Influence of external electric fields on multi-photon transitions between the 2s, 2p and 1s levels for hydrogen and antihydrogen atoms and hydrogen-like ions

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Abstract
One- and two-photon transitions in the hydrogen atom are analytically evaluated in the absence and in the presence of an external electric field. The emission probabilities in the external electric field are different for the hydrogen (H) and anti-hydrogen (\(\bar{\text{H}}\)) atoms due to the existence of contributions that are linear in the electric field. The magnitude of these contributions is evaluated within the nonrelativistic limit. The three-photon E1E1E1 2p-1s transition probability is also evaluated and possible applications of the results are discussed.

1. Introduction

Recent experimental success in the production of antihydrogen atoms [1, 2] opens realistic chances for a comparison of the atomic spectra for hydrogen (H) and anti-hydrogen (\(\bar{\text{H}}\)) atoms. One of the purposes for this comparison is the search for the CPT-violating effects [3]. The possibility of the CPT-tests is connected with the modern extra-accurate resonance frequency measurements in hydrogen [4, 5]. In [6–8] it was shown that a specific difference in the H and \(\bar{\text{H}}\) atomic spectra arises even in the absence of the CPT-violation, if an external electric field is present. In principle, a difference also arises for the frequency measurements if nonresonant (NR) corrections are taken into account. Actually, the NR corrections define the natural limit up to which the frequency measurements have meaning; beyond this limit the spectral line profile cannot be defined by the two parameters: resonance frequency and width. NR corrections are not just corrections to the level energy, but rather corrections to the spectral line profile. These corrections for the atoms placed in an external electric field contain terms that are linear in the electric field. Therefore, NR corrections appear to be different for H and \(\bar{\text{H}}\) atoms. However, this difference is very small and hence the existence of the electric stray field should not become a serious problem in performing experiments searching for CPT-violating effects. Another difference in spectroscopic properties of H and \(\bar{\text{H}}\) atoms in an external electric field is the difference in the transition probabilities, also caused by the terms that are linear in the electric field. This effect is much larger than the difference in the NR corrections and has not yet been discussed in detail.

In the present paper we will investigate particularly the difference in the one-photon 2s-1s emission probabilities for H and \(\bar{\text{H}}\) atoms in an external electric field and will find the optimal conditions for observing this effect. This investigation should confirm our understanding of fundamental symmetries in physics. Thus, going over from H to \(\bar{\text{H}}\) and changing simultaneously the sign of the electric field should not change the atomic spectra provided that CPT-symmetry is conserved.

The one-photon decay of the 2s state of the H atom in an external electric field was utilized in the experiments [4, 5] for the registration of the 2s-1s two-photon resonance absorption. The difference of the one-photon 2s-1s decay rate for H and \(\bar{\text{H}}\) atoms in an external electric field can be observable in the
similar experiments with $\overline{H}$ atoms. These studies are contained in sections 2 and 8 of the present paper.

In total, the goal of our paper is twofold. Apart from the studies of the one-photon (section 2) and two-photon (section 8) transition probabilities in an external electric field, we also investigated the exotic two-photon transitions E1M1 and E1E2. This is done in sections 5–7.

The probabilities for the spontaneous two-photon decay in hydrogen atoms and hydrogen-like ions have been under investigation since the theoretical formalism was introduced by G"opbert–Mayer [9] and the first evaluation for the two-photon E1E1 transition $2s \rightarrow 2\gamma(E1) + 1s$ was presented by Breit and Teller [10]. A highly accurate calculation of the E1E1 transition probability has been performed by Klarfeld [11]. Recently, Jentschura [12] performed a complete evaluation of the radiative corrections and presented a more accurate value for the E1E1 two-photon decay probability.

