1 = 1$, $n_2 = 3$ is larger than transition probability $\Omega(7g)$ into the state with $n_1 = n_2 = 2$. This difference results from the well-known fact that wavefunctions of the hydrogen atom in parabolic coordinates are symmetric about plane z = 0 when $n_1 = n_2$, but not symmetric when $n_1 \neq n_2$ (Landau & Lifshitz 1977). As a result, transition matrix element z_{if} with $n_1 \neq n_2$ is larger than z_{if} with $n_1 = n_2$.

Fig. 3 shows the ratio $\tau(i) = [\Omega'(i) - \Omega(i)]/\Omega(i)$ as a function of redshift z. Here, $\Omega'(i)$ and $\Omega(i)$ are calculated with and without the inclusion of the second term in equation (C5). The calculation revealed that $\tau(7g) = 3.7 \times 10^{-8}$ at z = 2000, $\tau(7g) = 4.2 \times 10^{-5}$ at z = 3000, $\tau(7g) = 1.4 \times 10^{-3}$ at z = 4000, and $\tau(7g) = 1.2 \times 10^{-2}$ at z = 5000. For free-bound transitions into the state with $n_1 = 1$, n_2 = 3, these probabilities are $\tau(8i) = 8.3 \times 10^{-5}$ at z = 2000, $\tau(8i) =$ 2.6×10^{-3} at z = 3000, $\tau(8i) = 1.5 \times 10^{-2}$ at z = 4000, and $\tau(7g)$ = 4.8×10^{-2} at z = 5000.

Multiplying $\Omega(i)$ and bound-bound transition probabilities defined by equations (7)–(9), one thereby obtains the absolute values of the recombination probability, W(i). Bound-bound transition probabilities do not depend on a redshift. Therefore, the dependence of W(i) on z is fully defined by the initial free-bound transition probability.

5 CONCLUSIONS

In this work, we have analysed quantitatively the recombination of an electron and a proton when the nearest neighbouring proton participates in the process. The system of colliding particles is considered as a quasi-molecule, H_2^+ , temporarily formed during a collision. This analysis has been implemented in an adiabatic approximation, in which the lowest 30 electronic states of H_2^+ with m = 0 (σ states) were involved. The presence of another proton reduces the symmetry of a field experienced by an electron from spherical to axial. This reduction of symmetry leads in turn to the radiative transitions that are forbidden in the recombination of an electron on an isolated proton.

In the developed scheme of calculation, our inclusion of higher electronic states leads to no qualitative new and formidable problem – it only complicates the treatment. We hence expect that $\eta(i)$ calculated for higher quasi-molecular states will be near obtained for states of the present large number, even though finite. Our expectation is based on the fact that the Franck–Condon factors decrease rapidly for highly excited attractive states as the locations of the energy minima are shifted towards large internuclear distances; accordingly, the participation of highly excited quasi-molecular states in the recombination declines.

The main results obtained in this work are that the QMR allows the formation of H_2^+ in its ground state and that the probability of this process is comparable with the probability of the formation of atomic hydrogen. Another important result is that the participation of a second proton in the process increases the binding energy of an electron. That in turn leads to increasing of *z* at which the recombination of hydrogen starts. We thus obtained that the quasimolecular treatment reduces the rate of recombination of hydrogen and it shifts beginning of the stage of the standard recombination towards earlier period.

An inspection of $\eta(i)$ shows that an inclusion of a molecular channel in the recombination accelerates the loss of free protons about 1.5 times but maintains an unchanged rate of disappearance of free electrons. Hence, conclusions made by previous authors concerning the fraction of free electrons in the recombination period (see e.g. Glover et al. 2014) remain valid.

