Two-photon decays of highly excited states in hydrogen

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Abstract

The relativistic and nonrelativistic approaches for the calculations of the two-photon decay rates of highly excited states in hydrogen are compared. The dependence on the principal quantum number \(n\) of the \(ns\), \(nd\) and \(np\) initial states is investigated up to \(n = 100\) for the nonresonant emissions. For the \(ns\) states together with the main \(E_1E_1\) channel the contributions of higher multipoles (\(M_1M_1\), \(E_2E_2\) and \(E_1M_2\)) are considered. For the \(np\) states the \(E_1M_1\) and \(E_1E_2\) channels are evaluated. Moreover, the simple analytical formula for the \(E_1M_1\) decay is derived in the nonrelativistic limit.

1. Introduction

The question about the role of the two-photon decays in the context of the hydrogen recombination in the early Universe was first raised in [1, 2]. It was shown that the electron recombination mainly occurs in the \(2s\) state, followed by the \(2s\) state decays via two-photon \(E_1E_1\) emission into the ground state. The transition frequencies of these photons are not resonant (the energy of each photon released will not excite any of the neighbouring atoms), and, therefore, the medium is transparent for these frequencies. The contribution of such a transition rate to the microwave background was further investigated in the literature, see, e.g., [3–5]. The recent success in the observation of the cosmic microwave background temperature and polarization anisotropy draws attention to the details of cosmological hydrogen recombination history. This, in turn, requires accurate knowledge of the two-photon decay processes.

The theoretical formalism for the two-photon decay has been introduced by Göppert–Mayer [6] and the first calculation of the two-photon \(E_1E_1\) transition \(2s \to 2\gamma(E_1) + 1s\) belongs to Breit and Teller [7]. Further improvements including relativistic corrections were performed in [8, 9]. The two-photon transition \(2p \to 1s\) occurring via \(E_1E_2\) and \(E_1M_1\) channels was first evaluated in [10, 11]. In a recent paper by Amaro et al [12] these results were confirmed and further two-photon transition rates from initial bound states with \(n = 2, 3\) have been evaluated.

In connection with increased accuracy of the astrophysical experiments (see, e.g., [13]) it might also become important to consider atomic recombination into highly excited states in hydrogen, as proposed by Dubrovich and Grachev in [4], and further developed in [14–16]. The magnitude of the nonresonant radiation from highly excited states is of the same order as for the \(2s \to 1s\) transition and, therefore, the same contribution to the emission escape can be anticipated. Highly excited states can decay by cascade emission (i.e. the transition occurs via the intermediate state) and by ‘pure’ (nonresonant) two-photon emission. In the case of the cascade transition, the emitted photons can be absorbed immediately by the neighbouring atoms and, therefore, the medium is not transparent for the resonant radiation, but it is for the nonresonant one. For this reason the question of separation of the ‘pure’ and cascade emission arises. There are some papers considering this problem (see, e.g., [17–20]). In [17, 18] the possibility of separation between cascade and ‘pure’ two-photon emission has been shown. However, in our paper [19] it has been demonstrated that it is impossible to divide resonant and nonresonant two-photon emission due to the interference term between them. Recently, in [20]...
Jentschura accepted our point of view on the treatment of this problem. The separation of the cascades and the ‘pure’ two-photon emission remains ambiguous. In [14, 16] the influence of the highly excited states on the Sobolev escape probability for Lyman-α photons was computed, employing the ‘1+1’ scheme. In the vicinity of the Lyman-α resonance the shape of the ‘1+1’ emission profile remains Lorentzian and the resonant/nonresonant or resonant/resonant interference terms do not appear. Another approach for the account of the two-photon processes from the highly excited states to the recombination problem was presented by Hirata in [15] introducing a distinction between regions with resonant photon contributions and those with ‘pure’ two-photon contributions.

The main aim of the present paper is to rigorously evaluate the dependence of the two-photon decay rates on the principal quantum number of the initial state \( n \). Since the nonresonant photons being transparent for the medium contributes to the microwave background, it is important to investigate the \( n \)-behaviour of the ‘pure’ two-photon emission. For this reason we calculate the differential transition rate for different \( n \) at the equal frequencies of the emitted photons; the energy region where the contribution of the cascades is almost negligible for high \( n \). In the calculations we employ both the relativistic and nonrelativistic approaches. By the nonrelativistic approach we mean (i) the long-wavelength approximation for the photon emission operator, in the case of dipole transitions this yields the dipole operators; therefore, we use the term ‘dipole approximation’ for this; (ii) matrix elements evaluated with the nonrelativistic (Schrödinger) electron wavefunctions. In the relativistic approach the full photon emission operator together with the relativistic electron wavefunctions is employed. Since the orbital size of the highly excited states increases quadratically with increasing \( n \), the long-wavelength (dipole) approximation seems to be inadequate [4]. The argument of the photon wavefunction is no longer small and, therefore, the restriction to the first term only in the power-series expansion of the Bessel function is under question. One could expect that the utilization of the full photon emission operator contributes essentially to the two-photon decay rates from the highly excited states. For the same reason the higher multipole contributions (besides the dominant E1E1 channel) of the two-photon transitions for the \( ns \) and \( nd \) levels could become important. Moreover, since the highly excited states are strongly mixed, we should consider the decays from the \( np \) states as well.