The present paper is also devoted to the evaluation of the probabilities for two-photon decays $2p \rightarrow \gamma(E1) + \gamma(M1) + 1s$ and $2p \rightarrow \gamma(E1)+\gamma(E2)+1s$. Evaluations of these two transitions were first accomplished in [13, 14] for hydrogen-like systems with nuclear charge numbers $Z$ within the range $1 \leq Z \leq 100$ by pure numerical methods. Here we present analytic calculations in the nonrelativistic limit and compare them with corresponding numerical results. For performing the summations over intermediate states (i.e., over the complete set of solutions of the Schrödinger equation describing electrons in the Coulomb field of the nucleus) we employ the Coulomb Green function [15]. The Green function method was first applied for deriving the general expression for the two-photon decay probability in H atom and H-like ions in [16, 17]. An alternative approach applicable for arbitrary states based on Schwinger’s analytical representation of the Coulomb Green function has been presented in [18, 19]. A very condensed survey on the Coulomb Green function theory, necessary for understanding our derivations, is given in section 4.

As has been indicated in [20], the nonrelativistic behaviour of E1M1 transitions as a function of $Z$ with the neglect of the interelectron interaction should be $W_{\text{E1M1}} = (8/9\pi\alpha^2Z)^2/100$ for the helium-like systems. This very small value arises due to the cancellation of contributions of the leading terms $2p_{1/2}$ and $2p_{3/2}$ in the summation over intermediate np-states. However, we should note that this result yields only a minor contribution for small nuclear charges $Z$ when it is evaluated within the ‘velocity’ form [20]. In this case a major contribution arises from the negative-energy intermediate states and scales like $(\alpha Z)^8$ in atomic units [13, 14].

The two-photon $2p_{1/2} \rightarrow \gamma(E1) + \gamma(E2) + 1s$ and $2p_{1/2} \rightarrow \gamma(E1) + \gamma(M1) + 1s$ transition rates for hydrogen and hydrogen-like ions are proportional to $ma^2(\alpha Z)^8$ while the leading contribution to the $2p_{1/2}$ level width is $ma(\alpha Z)^4$ in relativistic units. Thus, the two-photon transitions represent the higher order corrections to the life time of the $2p_{1/2}$ level when compared to the lowest order $(\alpha Z)^5 \ln(\alpha Z)$ (in relativistic units) radiative corrections derived in [21, 22]. A direct observation of the influence of the two-photon $2p_{1/2} \rightarrow \gamma(E1) + \gamma(E2) + 1s$ and $2p_{1/2} \rightarrow \gamma(E1) + \gamma(M1) + 1s$ transitions in the H atom does not look feasible due to the huge background arising from the one-photon transition $2p_{1/2} \rightarrow \gamma(E1) + 1s$. However, two-photon decays of the $2p_{1/2}$-level could be observed, in principle, in coincidence experiments.

In this paper we reevaluate the two-photon decay rate of the 2p-state in hydrogen, deriving the E1E2 and E1M1 contributions to the two-photon emission processes by means of analytical methods. These calculations are performed within different gauges and employ different forms for the expression of the transition probability. The connection between different ‘forms’ and ‘gauges’ was first clarified in [23] (see also [24]). In [23] these forms and gauges were investigated for the one-photon transitions, and in [24] for the two-photon transitions. In section 3 we briefly summarize the results obtained in [23, 24] with further application to some particular transitions. In sections 5–7 the two-photon E1M1 and E1E2 transition probabilities are given in the nonrelativistic limit in both ‘velocity’ and ‘length’ forms and in two different gauges.

In section 8 we perform the calculation of two-photon transition probabilities from the 2s and $2p_{1/2}$ hydrogenic levels in the presence of an external electric field. The mixing of the 2s and $2p_{1/2}$ levels results in additional terms linear in the electric field. The evaluation is performed within the nonrelativistic limit by the Coulomb Green function method [17] in the ‘length’ form. These terms linear in the electric field lead to the difference of the corresponding probabilities (see [25–27]) for the hydrogen and anti-hydrogen atoms. The magnitude of these contributions is evaluated and the possibility of the observation of this effect is discussed. It is important to stress that these linear field corrections even in a very small stray electric field can be larger than the radiative correction to the decay of 2s level, evaluated in [12].

Finally, in section 9, we evaluate three-photon emission probability for the hydrogen atom.