The presence of a second proton leads to the splitting of the hydrogen atom level with $n \gg 1$ and m = 0 into n levels and to the formation of H_2^+ in highly excited σ states. Among these states, half is repulsive and another half is attractive. In a repulsive state, H_2^+ rapidly dissociates into an excited hydrogen atom and a proton. In an attractive state, H_2^+ relaxes to the lowest vibrational level and then descends to lower lying quasi-molecular states according to the Franck-Condon principle. This process terminates with the formation of H or H_2^+ in the ground state. At large *R*, i.e. when *R* $\sim 2n^2 \gg 1$, the attractive potential is a value of the order of n^{-2} according to equation (1). Taking into account that $n \sim 10^2$ at z = 2500, one can assume that the formation of H_2^+ was efficient in the pre-recombination as well as in the recombination period of evolution of the Universe. We emphasize that our inclusion of the QMR in the calculations increases the initial free-bound transition probabilities, especially for z > 3000.

In the pre-recombination period of evolution of the Universe, the primordial plasma was thus composed of neutral hydrogen and helium atoms, hydrogen molecular ions H_2^+ , protons, and electrons, all exposed to the radiative field. Ions H_2^+ formed in the ground state were destructed through photoionization, photoexcitation in the repulsive quasi-molecular state, or a collision with other particles. This statement becomes evident by exploring the abundance of H_2^+ The quantitative analysis that we have performed confirms that the QMR plays an important role, and, accordingly, must be taken into account for a complete treatment of the cosmological recombination. As a possible significant outcome, we note that the inclusion of the quasi-molecular correction in the cosmological recombination can increase the Hubble constant estimated from analysis of the cosmic microwave background data and, accordingly, decrease the tension with local measurements (Beradze & Gogberashvili 2019).

In conclusion, we emphasize that our work does not solve completely the problem of the formation of hydrogen in the early Universe; rather, it is one step towards the solution of that problem. The next step is the calculation of matrix elements for the initial free–bound transitions using the precise two-Coulomb-centre wavefunctions defined for the continuous and discrete spectra (in this work, only an estimate of these matrix elements was undertaken). A knowledge of these data allows us to calculate precisely the populations of quasi-molecular states and thereby to determine the absolute values of probabilities of the formation of H and H_2^+ in the pre-recombination stage.

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DATA AVAILABILITY

The data underlying this article are available in the article and in its online supplementary material.

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APPENDIX A

For two harmonic oscillators with disparate both equilibrium position and vibrational frequency, the Franck–Condon factor is expressible as (Chang 2005)

$$\begin{aligned} \langle \chi_{\nu} | \ \chi_{\nu'} \rangle &= \left(\frac{Ae^{-s}}{2^{\nu+\nu'}\nu!\nu'!} \right)^{1/2} \sum_{k=0}^{\nu} \sum_{k'=0}^{\nu'} \binom{\nu}{k} \binom{\nu'}{k'} H_{\nu-k}(b) \\ H_{\nu'-k'}(b') (2\sqrt{\alpha})^{k} (2\sqrt{\alpha'})^{k'} I(K), \end{aligned}$$
(A1)

in which Hermite polynomial $H_{\nu}(x)$ corresponds to vibrational state χ_{ν} , $A = 2\sqrt{\alpha \alpha'}/(\alpha + \alpha')$, $s = \alpha \alpha' d^2/(\alpha + \alpha')$, $b = -\alpha' \sqrt{\alpha} d/(\alpha + \alpha')$, and $b' = \alpha \sqrt{\alpha'} d/(\alpha + \alpha')$ in which $\alpha = \omega/\hbar$, $\alpha' = \omega'/\hbar$, *d* is the displacement between the two oscillators, and ω is the angular frequency of the oscillator; I(K) = 0 for k + k' odd; $I(K) = (2K - 1)!!/(\alpha + \alpha')^K$ for k + k' even.

The wavefunction describing nuclear motion in a repulsive field that is defined with the first two terms in equation (1) reads

$$\Phi_f(R) = C_\kappa(\kappa R)^{-1/2} J_{\sqrt{\gamma+1/4}}(\kappa R), \qquad (A2)$$

in which $J_{\sqrt{\gamma+1/4}}(\kappa R)$ is a Bessel function of the first kind, $\kappa^2 = 2\mu[U_i(R_0) + 1/(2n^2)]$, $\gamma = 3\mu n(n_1 - n_2)$, μ is the reduced mass of two protons, and C_{κ} is a normalizing factor. A nuclear rotational motion is ignored in the derivation of equation (A2).