The paper is organized as follows. In section 2 we present the general formulas for the two-photon decay. In section 3 we calculate E1E1 differential transition rates \( ns/nd \to 1s \) at the equal photon frequencies in hydrogen atom. The influence of the higher multipoles (M1M1, E2E2 and E1M2) is also investigated. As a next step we consider the two-photon E1E2 and E1M1 transition rates of the \( np \) states (sections 4 and 5). The investigation of the dependence on \( n \) is performed for all these transitions. Moreover, in section 5 we derive a simple analytical formula for the E1M1 decay rates of the \( np \) states in the nonrelativistic limit.

Apart from sections 2 and 3 where the relativistic units are useful for convenience, the atomic units are used throughout the paper.

2. General formulas: two-photon decay

The two-photon transition probability \( A \to A' + 2\gamma \) corresponds to the following second-order \( S \)-matrix elements:

\[
\langle A'| \hat{S}^{(2)} | A \rangle = e^2 \int d^4x_1 \ d^4x_2 \\
\times (\bar{\psi}_{A'}(x_1) \gamma_\mu A_{\mu}^A(x_1) S(x_1,x_2) \gamma_\mu A_{\mu}^A(x_2) \psi_A(x_2)),
\]

where \( S(x_1,x_2) \) is the Feynman propagator for the atomic electron. In the Furry picture the eigennode decomposition for this propagator reads (e.g. [21], see also [19])

\[
S(x_1,x_2) = \frac{1}{2\pi i} \int_{-\infty}^{\infty} d\omega e^{i\omega(t_1-t_2)} \sum_{N} \frac{\psi_N(\vec{r}_1) \psi_N(\vec{r}_2)}{E_N(1-i\delta) + \omega},
\]

where the summation in equation (2) extends over the entire Dirac spectrum of the electron states \( N \) in the field of the nucleus, \( \psi_N(x) \) is the electron wavefunction and \( E_N \) is the electron energy. In equation (1) \( \gamma_\mu \) are the Dirac matrices. The wavefunction of the photon

\[
\hat{A}_{\mu}^k(x) = \sqrt{\frac{2\pi}{\omega_\mu}} e^{i\vec{k} \cdot \vec{r} - i\omega t} \hat{A}_{\mu}^k
\]

is characterized by the momentum \( \vec{k} \) (\( \omega = |\vec{k}| \)) and polarization vector \( e_\mu^0(\mu, \lambda) = 0, 1, 2, 3 \), \( x = (\vec{r}, t) \). For real transverse photons we have

\[
\hat{A}(x) = \sqrt{\frac{2\pi}{\omega}} e^{i\vec{k} \cdot \vec{r} - i\omega t} \equiv \frac{2\pi}{\omega} \hat{A}_{\vec{k}} \ e^{-i\omega t}.
\]

Integrating over time and frequency variables, taking into account photon permutation symmetry and introducing the amplitude \( U_{AA}^{(2)} \)

\[
S_{AA}^{(2)} = -2\pi i \delta(E_A - \omega + \omega' - E_A) U_{AA}^{(2)}
\]

yields the expression

\[
U_{AA}^{(2)} = \frac{2\pi e^2}{\sqrt{\omega_\omega \omega'}} \left\{ \sum_N \frac{(\vec{g} \cdot \vec{A}^+_k)_A N (\vec{g} \cdot \vec{A}^+_e)_k N_A}{E_N - E_A + \omega} \right\}^{\omega/\omega} + \sum_N \left\{ \frac{(\vec{g} \cdot \vec{A}^+_e)_N (\vec{g} \cdot \vec{A}^+_e)_k N_A}{E_N - E_A + \omega} \right\}^{\omega/\omega},
\]

where \( e \) is the electron charge and \( \vec{a} \) is the vector incorporating the Dirac matrices. The labels \( A, A' \) and \( N \) abbreviate the complete set of the atomic electron quantum numbers (principal quantum number \( n \), total angular momentum \( j \), its projection \( m \) and parity \( \ell \)) for the initial, final and intermediate states, respectively. The transition probability is defined via

\[
dW_{AA}^{(2)} = 2\pi \delta(E_A - E_{A'} - \omega - \omega') |U_{AA}^{(2)}|^2 \frac{d\vec{k}}{(2\pi)^3} \frac{d\vec{k}'}{(2\pi)^3}.
\]