In principle, the multiphoton transitions in hydrogen in the dipole approximation were intensely studied theoretically several decades ago in connection with the development of laser optics. Several general methods for the evaluation of the multiphoton transition rates and multiphoton ionization cross-sections were developed. One of these methods (application of the Coulomb Green function), and the relevant references, we have already mentioned above (see also the most recent review on the subject in [28]). Another approach was developed in [29, 30] where the solution of the chain of inhomogeneous Schrödinger equations, equivalent to multiple use of the Coulomb Green function, was employed. The so-called Dalgaro–Lewis approach [31] is also based on the solution of the inhomogeneous Schrödinger equations (see the recent application of this method in [32]). However, the main goal of all these numerous works was not the accurate evaluation of multiphoton transition rates for bound–bound transitions, but the evaluation of cross-sections of the multiphoton ionization processes, necessary for applications to laser optics. The most extensive evaluation of the various two-photon bound–bound transition rates in hydrogen was performed recently in [33]. However, our aim in section 9 is different. We present the
accurate three-photon transition rate for the process $2p \rightarrow 3\gamma(\text{E1}) + 1s$ in order to find out whether this process can be of importance for the recent studies of the cosmological recombination. As far as we know, this transition rate was never evaluated accurately before.

The recent success in the observation of the cosmic microwave background temperature and polarization anisotropy draws attention to the details of the cosmological hydrogen recombination history. This, in turn, has required the accurate knowledge of the two-photon decay processes in hydrogen (see [34, 35] for details and references). The main interest concentrates around the $2s\rightarrow 1s\ E1\ E1$ two-photon transition and the two-photon decays for the $n_s\ n_d$ excited states.

The smallness of the numerical coefficients in E1E2 and E1M1 two-photon expressions excludes any significant role of these transitions for astrophysics at the recent level of accuracy in the astrophysical observations. The same can be stated for the three-photon 3E1 $2p_{1/2}/2s$ decay. This was not clear from the pure parametric estimates and only the extremely small numerical coefficient ($\sim 10^{-3}$), first evaluated in this work for E1E1E1 decay, confirmed this conclusion. However, the values for the $2p_{1/2}/1s$ E1M1 and E1E2 transition rates appeared to be important for the determination of the theoretical accuracy limits [36, 37] for frequency measurements by means of optical resonance experiments with hydrogen [4, 5].

The following notations will be used throughout this paper. The $2p_{1/2}$ level is labelled as $2p$ because the $2p_{3/2}$ level will not be considered. Vectors with three components are in bold. The angular part of any vector $\mathbf{r}$ is defined by the unit vector $\mathbf{n}$, directed as $\mathbf{r}$. The Clebsch–Gordan coefficients $C_{jm}^{i\ell m}$ are introduced according to [38]. Other notations are the following:

$$\Delta = \sqrt{\Delta E_L^2 + \frac{i}{2}\Gamma_{2p}^2},$$

$$w^{(1\gamma)} = \sqrt{w^{(1\gamma)}_L / W_{2p}},$$

$$w^{(2\gamma)} = \sqrt{w^{(2\gamma)}_L / W_{2p}}.$$  

Here $\Delta E_L$ is the Lamb shift, $\Gamma_{2p}$ is the width of the $2p$ state, $w^{(1\gamma)}, w^{(2\gamma)}$ are the one-photon and two-photon decay probabilities for the corresponding $2s$ and $2p$ levels. The value $w^{(2\gamma)} = W_{2p}(\text{E1E2}) + W_{2p}(\text{E1M1})$ includes the probabilities for $2p \rightarrow \gamma(\text{E1}) + \gamma(\text{E2}) + 1s$ and $2p \rightarrow \gamma(\text{E1}) + \gamma(\text{M1}) + 1s$ decays.

### 2. One-photon decay of the $2s$-state for hydrogen and anti-hydrogen atoms in external electric fields

In the absence of an electric field, the M1 transition $2s \rightarrow 1s + \gamma$—strongly forbidden in the nonrelativistic limit—was first evaluated by Breit and Teller [10]. The value obtained in [10] was later improved by Drake [39] (see also [40]). In [39, 40] relativistic corrections to the Schrödinger wavefunctions and to the M1 photon emission operator were taken into account. Neglecting these corrections the $2s \rightarrow 1s + \gamma$ transition probability turns out to be zero due to the orthogonality of the radial wavefunctions. Accurate fully relativistic calculations for the $2s \rightarrow 1s + \gamma$ transition for the hydrogen-like ions with arbitrary nuclear charge $Z$ values were performed by Johnson [41].

