Formation of hydrogen in the early universe: quasi-molecular mechanism of recombination

Tamaz Kereselidze,¹* Irakli Noselidze² and John F. Ogilvie^{3,4}

¹Faculty of Exact and Natural Sciences, Tbilisi State University, Chavchavadze Avenue 3, 0179 Tbilisi, Georgia

²School of Science and Technology, University of Georgia, Kostava Str. 77a, 0171 Tbilisi, Georgia

³Centre for Experimental and Constructive Mathematics, Department of Mathematics, Simon Fraser University, 8888 University Drive, Burnaby, British Columbia V5A 1S6, Canada

⁴Escuela de Quimica, Universidad de Costa Rica, Ciudad Universitaria Rodrigo Facio, San Pedro de Montes de Oca, San Jose 11501-2060 Costa Rica

Accepted 2019 June 21. Received 2019 June 21; in original form 2019 May 14

ABSTRACT

The recombination of an electron and a proton is assumed to occur in the presence of another proton, which participates in the process. The system of colliding particles is considered as a quasi-molecule temporarily formed during a collision. This model is employed to treat the formation of atomic hydrogen in the pre-recombination period of evolution of the early universe. According to a quasi-molecular mechanism of recombination, two processes are responsible for the formation of hydrogen in the early universe – a radiative transition of an electron to an excited repulsive state of H_2^+ with a subsequent dissociation into a hydrogen atom and a proton, and a radiative transition of an electron to an excited attractive state of H_2^+ with a subsequent cascade downward to a low-lying repulsive state. The participation of the nearest neighbouring proton in the process is shown to decrease the probability of recombination on an isolated proton.

Key words: molecular processes – radiative transfer – early universe.

1 INTRODUCTION

The binding of a free electron with a proton accompanied by emission of radiation, i.e. a radiative recombination, is one of the most fundamental processes in atomic and molecular physics. This process occurs in natural and laboratory plasmas, in the Earth's atmosphere, in the interstellar medium, etc. The recombination of electrons and protons plays an important role in astrophysics as this process was responsible for the formation of atomic hydrogen in the early universe. In this work, we treat the recombination epoch, before the period of evolution of the universe when heavy atoms and molecules appeared.

As the universe expanded, it concurrently cooled, eventually to a point at which the formation of neutral hydrogen and helium atoms was favoured energetically. At redshift $z \simeq 5000 - 8000$, the recombination of doubly ionized helium occurred, He III \rightarrow He II; at $z \simeq 1600 - 3500$, the recombination of singly ionized helium occurred He II \rightarrow He I, and eventually at $z \simeq 500 - 2000$ recombination of hydrogen took place, H II \rightarrow H I. At the end of recombination epoch when $z \simeq 1000$ the temperature of matter and radiation decreased to $T \simeq 3000K$ and photons decoupled from matter in the universe.

* E-mail: tamaz.kereselidze@tsu.ge

According to a fundamental mechanism (Peebles, 1968; Zel'dovich, Kurt & Syunyaev 1968), a proton and an electron can combine efficiently into a hydrogen atom only in excited state, from which a rapid cascade occurs into a state with principal quantum number n = 2; a direct radiative combination into the ground state is inefficient because the resulting photon has energy greater than that sufficient to ionize an adjacent hydrogen atom that must hence dissociate, leaving no net result. A radiative decay from state 2^2P involving one photon or from state 2^2S involving two photons then yields a hydrogen atom in its ground state.

Because of the extreme importance of recombination for the determination of cosmological parameters, several research groups have revised the details of this scheme of calculation (Dubrovich & Grachev 2005; Chluba & Sunyaev 2006; Wong & Scott 2007; Hirata 2008; Ali-Haïmoud & Hirata 2010; Grin & Hirata 2010).

Using an effective multishell multilevel approach, Chluba and Thomas (2011) described the recombination problem for hydrogen, to which these authors added all important recombination corrections discussed in the literature. This work, together with the subsequent work (Chluba & Ali-Haïmoud 2016) marked important steps towards a new cosmological recombination code that is applicable in an analysis of the cosmological recombination radiation. With data sets from the *Planck Surveyor* cosmologists can determine key cosmological parameters with unprecedented precision, enabling one to distinguish between various models within the big bang theory. For a further discussion of the problem, see reviews (Sunyaev & Chluba 2009; Glover et al. 2014; Kurt & Shakhvorostova 2014).

The formation of hydrogen in the early universe is a process so fundamental and important that all possible mechanisms of recombination must be included in the calculation. Despite substantial refinement, the recombination of an electron and a proton in the presence of another proton, i.e. a quasi-molecular mechanism to form atomic hydrogen, has not been discussed in the literature, and has accordingly been excluded from calculations of the cosmological recombination radiation.