Setting \( d\vec{k} \equiv \omega^2 d\vec{n} d\omega \) and integrating over \( d\omega \) yields

\[
dW_{AA}^{(2)} (\omega', \vec{n}', \vec{n}, \vec{e}', \vec{e}) = e^{\omega'(E_A - E_{A'} - \omega')}
\]

\[
\times \sum_{m_A m_{A'}} \frac{1}{2J_A + 1} \left\{ \sum_N \frac{(\vec{g} \cdot \vec{A}^+_e)_N (\vec{g} \cdot \vec{A}^+_e)_k N_A}{E_N - E_A + \omega'} \right\}^{\omega/\omega} \right\}^{\omega/\omega}
\]

\[
+ \sum_N \left\{ \frac{(\vec{g} \cdot \vec{A}^+_e)_N (\vec{g} \cdot \vec{A}^+_e)_k N_A}{E_N - E_A + \omega} \right\}^{\omega/\omega} \right\}^{\omega/\omega} d\vec{n} d\vec{n}' d\omega'.
\]
Here the summation over \( N \) represents the summation over all sets of quantum numbers of the intermediate state \([nljm]\). The sums over the projections of the total angular momentum of the final state \( A' \) and the averaging over the projections of the total angular momentum of the initial state \( A \) in equation (8) are also included.

Expanding further the photon wavefunction in a multipole series (see, e.g., [21, 22]), we consider contributions with different multipole structures E1E1, E1M1, E1E2, E1M2, M1M1 and E2E2. The nonrelativistic limit can easily be obtained from equations (4) and (8), replacing the photon and electrons wavefunctions by their nonrelativistic analogues. In this way we describe electric dipole, magnetic dipole and electric quadrupole photons (see, e.g., [23]).

### 3. E1E1 decay of the \( ns, nd \) states

First, we focus on the decay rate of the \( ns \) and \( nd \) levels (\( A \equiv ns/nd \rightarrow A' \equiv 1s \)) in hydrogen. The common expression for the two-photon transition probability in relativistic evaluation can be written as

\[
dW^{(2)}_{AA'}(\omega) = e^4 \frac{32\pi \omega\omega'}{2J_A + 1} \times \sum_{J'} \sum_{MM'} \sum_{m_jm_{M'}} \sum_N \frac{(A^{(1)}_{JM})_{AN}(A^{(0)}_{JM'})_{NL}}{E_N - E_A + \omega'} + \sum_N \frac{(A^{(1)}_{JM})_{AN}(A^{(0)}_{JM'})_{NL}}{E_N - E_A + \omega} \, d\omega, \tag{9}
\]

where the summation over the photon polarization and the integration over the photon angles have been carried out, \( \omega' = E_A - E_N - \omega \). Here \( A^{(0)}_{JM}(\omega) \) are the multipole components of the transition operator; the symbol \( \lambda \) indicates the magnetic multipoles (\( \lambda = 0 \)) or electric multipoles (\( \lambda = 1 \)). The multipole components \( A^{(1)}_{JM}(\omega) \) are defined in the same way as in [21, 22, 24]. They are given in the transverse gauge by the expressions

\[
A^{(0)}_{JM}(\omega) = j_{\ell}(\omega) \alpha Y_{JM}(\vec{\omega}),
\]

\[
A^{(1)}_{JM}(\omega) = \left( j_{\ell}(\omega) + \frac{j_{\ell}(\omega)}{\omega'} \right) \alpha Y_{JM}(\vec{\omega}) + \sqrt{J(\omega + \omega')} Y_{JM}(\vec{\omega}), \tag{10}
\]

where \( j_{\ell}(x) \) is the spherical Bessel function and \( Y_{JM}(\vec{\omega}) \) are the vector spherical harmonics. The transverse gauge is also called the velocity gauge since the electric dipole matrix elements in this gauge turn into the velocity form dipole amplitudes in the nonrelativistic limit. In the length gauge the magnetic multipole components have the same form, whereas the electric multipole components are given by

\[
A^{(1)}_{JM}(\omega) = -j_{\ell+1}(\omega) \alpha Y_{JM}(\vec{\omega}) + \sqrt{\frac{J + 1}{J}} j_{\ell+1}(\omega) Y_{JM}(\vec{\omega}) - i \sqrt{\frac{J + 1}{J}} j_{\ell}(\omega) Y_{JM}(\vec{\omega}), \tag{11}
\]

where \( I \) is the identity operator and \( Y_{JM}(\vec{\omega}) \) are the spherical functions. Explicit formulas for the one-electron matrix elements \( A^{(1)}_{JM}(\omega) \) in the length and velocity gauges can be found in [22]. For the case of E1E1 transition one can easily obtain

\[
dW_{AA'}^{E1E1}(\omega) = e^4 \frac{8\omega^3}{27\pi} |S_{1s,ns}(\omega) + S_{1s,ns}(\omega')|^2 \, d\omega, \tag{13}
\]

and

\[
dW_{ns,1s}^{E1E1}(\omega) = e^4 \frac{16\omega^3}{\pi^3} |S_{1s,ns}(\omega) + S_{1s,ns}(\omega')|^2 \, d\omega, \tag{14}
\]

with notations

\[
S_{1s,ns,nd}(\omega) = \sum_{n,p} \langle R_{1s}|r| R_{n,p}\rangle \langle R_{n,p}|r| R_{ns,nd}\rangle E_{n,p} - E_{ns} + \omega,
\]

where \( R_{ns} \) are the radial parts of the nonrelativistic hydrogenic wavefunctions and \( E_{nl} \) are the corresponding energies.