Within QED theory the $S$-matrix element for the one-photon emission process reads [42]

$$S_{\gamma A} = e \frac{\sqrt{4\pi}}{\sqrt{2\omega}} \int dx \psi_A(x) e^{i\mathbf{p}\cdot\mathbf{r}} e^{-i(k\mathbf{r}-\omega t)} \psi_A(x),$$

where $\mathbf{k}$ is the wave vector of the photon, $\omega = |\mathbf{k}|$ is the photon frequency, $x = (\mathbf{r}, t)$ is the 4-vector of space-time coordinates, $e_\mu$ is the 4-vector of the photon polarization, $\psi_A(x)$ is the Dirac wavefunction for the bound electron in an atom, $\gamma_\mu$ are the Dirac matrices and $A'$, $A$ correspond to the relevant quantum numbers characterizing the final and initial states of the electron in an atom. In equation (4) $e$ is the electron charge and the relativistic units $\hbar = c = 1$ are used throughout this section.

We integrate over the time variable $t$ in equation (4) and employ the relation

$$S_{\gamma A} = -2\pi i \delta(E_A - E_A - \omega) U_{\gamma A}$$

for the transition amplitude $U_{\gamma A}$. In what follows, we define also the amplitude $U_{\gamma A}(\mathbf{k}, \epsilon)$ as

$$U_{\gamma A}(\mathbf{k}, \epsilon) = e \frac{\sqrt{2\pi}}{\omega} \langle A'|\epsilon\mathbf{\sigma} e^{-i\mathbf{k}\cdot\mathbf{r}}|A\rangle.$$  

Here $\epsilon$ is the transverse polarization vector and $\mathbf{\sigma}$ are the Dirac matrices.

Transition probability integrated over the photon emission directions and summed over the polarizations is

$$W_{\gamma A}^{(1\gamma)} = \frac{\epsilon \omega_{\gamma A}}{2\pi} \sum \int d\epsilon_\ell |U_{\gamma A}(\mathbf{k}, \epsilon)|^2,$$

$$w^{(1\gamma)} = \frac{\epsilon \omega_{\gamma A}}{2\pi} \sum \int d\epsilon_\ell |U_{\gamma A}(\mathbf{k}, \epsilon)|^2.$$  

Here $\epsilon_{\gamma A} = E_A - E_{A'}, E_{A'}, E_A$ are the Dirac eigenvalues for the atomic electron, $\langle A'|...|A\rangle$ is the matrix element with the Dirac 4-component wavefunctions. Summation over $\epsilon$ implies the transversality condition $\epsilon\mathbf{k} = 0$.

In the nonrelativistic limit the amplitude $U_{\gamma A}(\mathbf{k}, \epsilon)$ should be changed to the transition amplitude in the Pauli approximation defined via the matrix element of the corresponding emission operator [40]

$$U_{\gamma A}^{(1\gamma)}(\mathbf{k}, \epsilon) = \langle (\epsilon \mathbf{p} + i\mathbf{e} [\mathbf{k} \times \hat{\mathbf{s}}]) e^{-i\mathbf{k}\cdot\mathbf{r}} |A\rangle.$$  

The relation (8) involves the nonrelativistic electron momentum operator $\mathbf{p} = -i\nabla$, the electron spin operator $\hat{\mathbf{s}} = \frac{i}{2}\mathbf{\sigma}$ ($\mathbf{\sigma}$ are the Pauli matrices) and $(...)_{\gamma A}$ denotes the matrix element with the Schrödinger wavefunctions. In the dipole approximation the first term of the integrand in equation (7) describes the E1 photon emission, that in the case of $A' = 1s, A = 2s$ is forbidden by parity; the second term corresponds to the M1 photon emission. Due to the orthogonality of the radial wavefunctions $\psi_{2s}$ and $\psi_{1s}$ the M1 transition probability as described by equation (7) is nonzero only due to the factor $e^{-i\mathbf{k}\cdot\mathbf{r}}$ and due to the relativistic corrections to the Schrödinger wavefunctions. In relativistic units for the atomic electron $r \approx a_0 = 1/m\alpha Z$ ($a_0$ is Bohr's...
radius, \( m_r \) is the electron mass, \( \alpha \approx 1/137 \) is the fine structure constant), \( \omega \approx m (\alpha Z)^2 \) and \( k r \approx \alpha \). Thus, one can restrict the consideration to the lowest nonvanishing term of the multipole expansion of \( e^{-ikr} \), which turns out to be of the same order of magnitude as the relativistic corrections to the wavefunctions.