Here, we present a quasi-molecular mechanism for the formation of hydrogen in the early universe for its further inclusion into calculations. We assume that, before the recombination period ($z \simeq$ 2000 - 8000) when the temperature was greater than subsequently, the recombination of an electron and a proton and the consequent formation of atomic hydrogen in an excited state occurred in the presence of the nearest neighbouring proton, which participated in the process. The system of three colliding particles – an electron and two protons, we consider to act as a quasi-molecule temporarily formed during a collision. The influence of another proton was obviously efficient if, at the beginning of the recombination period, the average distance between protons was comparable with the radius of a hydrogen atom in an excited state.

In this article, after stating our objective, we estimate an average distance between protons at the beginning of the recombination period and analyse the quasi-molecular mechanism of recombination. We proceed to develop a scheme of calculation in Section 3, before a conclusion. Unless otherwise indicated, atomic units $(e = m = \hbar = 1)$ are used throughout the paper.

2 QUASI-MOLECULAR MECHANISM OF RECOMBINATION

To begin, we estimate the average distance between protons at the beginning of the recombination period. This distance is estimable if one assumes that, before recombination, the reaction $e + p \rightleftharpoons H + \hbar \omega$ was in statistical equilibrium, i.e. the rate of radiative recombination was balanced with the rate of photoionization.

In statistical equilibrium at temperature T, the number density n_a of particles with mass m_a is given according to the Maxwell–Boltzmann equation,

$$n_{\rm a} = g_{\rm a} \left(\frac{m_{\rm a} k_{\rm B} T}{2\pi\hbar^2}\right)^{3/2} {\rm e}^{-\frac{m_{\rm a}c^2}{k_{\rm B} T}},\tag{1}$$

containing statistical weight g_a of particle *a*, Boltzmann constant k_B , reduced Planck constant \hbar , and speed *c* of light. This expression applies in the non-relativistic regime, i.e. when $k_BT \ll m_a c^2$.

From equation (1) for the hydrogen atoms, protons, and free electrons, we obtain an equation that relates the number densities of these particles,

$$\frac{n_{\rm p} n_{\rm e}}{n_{\rm H}} = \frac{g_{\rm p} g_{\rm e}}{g_{\rm H}} \left(\frac{m_{\rm p} m_{\rm e}}{m_{\rm H}}\right)^{3/2} \times \left(\frac{k_B T}{2\pi\hbar^2}\right)^{3/2} {\rm e}^{-\frac{(m_{\rm p}+m_{\rm e}-m_{\rm H})c^2}{k_{\rm B}T}}.$$
 (2)

Equation (2) becomes simplified when one considers that the ratio of the statistical weights is unity, $m_{\rm H} \simeq m_{\rm p}$, and expression $(m_{\rm p} + m_{\rm e} - m_{\rm H})c^2$ in the exponential factor is the binding energy of the hydrogen atom, i.e. the ionization energy, I = 13.6 eV. With these simplifications, one obtains the Saha equation

$$\frac{n_{\rm p}n_{\rm e}}{n_{\rm H}} = \left(\frac{m_{\rm e}k_{\rm B}T}{2\pi\hbar^2}\right)^{3/2} \mathbf{e}^{-\frac{l}{k_{\rm B}T}}.$$
(3)



Figure 1. The average distance between protons as a function of *z*. Straight lines correspond to the radius $r_n = 2n^2a_0$ of the hydrogen atom in the excited state with principal quantum number n; $v_{n,n-1}$ is the redshifted by z = 1100 frequency of the emitted radiation corresponding to the α transition $n \rightarrow n-1$; $a_0 = 0.529 \times 10^{-8}$ cm is the first Bohr radius of hydrogen.

On substituting the values of constants into equation (3), the Saha equation becomes rewritten as

$$\frac{n_{\rm p}n_{\rm e}}{n_{\rm H}} = 2.415 \times 10^{15} T^{3/2} \exp\left(-\frac{157820}{T}\right). \tag{4}$$

The average distance between protons, \bar{R} is related to the number density of the protons according to $\bar{R} = n_p^{-1/3}$. Substituting in the latter equation n_p defined from equation (4), we obtain \bar{R} as a function of absolute temperature T and ratio n_H/n_e ,

$$\bar{R}/\mathrm{cm} = 7.45 \times 10^{-6} \left(\frac{n_{\mathrm{H}}}{n_{\mathrm{e}}}\right)^{-1/3} T^{-1/2} \mathbf{e}^{\frac{52606}{T}}.$$
 (5)

If we assume electrons to be in equilibrium with hydrogen atoms at the beginning of the recombination period, we determine the dependence of \bar{R} on redshift z. Fig. 1 shows \bar{R} as a function of z calculated using equation (5) in which $n_{\rm H} = n_{\rm e}$. The deviation of this obtained dependence from that calculated with recombination code COSMOREC (Chluba & Thomas 2011) is important for $z \leq$ 1500. For such z the recombination occurs more slowly than in the equilibrium case (see fig. 3 in Sunyaev and Chluba 2009). For $z \gtrsim$ 1500 equation (5) with $n_{\rm H} = n_{\rm e}$ hence reproduces satisfactorily the dependence of \bar{R} on z.