For a transition from an attractive electronic state with vibrational quantum number $\nu = 0$ to a repulsive state, the overlap integral is defined as

$$\left\langle \Phi_{f} \middle| \chi_{i} \right\rangle = \int_{0}^{\infty} \Phi_{f}(R) \chi_{0}(R) \mathrm{d}R,$$
 (A3)

in which

$$\chi_0(R) = C_0 \mathrm{e}^{-\frac{\alpha\mu(R-R_0)^2}{2}}$$
(A4)

and $C_0 = (\alpha \mu / \pi)^{1/4}$ is the normalizing factor.

APPENDIX B

Here are presented the simplified expressions: for $\eta(3d)$

$$\eta(3d) = \rho(2p \to 1s)\{\rho(3d \to 2p) + \rho(2p \to 1s)\}^{-1},\tag{B1}$$

for $\eta(5g)$

$$\eta(5g) = A(5g)\rho(2p \to 1s) \{\rho(5g \to 4f)$$
$$\times \rho(4f \to 3d)\rho(3d \to 2p) + A(5g)$$
$$\times \left[\rho(5g \to 2p) + \rho(2p \to 1s)\right] \}^{-1}, \tag{B2}$$

)

in which

$$\begin{split} A(5\mathrm{g}) &= \rho(5\mathrm{g} \to 4\mathrm{f})\rho(4\mathrm{f} \to 3\mathrm{d}) \\ &+ \left[\rho(5\mathrm{g} \to 4\mathrm{f}) + \rho(4\mathrm{f} \to 3\mathrm{d})\right]\rho(3\mathrm{d} \to 2\mathrm{p}), \end{split}$$

for $\eta(7i)$

$$\eta(7i) = A(7i)B(7i)\rho(2p \rightarrow 1s) \{\rho(7i \rightarrow 6h)$$

$$\times \rho(6h \rightarrow 5g) [A(7i)\rho(5g \rightarrow 4f)\rho(4f \rightarrow 3d)$$

$$\times \rho(3d \rightarrow 2p) + B(7i)\rho(5g \rightarrow 2p)] + A(7i)B(7i)$$

$$\times \rho(2p \rightarrow 1s)\}^{-1}, \qquad (B3)$$

in which

$$\begin{split} A(7i) &= \rho(7i \to 6h)\rho(6h \to 5g) + \rho(5g \to 2p) \\ &\times \left[\rho(7i \to 6h) + \rho(6h \to 5g)\right], \\ B(7i) &= \rho(7i \to 6h)\rho(6h \to 5g)\rho(5g \to 4f) \\ &\times \rho(4f \to 3d) + \rho(3d \to 2p) \left[\rho(6h \to 5g) \\ &\times \rho(5g \to 4f)\rho(4f \to 3d) + \rho(7i \to 6h) \\ &\times \rho(5g \to 4f)\rho(4f \to 3d) + \rho(7i \to 6h) \\ &\times \rho(6h \to 5g)\rho(4f \to 3d) + \rho(7i \to 6h) \\ &\times \rho(6h \to 5g)\rho(5g \to 4f)\right]. \end{split}$$

and for $\eta(i)$ (i = 7g, i = 8i)

$$\eta(i) = A'(i)B'(i)C'(i)\rho(2p \to 1s) \{A(i)B'(i)C'(i) + A'(i)B(i)C'(i) + A'(i)B'(i)C(i) + A'(i)B'(i)C'(i) + A'(i)B'(i)C'(i)\rho(2p \to 1s)\}^{-1},$$
(B4)