The corresponding decay rate for the two-photon transitions \( ns/nd \rightarrow 1s \) can be obtained by integration of equation (12) (in the nonrelativistic case equations (13) and (14)) over the entire frequency interval

\[
W_{AA'}^{E1E1} = \frac{1}{2} \int_0^\infty dW_{AA'}^{E1E1}(\omega), \tag{17}
\]

where \( \omega_0 = E_A - E_{ns} \). The gauge invariance of the transition probability was investigated in [25] for the one-photon transitions. The two different forms for the E1E1 multipolar coefficients in combination with different gauges were obtained in [26]. In our paper [11] the results of [26] were applied for the evaluation of the two-photon transition probabilities. The gauge invariance serves as a tool for testing the numerical evaluation procedure in both relativistic and nonrelativistic cases.

The aim of this paper is the investigation of the nonresonant two-photon decay rates from the highly excited hydrogenic states, since these transitions could play an important role in studies of the anisotropy of the cosmic microwave background. It was expected that two-photon transitions from the highly excited states could contribute essentially in the recombination process. Accordingly, we study the behaviour of the frequency distribution function of the transition probability of the initial state with the increasing principal quantum number \( n \). Comparison between the relativistic and nonrelativistic calculations is performed.
in order to examine the possible deviation from the dipole approximation. The results of numerical calculations are presented in Table 1 for the $n - 1s$ two-photon E1E1 transitions. For the analysis of the $n$-behaviour of the ‘pure’ two-photon decays we present the results in terms of the normalized distribution function

$$Q_{E1}^{E1} = \frac{1}{2} \frac{dW_{E1}^{E1}}{W_{E1}^{E1}} n^3$$

(18)

at the equal frequencies of the emitted photons $x = \omega/\omega_0 = 0.5$. The choice of the frequency is caused by the absence of the cascades in this region. The E1E1 two-photon transition probability $W_{E1}^{E1} = 8.229$ s$^{-1}$ is taken as the normalization factor. Moreover, the normalized distribution function is multiplied by the factor $n^3$ in order to emphasize the dominant behaviour of $Q_{E1}^{E1}$ for large $n$ values. In Table 1 we also present the corresponding quantity $Q_{E1}^{E1}$ for the E1E1 two-photon $nd - 1s$ transitions. Again the normalization factor $W_{E1}^{E1}$ for the frequency distribution function is taken.

These results reveal that for large values of $n$ the scaling of the frequency distribution function for the E1E1 two-photon $ns/nd - 1s$ transitions is close to $1/n^3$ and the dipole approximation holds even for the large $n$. This means the decrease of the nonresonant two-photon transitions’ contribution for large values of $n$ to the recombination dynamics of the primordial hydrogen in the Universe. The relativistic corrections appear not to be essential for considering two-photon transitions from the highly excited levels to the ground state. Table 1 also shows that two-photon E1E1 $ns - 1s$ transition probabilities decrease faster than $1/n^3$ for the low values $n$ and picture changes for $n \approx 10$ when the normalized quantity $Q_{E1}^{E1}$ reaches the asymptotic value $\approx 6.6$. For the $nd - 1s$ E1E1 two-photon transitions behaviour is quite different. Namely, for $n \leq 40$, the values of the transition rates decrease slower than $1/n^3$ and then, as in the case of $ns - 1s$ transitions, reach the $1/n^3$ asymptotics.

| $n$  | $Q_{E1}^{E1}$ (relativistic) | $Q_{E1}^{E1}$ (nonrelativistic) | $Q_{E1}^{E1}$ (relativistic) | $Q_{E1}^{E1}$ (nonrelativistic) |
|------|-----------------------------|---------------------------------|-------------------------------|-------------------------------|
| 2    | 10.35                       | 10.35                           | 10.35                         | 10.35                         |
| 3    | 8.527                       | 8.528                           | 32.21                         | 32.21                         |
| 5    | 7.255                       | 7.255                           | 49.97                         | 49.97                         |
| 8    | 6.674                       | 6.765                           | 56.39                         | 56.46                         |
| 10   | 6.591                       | 6.648                           | 57.97                         | 58.00                         |
| 20   | 6.595                       | 6.490                           | 60.13                         | 60.08                         |
| 30   | 6.576                       | 6.460                           | 60.51                         | 60.46                         |
| 40   | 6.567                       | 6.450                           | 60.65                         | 60.60                         |
| 50   | 6.562                       | 6.445                           | 60.71                         | 60.66                         |
| 60   | 6.559                       | 6.442                           | 60.71                         | 60.70                         |
| 70   | 6.558                       | 6.441                           | 60.73                         | 60.72                         |
| 80   | 6.557                       | 6.439                           | 60.74                         | 60.73                         |
| 90   | 6.556                       | 6.439                           | 60.74                         | 60.74                         |
| 100  | 6.556                       | 6.438                           | 60.75                         | 60.75                         |