Fig. 1 shows clearly that, for $z \gtrsim 2000$, the average distance between protons is comparable with a radius of the hydrogen atom in a highly excited state. We thus deduce that, at the beginning of the recombination period, two protons participated in the recombination; i.e. the quasi-molecular mechanism of recombination was responsible for the formation of atomic hydrogen in the pre-recombination period. The quasi-molecular mechanism of recombination is thus efficient at $z \simeq 2000$ mainly for $n \gtrsim 100$.

After the emission of a photon, the electron and two protons formed the hydrogen molecular ion H_2^+ in a highly excited electronic state. The formation of H_2^+ in ground state $1s\sigma_g$ and first excited



Figure 2. Energy terms $U_{g,u}(R)$ of H_2^+ as functions of distance R between protons. Solid curves denote σ terms; dotted curves denote π terms; and g and u stand for the even and odd electronic states, respectively; $\varepsilon_0 = m_e e^4 / \hbar^2$.

state $2p\sigma_u$ (the quasi-molecular states are specified with quantum numbers n_u , l_u , m_u that characterize an electron in the *united atom*, R = 0) was inefficient because in that case the emitted photon was so energetic that it almost immediately re-ionized a neighbouring hydrogen molecular ion.

In the pre-recombination stage, the duration of a collision of two protons was about 10^{-14} s or less, whereas the time of an electronic transition in H_2^+ is of order 10^{-8} s. Hence, if H_2^+ were formed in a repulsive (antibonding) state (states $2p\sigma_u$, $2s\sigma_g$, $3d\pi_g$, $3p\sigma_u$, $4f\sigma_u$, and $3s\sigma_g$ in Fig. 2), it would rapidly dissociate into an excited hydrogen atom and a proton,

whereas, from an attractive (bonding) state $(3d\sigma_g, 2p\pi_u, 4f\sigma_u, 4f\pi_u, and 4d\sigma_g$ in Fig. 2), H_2^+ would cascade downward to the low-lying states,

$$H_2^+(n) \to H_2^+(n-1) + \hbar\omega.$$
 (7)

In the latter case atomic hydrogen might be formed in a transition from the bound to an unbound quasimolecular state.

The quasi-molecular mechanism thus leads to a radiative transition of two types: free-bound with a subsequent formation of a hydrogen atom (reaction 6), and bound–bound (reaction 7). One should note that a direct electronic transition from an excited bonding state to state $1s\sigma_g$ leads to the formation of H_2^+ in the ground state, but these transitions have small Franck–Condon factors, because the minimum of potential energy for the ground state occurs at an internuclear distance much smaller than those of excited states. From an excited bound state, a cascade downward is likely a more effective process for the formation of H_2^+ in the ground state. This quasi-molecular mechanism of recombination hence allows the creation of a hydrogen molecular ion, whereas the formation of H_2^+ is impossible in an electron–proton recombination.

3 SCHEME OF CALCULATION

Our approach is based on an adiabatic representation of the process. This representation is valid for the temperatures and densities characteristic of the recombination epoch. The objective is to calculate the probability of a free–bound and a bound–bound radiative transition of an optimally maximum number of channels in equations (6) and (7). Because a configuration of protons experiences no significant changes when an electron is undergoing a transition from the continuous to the discrete spectrum, the probability depends on R— the distance between protons at which the radiative transition occurs.

The probability of a free-bound and bound-bound radiative transition is defined as (Heitler 1954)

$$W_{\rm if}(R) = \frac{4\omega_{\rm if}^3}{3c^3} |\boldsymbol{d}_{\rm if}(R)|^2, \tag{8}$$

in which ω_{if} is the frequency of an emitted photon,

$$\boldsymbol{d}_{\rm if}(\boldsymbol{R}) = \int \Psi_{\rm i}^*(\boldsymbol{r}, \boldsymbol{R}) \boldsymbol{r} \Psi_{\rm f}(\boldsymbol{r}, \boldsymbol{R}) \mathrm{d}\boldsymbol{r}$$
⁽⁹⁾

is the transition matrix element given in the dipole approximation, r denotes the position vector of an electron; $\Psi_i(r, R)$ and $\Psi_f(r, R)$ are the wavefunctions of an electron in the initial and final states, respectively.