in which

$$\begin{split} A(i) &= \rho(i \rightarrow 7\mathrm{h})\rho(7\mathrm{h} \rightarrow 7\mathrm{i})\rho(7\mathrm{i} \rightarrow 2\mathrm{p}), \\ B(i) &= \rho(i \rightarrow 7\mathrm{h})\rho(7\mathrm{h} \rightarrow 7\mathrm{i})\rho(7\mathrm{i} \rightarrow 6\mathrm{h}) \\ &\times \rho(6\mathrm{h} \rightarrow 5\mathrm{g})\rho(5\mathrm{g} \rightarrow 2\mathrm{p}), \\ C(i) &= \rho(7\mathrm{g} \rightarrow 7\mathrm{h})\rho(7\mathrm{h} \rightarrow 7\mathrm{i})\rho(7\mathrm{i} \rightarrow 6\mathrm{h})\rho(6\mathrm{h} \rightarrow 5\mathrm{g}) \\ &\times \rho(5\mathrm{g} \rightarrow 4\mathrm{f})\rho(4\mathrm{f} \rightarrow 3\mathrm{d})\rho(3\mathrm{d} \rightarrow 2\mathrm{p}), \\ A'(i) &= \rho(i \rightarrow 7\mathrm{h})\rho(7\mathrm{h} \rightarrow 7\mathrm{i}) + [\rho(i \rightarrow 7\mathrm{h}) \\ &+ \rho(7\mathrm{h} \rightarrow 7\mathrm{i})]\rho(7\mathrm{i} \rightarrow 2\mathrm{p}), \\ B'(i) &= \rho(i \rightarrow 7\mathrm{h})\rho(7\mathrm{h} \rightarrow 7\mathrm{i})\rho(7\mathrm{i} \rightarrow 6\mathrm{h})\rho(6\mathrm{h} \rightarrow 5\mathrm{g}) \\ &+ [\rho(i \rightarrow 7\mathrm{h})\rho(7\mathrm{h} \rightarrow 7\mathrm{i})\rho(7\mathrm{i} \rightarrow 6\mathrm{h}) \\ &+ \rho(i \rightarrow 7\mathrm{h})\rho(7\mathrm{h} \rightarrow 7\mathrm{i}) \\ &\times \rho(6\mathrm{h} \rightarrow 5\mathrm{g}) + \rho(i \rightarrow 7\mathrm{h})\rho(7\mathrm{i} \rightarrow 6\mathrm{h})\rho(6\mathrm{h} \rightarrow 5\mathrm{g}) \\ &+ \rho(7\mathrm{h} \rightarrow 7\mathrm{i})\rho(7\mathrm{i} \rightarrow 6\mathrm{h})\rho(6\mathrm{h} \rightarrow 5\mathrm{g})]\rho(5\mathrm{g} \rightarrow 2\mathrm{p}). \end{split}$$

$$C' = \rho(7g \rightarrow 7h)\rho(7h \rightarrow 7i)\rho(7i \rightarrow 6h)\rho(6h \rightarrow 5g)$$

$$\times \rho(5g \rightarrow 4f)[\rho(4f \rightarrow 3d) + \rho(3d \rightarrow 2p)] + \rho(7g \rightarrow 7h)$$

$$\times \rho(7h \rightarrow 7i)\rho(7i \rightarrow 6h)\rho(4f \rightarrow 3d)[\rho(6h \rightarrow 5g)$$

$$+ \rho(5g \rightarrow 4f)] \times \rho(3d \rightarrow 2p) + \rho(7g \rightarrow 7h)[\rho(7h \rightarrow 7i)$$

$$+ \rho(7i \rightarrow 6h)]\rho(6h \rightarrow 5g) \times \rho(5g \rightarrow 4f)\rho(4f \rightarrow 3d)$$

$$\times \rho(3d \rightarrow 2p) + \rho(7h \rightarrow 7i)\rho(7i \rightarrow 6h)$$

$$\times \rho(6h \rightarrow 5g)\rho(5g \rightarrow 4f)\rho(4f \rightarrow 3d)\rho(3d \rightarrow 2p),$$

APPENDIX C

At large distance R between protons, the wavefunction of a colliding electron is representable as

$$\Psi_i = \frac{1}{\sqrt{2}} (\psi_a - \psi_b), \tag{C1}$$

in which ψ_a and ψ_b are wavefunctions describing the motion of an electron in the Coulomb field of protons at the left *a* and right *b*, respectively.