Table 2. The relativistic values of the normalized distribution functions $Q_{E2}^{E2}$, $Q_{M1}^{M1}$ and $Q_{E1}^{E1}$, at the equal frequencies of the emitted photons $x = 0.5$ for the interval of the principal quantum number $n = [2, 100]$.

| $n$  | $Q_{E2}^{E2}$ (relativistic) | $Q_{M1}^{M1}$ (relativistic) | $Q_{E1}^{E1}$ (relativistic) |
|------|------------------------------|------------------------------|------------------------------|
| 2    | $1.168 \times 10^{-11}$     | $3.019 \times 10^{-11}$     | $2.581 \times 10^{-10}$     |
| 5    | $1.907 \times 10^{-11}$     | $5.277 \times 10^{-11}$     | $2.962 \times 10^{-10}$     |
| 10   | $2.967 \times 10^{-11}$     | $5.620 \times 10^{-11}$     | $2.866 \times 10^{-10}$     |
| 20   | $3.265 \times 10^{-11}$     | $5.916 \times 10^{-11}$     | $2.861 \times 10^{-10}$     |
| 40   | $3.342 \times 10^{-11}$     | $5.932 \times 10^{-11}$     | $2.853 \times 10^{-10}$     |
| 60   | $3.356 \times 10^{-11}$     | $5.932 \times 10^{-11}$     | $2.853 \times 10^{-10}$     |
| 80   | $3.361 \times 10^{-11}$     | $5.932 \times 10^{-11}$     | $2.852 \times 10^{-10}$     |
| 90   | $3.363 \times 10^{-11}$     | $5.932 \times 10^{-11}$     | $2.851 \times 10^{-10}$     |
| 100  | $3.364 \times 10^{-11}$     | $5.932 \times 10^{-11}$     | $2.851 \times 10^{-10}$     |

To make the picture complete the relativistic evaluations have also been performed for E2E2, M1M1 and E1M2 transitions as the corrections to the E1E1 ns-level decay. Their contributions are compiled in Table 2 and appear to be negligible. Table 2 shows that the contributions of the higher multipoles to the nonresonant two-photon emission for the $n - 1s$ decays are negligible. The parametric estimation for these transition rates is $(\alpha Z)^{10}$ in atomic units. The values of the M1M1, E2E2 and E1M2 transition probabilities are in good accordance with those reported in [12]. It is obvious that the corresponding values of the transition probabilities for the two-photon emission of the $nd$ states are also negligible and all of them can be omitted in astrophysical investigations.

4. E1E2 decay of the np states

In this section we evaluate the two-photon E1E2 transition rates $np \rightarrow 1s$. Relativistic and nonrelativistic calculations for the $2p - 1s$ E1E2 transition were previously performed in [9, 10]. We follow [11], where two-photon E1E2 transition probability was evaluated in different forms and gauges. For reasons of simplicity in this section we present the evaluation of the transition rate within the nonrelativistic length form. The electric multipole operators can be written as (nonrelativistic limit)

$$V_{EA}^{E1}(\omega) = \sqrt{\frac{k + 1}{k}} \frac{2\omega^{k+1}}{(2k+1)!!} r^k Y_{k-M}$$

(19)

where $Y_{k-M}$ is a spherical harmonic. Accordingly, the two-photon decay rate of the atomic state $A$ with the emission of two electric photons can be written as (see, e.g., [11])

$$dW_{AA}^{E1E2}(\omega, \omega') = \sum_{M,W,|\omega',\omega|} \left[ \sum_N \frac{(A'|V_{EA}^{E1}(\omega)|N)(N|V_{EA}^{E1}(\omega')|A)}{E_N - E_A + \omega'} + \sum_N \frac{(A'|V_{EA}^{E1}(\omega')|N)(N|V_{EA}^{E1}(\omega)|A)}{E_N - E_A + \omega} \right]$$

$$+ \sum_N \frac{(A'|V_{EA}^{E1}(\omega')|N)(N|V_{EA}^{E1}(\omega)|A)}{E_N - E_A + \omega}$$