These wavefunctions are solutions of the Schrödinger equation

$$\left(-\frac{1}{2}\Delta_{\boldsymbol{r}} - \frac{1}{r} - \frac{1}{|\boldsymbol{r} - \boldsymbol{R}|}\right)\Psi = \varepsilon\Psi,\tag{10}$$

in which ε is the electron energy; $\Psi = \Psi_i(\boldsymbol{r}, R)$ with $\varepsilon = p^2/2 > 0$ for the initial continuous state and $\Psi = \Psi_f(\boldsymbol{r}, R)$ with $\varepsilon = \varepsilon_f(R) < 0$ for the final discrete state.

The variables in equation (10) are known to be separable in prolate spheroidal coordinates $\xi = (r + |\mathbf{r} - \mathbf{R}|)/R$, $\eta = (r - |\mathbf{r} - \mathbf{R}|)/R$, $\varphi = \arctan(y/x)$ $(1 \le \xi < \infty, -1 \le \eta \le 1, 0 \le \varphi < 2\pi)$. The eigenfunctions are representable as a product of three functions, of which two contain *R* as a parameter. These functions are solutions of the 1D equations, which become the familiar radial and angular equations when $R \to 0$. The functions with non-zero *R* might hence be called spheroidal quasi-radial and quasi-angular functions.

In our treatment, we assume that the foci of spheroidal coordinates are located on axis z with coordinates $z_1 = 0$ and $z_2 = R$; an electron with a momentum $p(p, \theta_p, \varphi_p)$ collides with two protons that are situated at the foci. We expand the wavefunction of the colliding electron in the basis of spheroidal functions, $\psi_{pqm_i}(\xi, \eta, \varphi, R) = X_{pm_i}(\xi, R)Y_{qm_i}(\eta, R)\Phi_{m_i}(\varphi)$, which correspond to the continuous spectrum

$$\Psi_{i} = \sum_{q} \sum_{m_{i}} \int_{0}^{\infty} C_{pqm_{i}}(\theta_{p}, \varphi_{p}, R) \psi_{pqm_{i}} p^{2} dp.$$
(11)

In equation (11), C_{pqm_i} are expansion coefficients, $\Phi_{m_i} = e^{\pm im_i\varphi}/\sqrt{2\pi}$, m_i is the modulus of the projection of electron angular momentum along axis z, and q stands for a number of nodal surfaces of quasi-angular function $Y_{qm_i}(\eta, R)$. Taking into account that spheroidal functions are orthogonal and normalized, one can

readily obtain that

$$C_{pqm_{i}}(\theta_{p},\varphi_{p},R) = \frac{R^{3}}{8} \int_{1}^{\infty} \int_{-1}^{1} \int_{0}^{2\pi} \psi_{pqm_{i}}^{*}(\xi,\eta,\varphi,R)$$
$$\times \Psi_{i}(\boldsymbol{r},R)(\xi^{2}-\eta^{2})d\xi d\eta d\varphi.$$
(12)

Substituting in equation (12) expression (A2) derived in the appendix for $\Psi_i(\boldsymbol{r}, R)$ and performing integration over spheroidal coordinates makes evident that expansion coefficients C_{pqm_i} depend on the orientation of the colliding electron.

The wavefunction of the final state is taken to be

$$\Psi_{\rm f} = X_{{\rm n}_{\xi}m_{\rm f}}(\xi, R) Y_{{\rm n}_{\eta}m_{\rm f}}(\eta, R) \Phi_{m_{\rm f}}(\varphi).$$
(13)

Here, $X_{n_{\xi}m_{f}}(\xi, R)$ and $Y_{n_{\eta}m_{f}}(\eta, R)$ are the spheroidal quasi-radial and quasi-angular functions corresponding to the discrete spectrum, n_{ξ} and n_{η} denote numbers of nodal surfaces, and m_{f} is defined as in equation (11). Spheroidal quantum numbers n_{ξ} , n_{η} , and m_{f} are related to the *united-atom* quantum numbers according to the correlation rules $n_{u} = n_{\xi} + n_{\eta} + m_{f} + 1$, $l_{u} = n_{\eta} + m_{f}$, and $m_{u} = m_{f}$ (Bates & Reid 1968; Kereselidze 1987).