If protons are located on the axis z with coordinates $z_a = -R/2$, $z_b = R/2$ and a colliding electron is moving parallel to the axis z with momentum p, wavefunctions ψ_a and ψ_b can be represented as a product of Coulomb spheroidal quasi-radial and quasi-angular functions corresponding to the continuous spectrum. Expanding spheroidal functions in powers of small values $\mu_{a,b}/R$ and $\nu_{a,b}/R$, in which μ_a , ν_a and μ_b , ν_b are parabolic coordinates centred on protons a and b, respectively, we obtain, within the accuracy of the main term, that

$$\Psi_{i} = \frac{C_{i}}{\sqrt{2}} \left[\left(e^{-i\frac{p}{2}(\mu_{a}-\nu_{a})} - e^{-i\frac{p}{2}(\nu_{b}-\mu_{b})} \right) + O(R^{-1}) \right].$$
(C2)

In equation (C2), $C_i = (2\pi)^{-1/2}$ is a normalizing factor.

At $R \gg 2n^2$, wavefunctions of quasi-molecule H₂⁺ with parabolic quantum numbers $n_1, n_2 \le 4$ and m = 0 ($n = n_1 + n_2 + m + 1$) are representable as

$$\psi_f = \frac{C_f}{\sqrt{2}} \left[f_{n_1}(\mu_a) f_{n_2}(\nu_a) + f_{n_1}(\mu_b) f_{n_2}(\nu_b) \right],$$

$$f_{n_{1,2}}(x) = f_{n_{1,2}}^{(0)}(x) \pm \frac{1}{2R} f_{n_{1,2}}^{(1)}(x) + O(R^{-2}),$$
(C3)

in which

$$f_{n_{1,2}}^{(0)}(x) = e^{-\frac{x}{2n}} F\left(-n_{1,2}, 1, \frac{x}{n}\right),$$

$$f_{n_{1,2}}^{(1)}(x) = e^{-\frac{x}{2n}} x \times \left[n_{2,1} F\left(-n_{1,2}, 1, \frac{x}{n}\right) - (2n_{2,1} + 1)\left(\frac{\mathrm{d}F(-n_{1,2}, 1, t)}{\mathrm{d}t}\right)_{t=\frac{x}{n}}\right],$$
(C4)

where $F(-n_{1,2}, 1, x/n)$ is a confluent hypergeometric function and C_f is a normalizing factor.

Employing the derived wavefunctions, we obtain for the freebound transition matrix elements $u \rightarrow g$ that

$$z_{if} = z_{if}^{(0)} - \frac{1}{2R} z_{if}^{(1)} + O(R^{-2}),$$
(C5)

in which

$$z_{if}^{(0)} = C \int_{0}^{\mu_{\max}} \int_{0}^{\nu_{\max}} e^{-i\frac{p}{2}(\mu-\nu)} f_{n_{1}}^{(0)}(\mu) f_{n_{2}}^{(0)}(\nu)(\mu^{2}-\nu^{2}) \,\mathrm{d}\mu \,\mathrm{d}\nu,$$

$$z_{if}^{(1)} = C \int_{0}^{\mu_{\max}} \int_{0}^{\nu_{\max}} e^{-i\frac{p}{2}(\mu-\nu)} \times \left[f_{n_{1}}^{(0)}(\mu) f_{n_{2}}^{(1)}(\nu) - f_{n_{1}}^{(1)}(\mu) f_{n_{2}}^{(0)}(\nu) \right] (\mu^{2}-\nu^{2}) \,\mathrm{d}\mu \,\mathrm{d}\nu, \quad (C6)$$

where μ_{max} , $\nu_{\text{max}} \gg 2n^2$ and $C = (\pi/32)^{1/2}C_f$. In equation (C6), parabolic coordinates might be centred on either of protons.

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