4
the distribution function $R_L$ where $\omega$ takes the form \[11\]
decomposition of the Coulomb Green function, the probability\[\text{intermediate states we employ the explicit expression for the} \]
To perform the summation over the complete set of\[\text{gl}(\nu \rightarrow \omega)\]
\[
W(\omega) = \frac{2p}{\sqrt{\pi}} \omega^{1/2} |I_1(\omega') + I_2(\omega)|^2 \]
\[
I_1(\omega) = \frac{1}{\sqrt{6}} \int_0^\infty \int_0^\infty dr_1 dr_2 r_1^{\nu/2} e^{-r_1 - \frac{r_2}{2}} g_1(E_A - \omega; r_1, r_2) \]
\[
I_2(\omega) = \frac{1}{\sqrt{6}} \int_0^\infty \int_0^\infty dr_1 dr_2 r_1^{\nu/2} e^{-r_1 - \frac{r_2}{2}} g_2(E_A - \omega; r_1, r_2).\]
The decomposition of the radial part of the Coulomb Green function reads\[\text{g}_l(v; r, r') = \frac{4Z}{\nu} \left( \frac{4}{\nu r} \right)^{l/2} \exp \left( -\frac{r + r'}{\nu} \right) \]
\[
\times \sum_{n=0}^\infty \frac{n!L_n^{(1)}(\frac{1}{\nu}) L_{n+l}^{(1)}(\frac{1}{\nu})}{(2l + 1 + n)! (n + l + 1 - \nu)} \]
\[\text{where } L_n^{(1)} \text{ are the generalized Laguerre polynomials. The corresponding radial integrals can be evaluated analytically.} \]
\[\text{Equations (22) and (23) can easily be generalized for the case of } np \rightarrow \gamma(E1) + \gamma(E2) + 1s \text{ transitions by replacing the radial function } 2p \text{ state, which is equal to } R_{2l}(r) = \frac{r}{2\sqrt{\pi}} e^{-r^2/2}. \]
\[\text{by the required one.} \]
\[\text{Finally, integrating over frequencies } \omega \text{ yields } (\omega_0 = E_{2p} - E_{1s}) \]
\[
W_{2p,1s} = \frac{1}{2} \int_0^{\infty} dW_{E1E2}(\omega) = 1.98896 \times 10^{-5} (\alpha Z)^8 \text{ au} \]
\[= 6.611947 \times 10^{-6} \text{ s}^{-1} (Z = 1). \]

The Z-dependence of the $W_{E1E2}$ transition probability is also indicated. Compared with the relativistic result, the relative discrepancy is about 0.1%. The parametric estimation of the transition rate $W_{E1E2}$ is $(\alpha Z)^8$ in atomic units. This is $\sigma^2$ times less than the corresponding parametric estimate for the E1E1 transition probability, which is $(\alpha Z)^6$. However, with respect to the achieved accuracy of the astrophysical experiments, the E1E2 transition rates could be considered as a correction to the two-photon processes.

In table 3 the relativistic results for the $np_{1/2} \rightarrow \gamma(E1) + \gamma(E2) + (n-1)s$ transition rates are presented. Good agreement with the corresponding nonrelativistic results is found. Bad convergence properties of the finite basis set representation restrict our calculations of the transitions between neighbouring states to $n = 5$. This can be checked by considering the level of accuracy up to which gauge invariance is preserved in the numerical evaluations. For the $nl \rightarrow 2\gamma + 1s$ transitions the gauge invariance is preserved with good accuracy up to $n = 100$. In table 3 we also display the relativistic and nonrelativistic values for the E1E2 normalized distribution function
\[Q_{E1E2}^{E1E2} = \frac{1}{2} \int_0^{\infty} dW_{E1E2}(\omega) n^3 \]
at the equal frequencies of the emitted photons $x = \omega/\omega_0 = 0.5$. One can see from the table that the behaviour of the nonresonant E1E2 two-photon emission with the increasing $n$ values is the same as for E1E1 probability of the ns/nd-states emission. And again the nonrelativistic dipole approximation works well.

| $n$ | $W_{E1E2}^{np_{1/2},(n-1)s}$ (relativistic) | $Q_{E1E2}^{np_{1/2},(n-1)s}$ (relativistic) | $Q_{E1E2}^{np_{1/2},(n-1)s}$ (nonrelativistic) | $W_{E1E2}^{np_{1/2},(n-1)s}$ (relativistic) | $Q_{E1E2}^{np_{1/2},(n-1)s}$ (relativistic) | $Q_{E1E2}^{np_{1/2},(n-1)s}$ (nonrelativistic) |
|-----|------------------------------------------|------------------------------------------|------------------------------------------|------------------------------------------|------------------------------------------|------------------------------------------|
| 2   | $6.612 \times 10^{-06}$                  | $15.31$                                  | $15.32$                                  | $9.682 \times 10^{-06}$                  | $9.99$                                  | $13.33$                                  |
| 3   | $3.737 \times 10^{-08}$                  | $3.31$                                   | $3.32$                                   | $1.189 \times 10^{-08}$                  | $12.65$                                 | $14.24$                                  |
| 4   | $9.755 \times 10^{-10}$                  | $14.26$                                  | $14.27$                                  | $1.989 \times 10^{-10}$                  | $13.60$                                 | $14.51$                                  |
| 5   | $6.221 \times 10^{-11}$                  | $21.91$                                  | $21.91$                                  | $1.025 \times 10^{-11}$                  | $14.04$                                 | $14.63$                                  |
| 10  | $-34.64$                                 | $34.53$                                  | $-14.83$                                 | $14.63$                                  | $14.78$                                 | $14.82$                                  |
| 20  | $-38.28$                                 | $38.45$                                  | $-14.82$                                 | $14.82$                                  | $14.83$                                 | $14.83$                                  |
| 30  | $-39.36$                                 | $39.13$                                  | $-14.82$                                 | $14.82$                                  | $14.83$                                 | $14.83$                                  |
| 40  | $-39.39$                                 | $39.52$                                  | $-14.82$                                 | $14.82$                                  | $14.83$                                 | $14.83$                                  |
| 50  | $-39.46$                                 | $39.58$                                  | $-14.82$                                 | $14.82$                                  | $14.83$                                 | $14.83$                                  |
| 60  | $-39.47$                                 | $39.60$                                  | $-14.82$                                 | $14.82$                                  | $14.83$                                 | $14.83$                                  |
| 70  | $-39.43$                                 | $39.56$                                  | $-14.82$                                 | $14.82$                                  | $14.83$                                 | $14.83$                                  |
| 80  | $-39.46$                                 | $39.58$                                  | $-14.82$                                 | $14.82$                                  | $14.83$                                 | $14.83$                                  |
| 90  | $-39.47$                                 | $39.60$                                  | $-14.82$                                 | $14.82$                                  | $14.83$                                 | $14.83$                                  |
| 100 | $-39.48$                                 | $39.61$                                  | $-14.82$                                 | $14.82$                                  | $14.83$                                 | $14.83$                                  |
5. E1M1 decay of the np states