Substituting equations (11) and (13) in equation (9) and performing integration over the azimuthal angle φ , we obtain that

$$\boldsymbol{d}_{\rm if} = \boldsymbol{i}(x)_{\rm if} + \boldsymbol{j}(y)_{\rm if} + \boldsymbol{k}(z)_{\rm if},\tag{14}$$

$$(x)_{if} = \pm i (y)_{if} = \frac{R^4}{32} \sum_{q} C_{qm_i} \left(\int_{1}^{\infty} X_{pm_i} X_{n_{\xi}m_f} \times \sqrt{\xi^2 - 1} \xi^2 d\xi \int_{-1}^{1} Y_{qm_i} Y_{n_{\eta}m_f} \sqrt{1 - \eta^2} d\eta - \int_{1}^{\infty} X_{pm_i} X_{n_{\xi}m_f} \sqrt{\xi^2 - 1} d\xi \times \int_{-1}^{1} Y_{qm_i} Y_{n_{\eta}m_f} \sqrt{1 - \eta^2} \eta^2 d\eta \right),$$
(15)

$$(z)_{if} = \frac{R^4}{16} \sum_{q} C_{qm_i} \times \left(\int_{1}^{\infty} X_{pm_i} X_{n_{\xi}m_f} \xi^3 d\xi \int_{-1}^{1} Y_{qm_i} Y_{n_{\eta}m_f} \eta d\eta - \int_{1}^{\infty} X_{pm_i} X_{n_{\xi}m_f} \xi d\xi \int_{-1}^{1} Y_{qm_i} Y_{n_{\eta}m_f} \eta^3 d\eta \right).$$
(16)

The derived matrix elements satisfy the selection rules for the magnetic quantum number; namely, $(x)_{if}$ and $(y)_{if}$ are not equal to zero when $m_i = m_f \pm 1$, whereas $(z)_{if} \neq 0$ when $m_i = m_f$.

Equations (14)–(16) describe the radiative transition from a continuous to a discrete quasimolecular state. For the boundbound radiative transition the dipole-moment matrix elements are given in equations (14)–(16), in which a summation over q is omitted and both the initial and final states are described with spheroidal wavefunctions corresponding to the discrete spectrum. These derived equations allow us to calculate the dipolemoment matrix elements of free-bound and bound-bound radiative transitions for arbitrary R including $R \to \infty$. These outcomes, together with the energy terms of H₂⁺, enable one to obtain the various characteristics of processes (6) and (7), such as transition probabilities, cross-sections, rate constants, profiles of spectral lines, etc.

A precise quantum-mechanical calculation thus requires a knowledge of the correct wavefunctions of an electron moving in the Coulomb field of two fixed protons, for both discrete and continuous spectra. Several algorithms have been elaborated to calculate the discrete energy terms and wavefunctions of the quasi-molecule formed from an electron and two bare nuclei. For H_2^+ , the most detailed description of the elaborated algorithm and the results of extensive calculations are presented by Bates & Reid (1968); this algorithm might serve to calculate wavefunctions describing an electron in the bound state.

More challenging is to obtain the wavefunction that correctly describes an electron in the initial continuous state. Wavefunctions of this type mostly are calculated numerically. An application of numerical wavefunctions to recombination involves cumbersome and tedious calculations. The problem hence requires an alternative treatment. The purpose is thus to find solutions corresponding to the continuous spectrum in a closed algebraic form. This problem is solved in our recent paper (Kereselidze, Noselidze & Devdariani 2019) for large distances between protons.

For the discrete spectrum spheroidal quasi-radial and quasiangular functions were derived in a closed algebraic form by Ovchinnikov and Sukhanov (1965) and Kereselidze, Noselidze & Chibisov (2003). Describing the colliding electron with an explicit algebraic wavefunction, we thereby accelerate the recombination calculation and achieve a realistic runtime.

To our knowledge, calculations of matrix elements corresponding to a free–bound radiative transition with explicit wavefunctions are absent from the literature. An algorithm to calculate matrix elements of a bound–bound radiative transition in H_2^+ has been developed (Ramaker & Peek, 1972, 1973), motivated by problems arising in astrophysics. The transition matrix elements but for a one-electron heteronuclear quasimolecule were calculated by Devdariani et al. (2005).