The zero-order wavefunctions which should be employed for the evaluation of the matrix elements in equation (7) look like

\[
\psi_A(r) = \psi_{nlm}(r) = \sum_{m_l} C_{nlm}^{jm} R_{ml}(r) Y_{lm}(n_r) x_{lm}, \quad (9)
\]

where the standard set of one-electron quantum numbers is introduced: principal quantum number \( n \), total electron angular momentum \( j \) and its projection \( m_l \), orbital electron angular momentum \( m \). The function \( x_{lm} \) is the Pauli spinor. For the 2s and 1s electron states \( l = 0 \) and the transition amplitude in equation (7) reduces to [40]

\[
U_{2p, 1s}^P = -ik^2 (m_s \mathbf{e} \mathbf{k}) j a (z Z)^{12} R_{2s, 1s}, \quad (10)
\]

where \( |m_l| \) are the spin wavefunctions, \( R_{2s}(r) \) and \( R_{1s}(r) \) are the nonrelativistic radial wavefunctions. Inserting equation (10) into equation (7), we have to sum over \( m_l \) and average over \( m_s \). For summation over \( \mathbf{e} \) the standard formula [42]

\[
\sum_{\mathbf{e}} e_i e_i = \delta_{ij} - n_i n_k \quad (12)
\]

is used, where \( n_i \) and \( n_k \) are the Cartesian components of the vector \( n \). After integration over the photon emission directions \( n \) one finds

\[
W_{2s, 1s}^{(1y)} = \frac{3^5}{2^2 \pi a^5} (z Z)^{14} R_{2s, 1s}^2, \quad (13)
\]

respectively. The evaluation of the radial integral in equation (13) results

\[
W_{2s, 1s}^{(1y)} = \frac{1}{972} m (a Z)^{10} = 2.4957 10^{-6} \text{ s}^{-1}. \quad (14)
\]

The decay rate of the 2s state of a hydrogen atom in the presence of an external electric field was studied in [25–27]. The external electric field mixes the states 2s and 2p. A 100% presence of an external electric field was studied in [25–27]. In what follows we will consider weaker fields \( D < D_c \) such that admixtures of all other states, apart from 2p can be neglected. The ground state \( 1s \) will be assumed to be unaffected by the field. We will denote the mixed states 2s and 2p as \( 2s \) and \( 2p \), respectively. For the wavefunction of the 2s state we can write [26]

\[
\langle 2s | m_s \rangle = \langle 2s | m_s \rangle + \eta \sum_{m_l} \langle 2p | m_s \rangle (e \mathbf{D} | 2s | m_s \rangle | 2p | m_s \rangle, \quad (15)
\]

where \( \eta = (\Delta E_1 + i \Gamma_{2p} / 2)^{-1} \) and \( \mathbf{D} \) is the electric field vector. The transition amplitude (10) in an external electric field looks like

\[
U_{2s, 1s}^{P} (\mathbf{k}, \mathbf{e}) = U_{2s, 1s}^{P} (\mathbf{k}, \mathbf{e}) + \eta \sum_{m_l} \langle 2s | m_s \rangle (e \mathbf{D} | 2p | m_s \rangle U_{2p, 1s}^{P} (\mathbf{k}, \mathbf{e}), \quad (16)
\]

where

\[
U_{2p, 1s}^{P} (\mathbf{k}, \mathbf{e}) = \frac{e \omega_{2s, 1s} | 2p | m_s \rangle \mathbf{e} \mathbf{r} | 1s | m_s \rangle. \quad (17)
\]