A parametric estimate shows that the E1M1 transition probability is of the same order of magnitude as for E1E2; therefore, it should be included in our consideration. For the first time the E1M1 transition rate for the $2p_{1/2} \rightarrow 1s$ emission process was evaluated in [10, 11]. Our results were later confirmed by Amaro et al [12].

The expression for the E1M1 two-photon transition probability is given by

$$dW_{E1M1}^A(\omega) = \sum_{M_nM_{m1}m'_1} \sum_N \left( \frac{\langle A'|V^{E1}(\omega)|N\rangle\langle N|V^{M1}(\omega')|A \rangle}{E_N - E_A + \omega'} \right) \frac{d\omega'}{E_N - E_A + \omega} \frac{d\omega}{E_N - E_A + \omega'}$$

for the nonrelativistic limit the corresponding magnetic dipole operator reads $V^{M1}(\omega) = \sqrt{\frac{4\pi}{\mu_0}}(j_{3,1}m_A + \delta_{3,0}m_A)$, where $\mu_0 = \alpha/2$ is the Bohr magneton, $j_{3,1}m_A$ and $\delta_{3,0}m_A$ are the spherical components of the total angular momentum and the spin operator (spherical tensors of rank 1) of the electron. Since the operator for the magnetic photon includes total angular momentum and spin operator, coupled wavefunctions characterized by the set of quantum numbers $N = (nljm)$ should be used, i.e.

$$\phi_{nljm} = \sum_{m_lm_j} C_{lm1m_j}^{jm} R_{jl}(r)Y_{jm}(\hat{r}) \chi_{lm},$$

where $\chi_{lm}$, $(s = 1/2)$ is the spin function. The magnetic potentials in equation (27) do not depend on radial variables. Thus, only the intermediate states with $nl = n_Al_A$ or $nl = n_Al_A'$ will contribute to the transition probability in equation (27). Performing angular integrations and summations over all projections one arrives at the expressions

$$dW_{E1M1}^{2p_{1/2}1s}(\omega) = \frac{\alpha^8}{27\pi} \left( \frac{2}{3} \right)^{12} \omega^2 \exp^4 \omega^3 \frac{d\omega}{\omega}$$

and

$$W_{E1M1}^{2p_{1/2}1s} = \frac{1}{2} \int_0^{\omega_0} dW_{E1M1}^{2p_{1/2}1s}(\omega) = \frac{\alpha^8}{27\pi} \left( \frac{2}{3} \right)^{12} \frac{2}{3} \int_0^{\omega_0} \omega^2 \frac{d\omega}{\omega} \exp^4 \omega^3,$$

with $\omega_0 = E_{2p_{1/2}} - E_{1s}$. As the final result we obtain (see also [11])

$$W_{E1M1}^{2p_{1/2}1s} = \frac{\exp^4}{27\pi} \left( \frac{2}{3} \right)^{12} \omega^2 \exp^4 \omega^3 \frac{d\omega}{\omega}$$

In the case of arbitrary principal quantum number $n$ due to the condition

$$\langle R_{nl}|M1|R_{n'1'} \rangle \sim \delta_{nn'} \delta_{l'l'}$$

only the diagonal matrix elements remain in the sum over the intermediate states in equation (27). Therefore, in the nonrelativistic limit no cascades will arise in considering processes involving the magnetic dipole photons. We should note that in the relativistic case the cascades will arise; however, the contribution of the cascades appears to be negligible in the case of hydrogen atom.

For the E1M1 transition probability we have

$$dW_{E1M1}^{2p_{1/2}1s}(\omega) = \frac{\alpha^8}{27\pi} \left( \frac{2}{3} \right)^{12} \omega^2 \exp^4 \omega^3 \frac{d\omega}{\omega}$$

After the integration over the radial variable $r$ and the frequency $\omega$ within the interval $[0, E_{2p_{1/2}} - E_{1s}]$ we obtain

$$W_{E1M1}^{2p_{1/2}1s} = \frac{8}{135\pi n^3} \left( \frac{n - 1}{n + 1} \right)^2 \left( \alpha Z \right)^8.$$

For $n \gg 1$ it follows $W_{E1M1}^{2p_{1/2}1s} \approx \frac{n^2}{135\pi} \left( 1 - \frac{1}{n} \right)^2 \left( \frac{\alpha Z}{\exp^4} \right)^8$, i.e. the same scaling law arises as for E1E1 transitions.