We proceed to investigate probability $W_{if}(R)$ of free-bound radiative transition at large distances between protons. When *R* tends to infinity an electron might be attached to either proton. The unnormalized spheroidal wavefunction that is symmetric or antisymmetric with respect to a reflection in the plane normal to and bisecting molecular axis *R* is hence represented as a sum or difference of the appropriate parabolic wavefunctions centred on each nucleus,

$$\Psi_{\mathbf{n}_{\xi}\mathbf{n}_{\eta}m_{\mathrm{f}}}^{(\pm)}(\xi,\eta,\varphi) = \psi_{\mathbf{n}_{1}\mathbf{n}_{2}m_{\mathrm{f}}}(\mu_{1},\nu_{1},\varphi) \pm \psi_{\mathbf{n}_{1}\mathbf{n}_{2}m_{\mathrm{f}}}(\mu_{2},\nu_{2},\varphi).$$
(17)

In (17) μ_1 , ν_1 , φ and μ_2 , ν_2 , φ are parabolic coordinates; n_1, n_2, m_f are parabolic quantum numbers. Spheroidal coordinates are related to parabolic coordinates as $\xi \to 1 + \mu_1/R = 1 + \mu_2/R$ and $\eta \to -1 + \nu_1/R = 1 - \nu_2/R$ as $R \to \infty$. Spheroidal quantum numbers $n_{\xi} = n_1, n_{\eta} = 2n_2$ apply to symmetric and $n_{\eta} = 2n_2 + 1$ to antisymmetric states, respectively. Employing the known relation between the parabolic and spherical functions (Tarter 1970), we obtain that when $R \to \infty$,

$$\Psi_{\mathbf{n}_{\xi}\mathbf{n}_{\eta}m_{\mathrm{f}}}^{(\pm)} \to \psi_{\mathbf{n}_{1}\mathbf{n}_{2}m_{\mathrm{f}}} = \sum_{l_{\mathrm{s}}=m_{\mathrm{s}}}^{n_{\mathrm{s}}-1} \left\langle \frac{n_{\mathrm{s}}-1}{2}, \frac{n_{\mathrm{s}}-1}{2}, \frac{\tau_{\mathrm{s}}}{2}, \frac{\tau_{\mathrm{2}}}{2} \right| l_{\mathrm{s}}, m_{\mathrm{s}} \right\rangle \psi_{n_{\mathrm{s}}l_{\mathrm{s}}m_{\mathrm{s}}},$$
(18)

in which $\tau_1 = n_2 - n_1 + m_s$, $\tau_2 = n_1 - n_2 + m_s$, $\langle | \rangle$ are the Clebsch–Gordan coefficients and $\psi_{n_s l_s m_s}$ are spherical wavefunctions of an isolated hydrogen atom. Hence when $R \to \infty$ spheroidal wavefunction $\Psi_{n_s n_n m_f}^{(\pm)}$ transforms into a linear combination of spherical wavefunctions $\psi_{n_s l_s m_s}$ with principal quantum number $n_s = n_1 + n_2 + m_s + 1$, orbital angular-momentum quantum number $l_s = m_s, m_s + 1, \dots n_s - 1$, and magnetic quantum number $m_s = m_f$.

In the approximation when a splitting between symmetric and antisymmetric energy terms is neglected, an asymptotic expansion for the energy of H_2^+ is given by (Bates & Reid 1968)

$$U_{n_1 n_2 m_8}(R) = -\frac{1}{2n_8^2} + \frac{3n_8(n_1 - n_2)}{2R^2} + O(R^{-3}).$$
 (19)

Equation (19) shows that the energy terms with $n_2 > n_1$ are attractive, whereas the energy terms with $n_2 < n_1$ are repulsive at large distances between protons. For the energy terms with $n_2 = n_1$, symmetric terms are attractive and antisymmetric are repulsive. Hence, if H_2^+ is formed in an excited attractive state, it does not dissociate. From an attractive state H_2^+ would descend to a lower lying (repulsive or attractive) state with a subsequent dissociation or cascade down. Only the repulsive quasimolecular states thus create a hydrogen atom directly. The attractive states form the hydrogen atom through the intermediate state; these channels accordingly require an appropriate treatment.

Our objective is thus to calculate the value of $\sum W_{if}(R)$, in which the summation is taken over the repulsive quasimolecular states only. For given n_s and m_s one can write that, for large R,

$$W_{\rm rep}(R) = \sum_{n_2=0}^{n_{\rm s}-m_{\rm s}-1} W_{\rm if}(R) - W_{\rm atr}(R), \qquad (20)$$

in which $W_{\text{rep}}(R) = \sum_{n_2=0}^{n_1} W_{\text{if}}(R)$ and $W_{\text{atr}}(R) = \sum_{n_2=n_1}^{n_s-m_s-1} W_{\text{if}}(R)$ are the probabilities of a radiative transition to repulsive and attractive quasimolecular states, respectively.

Substituting equations (8) and (18) in equation (20) and taking into account that the Clebsch–Gordan coefficients are orthogonal and normalized, we obtain that

$$W_{\rm rep}(R) = W_{\rm tot}(R) - W_{\rm atr}(R), \qquad (21)$$

in which

$$W_{\rm tot}(R) = \frac{4\omega_{\rm if}^3}{3c^3} \sum_{l_{\rm s}=0}^{s_{\rm s}-1} \left| \langle \Psi_{\rm i} | \boldsymbol{d} | \psi_{\rm n_s l_s m_s} \rangle \right|^2$$
(22)

is the total probability of free-bound radiative transitions and

$$W_{\rm atr}(R) = \frac{4\omega_{\rm if}^3}{3c^3} \sum_{n_2=n_1}^{n_s-m_s-1} \left| \langle \Psi_{\rm i} | \, \boldsymbol{d} \, \left| \psi_{n_{\xi} n_{\eta} m_s} \right\rangle \right|^2 \tag{23}$$

is the probability of transitions to the attractive quasimolecular states.

We thus obtain that the quasi-molecular mechanism of recombination leads to an appearance of two terms in expression (21) derived for the recombination probability. Term $W_{tot}(R)$ clearly coincides at $R \to \infty$ with the probability calculated for the recombination on an isolated proton, whereas $W_{atr}(R)$ determines the

probability of transitions to the bound quasi-molecular states. The latter term reduces the probability of recombination on an isolated proton.

Equations (14)–(16) can be readily generalized for the calculation of free–bound and bound–bound radiative transitions in a quasimolecule formed of an electron and two ions He^{2+} . This can be achieved by making the scale transformation (Kereselidze & Firsov 1974) and linking the wavefunctions and energy terms of quasimolecules He_2^{3+} and H_2^+ .

4 CONCLUSIONS

The theoretical investigations over the past two decades provide a comprehensive representation of the cosmological recombination and related processes. It is now recognized that all physical processes that occurred in the early universe during the recombination epoch are essentially understood. For a precise determination of the cosmological parameters, a particular interest is an accurate calculation of the cosmological recombination radiation. To achieve this purpose all important physical processes must be incorporated in the calculation.

In the present work, we have demonstrated that at the beginning of the recombination period the recombination of an electron and a proton occurred in the presence of the nearest neighbouring proton, which participated in the process. According to a quasi-molecular mechanism of recombination, two processes are responsible for the formation of atomic hydrogen in the early universe – the radiative transition of an electron to an excited repulsive state of H_2^+ with a subsequent dissociation into an excited hydrogen atom and a proton, and the radiative transition of an electron to an excited attractive state of H_2^+ with a following cascade downward to low-lying quasimolecular states.

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 bound–bound radiative transitions that are forbidden in the case of an isolated hydrogen atom (Devdariani et al. 2005). This fact should be included in a calculation of the cosmological recombination radiation.

In accordance with these results, we contend that the existence of another proton that participated in the process, i.e. the quasimolecular mechanism of recombination, must be taken into account for a complete treatment of the cosmological recombination problem. We expect an appearance of quasi-molecular features to be similar to that of a superdense astrophysical plasma. As an example, we indicate the change of spectral profile in the absorption spectra of hydrogen-rich white dwarfs. In the far wings of spectral lines in the Lyman series are exhibited satellites (enhancements) that are caused exclusively by the quasi-molecular character of radiative transitions (Allard et al. 1999; Alard, Noselidze & Kruk 2009).

The results of calculations using equations (14)–(16) with spheroidal wavefunctions derived for the continuous spectrum in a closed algebraic form will be reported separately.

ACKNOWLEDGEMENTS

One of us (TK) thanks Professor Raffaella Schneider for helpful discussion during a visit at Sapienza University of Rome and for supplying references related to the problem. We express our gratitude to a referee for suggestions that substantially improve the presentation of the obtained results.