For the $np_{1/2} \rightarrow \gamma(E1) + \gamma(M1) + 2s$ emission process we obtain in the same way

$$W_{E1M1}^{np_{1/2}2s} = \frac{4}{135\pi n^2} \left( \frac{n - 1}{n + 2} \right)^2 \left( \frac{\alpha Z}{\exp^4} \right)^8.$$

Similarly, for $n \gg 1$ the scaling is

$$W_{E1M1}^{np_{1/2}2s} \approx \frac{4}{135\pi} \left( \frac{1}{3n^2} \right)^2 \left( \alpha Z \right)^8.$$

In table 3 the relativistic results for the $np_{1/2} \rightarrow \gamma(E1) + \gamma(M1) + (n - 1)s$ transition rates are presented. These results are in good agreement with the corresponding nonrelativistic values, which can easily be obtained in terms of equations (33)–(35). Again we restrict ourselves to $n = 5$ for the transitions between neighbouring states ($np_{1/2}$ and $(n - 1)s$). In table 3 we also display the relativistic and nonrelativistic values for the E1M1 normalized distribution function

$$Q_{E1M1}^{np_{1/2}1s} = \frac{1}{2} W_{E1M1}^{np_{1/2}1s} \frac{d\omega}{\omega} \omega^3 \exp^4 \omega^2$$

at the equal frequencies of the emitted photons $x = \omega/\omega_0 = 0.5$. As in previous cases the behaviour of the nonresonant E1M1 two-photon emission is $1/n^3$. The nonrelativistic dipole approximation holds in this case as well.

6. Conclusions

Relativistic and nonrelativistic calculations have been performed and compared. The numerical evaluation has been carried out employing the dual-kinetic-balance finite basis set method [28] with basis functions constructed from B-splines [29]. For the nonrelativistic calculations the analytical
expression for the nonrelativistic Coulomb Green function has been utilized.

We have proved that the dependence of the transition probabilities on the principal quantum number of the initial state $n$ out of the cascade regions is close to $1/n^3$. Therefore, the contribution of the highly excited states turns out to be much less significant for the astrophysical purposes as expected. Previously, the $n$-dependence of the nonresonant contribution was estimated in [4, 14]. It was found that the nonresonant transition rates scale roughly linear, when increasing towards larger $n$. The nonresonant two-photon rates were defined, e.g., in [14], via neglecting the resonant state in the summation over the entire spectrum of the intermediate states. However, the term with the resonant state alone contributes both to the resonant rate and to the nonresonant one. Therefore, to our mind, the investigation of the $n$-behaviour of the nonresonant emission should be performed by analysing the differential transition rate in the region, where the contribution of the cascades is negligible.

The relativistic calculations were performed aiming for the search of the influence of effects beyond the nonrelativistic dipole approximation. The gauge invariance served as a check of the calculations. The nonrelativistic calculations were performed in the length gauge. In principle, the gauge invariance could also be used in this case (see, for example, [11]), but comparison with the corresponding relativistic values is enough for our purposes here. We have compared the relativistic and nonrelativistic results to understand whether it is necessary to go beyond the dipole approximation. It was expected that for the highly excited states ($n \gg 1$) the dipole approximation might be not very accurate due to the large argument of the Bessel function. However, we were able to show that even for the $n = 100$ the deviation between the nonrelativistic dipole approximation and relativistic theory is not significant. The relative difference for the corresponding values does not exceed 1.8%. Since we always consider the two-photon decays into the ground state, this can be the reason that the dipole approximation is valid even for such high values of $n$. The presence of the ground state provides a short-range cutoff for one of the radial variables ($r$, for instance, in equation (24)); then the range of the second radial variable $r'$ will also be small, because of the exponential suppression factor exp$[-(r + r')]$ coming from the Green’s function (24).

Moreover, we have evaluated M1M1, E2E2 and E1M2 transition rates. It was shown that they also behave like $1/n^3$ and the parametric estimation for them is $(aZ)^{10}$ in atomic units.

On the score of the highly excited states which are fully mixed, we have also considered $np \rightarrow \rightarrow n s$ transition rates. It was shown that they also behave like $1/n^3$ and the parametric estimation for them is $(aZ)^{10}$ in atomic units.

The main conclusion that we can state is the rapid reduction for the all considered nonresonant two-photon transition rates with the increase of $n$. The dependence $1/n^3$ has been established for ‘pure’ two-photon transition rates, corresponding to the radiation escape from the interaction with the matter. It was shown that the nonrelativistic dipole consideration of the two-photon transition rates from the highly excited states is valid even for large $n$, in the case that the final state is one of the lowest states of the atom.

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