REFERENCES

- Ali-Haïmoud Y, Hirata C. M., 2010, Phys. Rev. D, 82, 063521
- Allard N. F., Royer A., Kielkopf J. F., Feautrier N., 1999, Phys. Rev. A, 60, 1021
- Alard N., Noselidze I., Kruk W., 2009, A&A, 506, 993
- Bates D. R., Reid R. H. G., 1968, in Bate D.R., Esterman I., eds, Advances in Atomic and Molecular Physics, v. IV. Academic Press, New York, USA
- Chluba J., Sunyaev R. A. 2006, A&A, 446, 39
- Chluba J., Thomas R. M., 2011, MNRAS, 412, 748
- Chluba J., Ali-Haïmoud Y., 2016, MNRAS, 456, 3494
- Devdariani A., Kereselidze T. M., Noselidze I. L., Dalimier E., Sauvan P., Angelo P., Schott R., 2005, Phys. Rev. A, 71, 022512
- Dubrovich V. K., Grachev S. I., 2005, Astron. Lett., 32,359
- Glover S. C. O., Cluba J., Furlanetto S. R., Pritchard J. R., Savin D. W., 2014, Adv. At. Mol. Opt. Phys., 63, 135
- Grin D., Hirata C. M., 2010, Phys. Rev. D, 81, 083005
- Heitler W., 1954, The Quantum Theory of Radiation, third edition. Clarendon Press, Oxford
- Hirata C. M., 2008, Phys. Rev. D, 78, 023001
- Hostler L., Pratt R., 1963, Phys. Rev. Lett., 10, 469
- Kereselidze T. M., 1987, J. Phys. B: At. Mol. Phys., 20, 1891
- Kereselidze T. M., Firsov O. B., 1974, Sov. Phys. JETP, 38, 46
- Kereselidze T. M., Noselidze I. L., Chibisov M. I., 2003, J. Phys. B: At. Mol. Opt. 36, 853
- Kereselidze T., Noselidze I., Devdariani A., 2019, J. Phys. B: At. Mol. Opt. Phys., 52, 105003
- Kurt V. G., Shakhvorostova N. N., 2014, Phys. Usp., 57, 4
- Landau L. D., Lifshitz E. M., 1977, Quantum Mechanics: Non-Relativistic Theory, third edition. Pergamon, Oxford, UK
- Ovchinnikov A. A., Sukhanov A. D., 1965, Sov.-Dokl., 9, 685
- Peebles P. J. E., 1968, ApJ, 153, 1
- Ramaker D. E., Peek J. M., 1972, J. Phys. B, 5, 2175
- Ramaker D. E., Peek J. M., 1973, At. Data, 5, 167
- Sunyaev R. A., Chluba J., 2009, Astron. Nachr., 330, 657
- Tarter C. B., 1970, J. Math. Phys., 11, 3192
- Wong W. Y., Scott D., 2007, MNRAS, 375, 1441
- Zel'dovich Y. B., Kurt V. G., Syunyaev R. A., 1968, ZhETF, 55, 278

APPENDIX:

For the initial continuous state, equation (10) can be written in the form

$$\left(\Delta_{\boldsymbol{r}} + \frac{2}{r} + p^2\right)\Psi_{i} = V(\boldsymbol{r})\Psi_{i},\tag{A1}$$

in with $p = \sqrt{2\varepsilon}$ and $V = -2|\boldsymbol{r} - \boldsymbol{R}|^{-1}$.

In the Coulomb–Born approximation, the solution of equation (A1) is expressible as

$$\Psi_{i}(\boldsymbol{r}, R) = f_{\boldsymbol{p}}(\boldsymbol{r}) + \int G_{\varepsilon}(\boldsymbol{r}, \boldsymbol{r}') V(\boldsymbol{r}') f_{\boldsymbol{p}}(\boldsymbol{r}') d\boldsymbol{r}', \qquad (A2)$$

in which the first term in the right-hand side is a solution of the appropriate homogeneous equation (Landau & Lifshitz 1977),

$$f_p(\vec{r}) = \mathbf{e}^{\pi/2p} \Gamma \left(1 - i/p\right) \mathbf{e}^{i \, pr \cos \Theta} \\ \times F \left(i/p, 1, \, i \, pr(1 - \cos \Theta)\right), \tag{A3}$$

 $F(i/p, 1, i pr(1 - \cos \Theta))$ is the confluent hypergeometric function and $\Theta = \arccos(\cos \theta \cos \theta_p + \sin \theta \sin \theta_p \cos(\varphi - \varphi_p))$ is the angle between position vector \mathbf{r} and momentum \mathbf{p} . In equation (A2) $G_{\varepsilon}(\mathbf{r}, \mathbf{r}')$ is the non-relativistic Coulomb Green's function, which in a closed form is expressible as (Hostler & Pratt 1963)

$$G_{\varepsilon}(\boldsymbol{r},\boldsymbol{r}') = \frac{\Gamma(1-\boldsymbol{i}/p)}{2\pi|\boldsymbol{r}-\boldsymbol{r}'|} \frac{1}{\boldsymbol{i}p} \left(\frac{\partial}{\partial x} - \frac{\partial}{\partial y}\right) \\ \times W_{\frac{i}{p},\frac{1}{2}}(-\boldsymbol{i}px)M_{\frac{i}{p},\frac{1}{2}}(-\boldsymbol{i}py);$$
(A4)

here $x = r + r' + |\mathbf{r} - \mathbf{r}'|$, $y = r + r' - |\mathbf{r} - \mathbf{r}'|$, and $W_{1/ip,1/2}(ipx)$, $M_{1/ip,1/2}(ipy)$ are Whittaker functions.

This paper has been typeset from a Microsoft Word file prepared by the author.