Direct evaluation of the integral in equation (17) results in

\[
U_{2p, 1s}^{P} (\mathbf{k}, \mathbf{e}) = \frac{e \omega_{2s, 1s}}{q} \sum_{m_l} \langle 2s | m_s \rangle \mathbf{e} \mathbf{D} | 2p | m_s \rangle (e \mathbf{r} | 1s | m_s \rangle \mathbf{r} | 1s | m_s \rangle, \quad (18)
\]

where \( e_q \) are the spherical components of the vector \( \mathbf{e} \) and \( q = -q \). Similarly,

\[
\langle 2s | m_s \rangle (e \mathbf{D} | 2p | m_s \rangle = 3 e \sum_{q} \langle 2s | m_s \rangle (e \mathbf{D} | 2p | m_s \rangle \mathbf{r} | 1s | m_s \rangle \mathbf{r} | 1s | m_s \rangle, \quad (19)
\]

Further evaluation requires the insertion of the amplitude (10) in equation (7) and summation over \( \mathbf{e} \). For this purpose the formula (12) should be used and then the representation of the scalar and vector products in spherical components should be employed. The final result is (here we do not integrate over the directions \( m \))

\[
d W_{2s, 1s}^{(1y)} (n_k) = \frac{3}{8 \pi} W_{2s, 1s}^{(1y)} \times \left[ 1 + e \mathbf{D} n_k \left( \frac{\Gamma_{2p}}{(\mathbf{w}^{(1y)} \Delta \gamma)^2} + \frac{e^2 D^2}{(\mathbf{w}^{(1y)} \Delta \gamma)^2} \right) \right] d n_k. \quad (20)
\]

Although formula (20) was obtained earlier in [25–27], we present here our method for its derivation.

The formal T-nonvariance of the factor \( \mathbf{D} n_k \) in equation (20) \( (n_k \text{ and } D \text{ are T-odd and T-even vectors, respectively}) \) is compensated for by the dependence on \( \Gamma_{2p} \): this is the imitation of T-nonvariance in unstable systems, as predicted by Zeldovich [44]. Rewriting equation (20) into the form [25]

\[
d W_{2s, 1s}^{(1y)} (n_k) = W_0 + |\mathbf{e}| \Gamma_{2p} n_k \frac{u^{(1y)}}{(\mathbf{w}^{(1y)} \Delta \gamma)^2} + e^2 D^2, \quad (21)
\]

where

\[
W_0 = \frac{3}{8 \pi} W_{2s, 1s}^{(1y)} \left( 1 + \frac{e^2 D^2}{(\mathbf{w}^{(1y)} \Delta \gamma)^2} \right), \quad (22)
\]

\[
\beta (D) = \frac{|\mathbf{e}| \Gamma_{2p} u^{(1y)}}{(\mathbf{w}^{(1y)} \Delta \gamma)^2} + e^2 D^2, \quad (23)
\]

we find the maximum value \( \beta (D) \) at [25]

\[
D_{\max} = \frac{\mathbf{w}^{(1y)} \Delta \gamma}{|\mathbf{e}|} \approx 0.3 \times 10^{-4} \text{ V cm}^{-1}. \quad (24)
\]

The value \( \beta_{\max} = \beta (D_{\max}) \) is equal to

\[
\beta_{\max} = \frac{\Gamma_{2p}}{2 \Delta} \approx \frac{1}{20}, \quad (25)
\]

The \( (-) \) and \( (+) \) signs in equation (21) correspond to the \( \mathbf{H} \) and \( \mathbf{H} \) atoms, respectively, \( n_D = D / |D| \).

The relative difference for the decay rates in \( \mathbf{H} \) and \( \mathbf{H} \) atoms at the maximum value \( D_{\max} \) equals

\[
\frac{d W_{2s, 1s}^{(1y)} (\mathbf{H})}{d W_{2s, 1s}^{(1y)} (\mathbf{H})} = \frac{d W_{2s, 1s}^{(1y)} (\mathbf{H})}{d W_{2s, 1s}^{(1y)} (\mathbf{H})} = \frac{W_0 (D_{\max}) \beta (D_{\max}) n_B n_B}{3 \frac{1}{6} W_{2s, 1s}^{(1y)} (\mathbf{H})} \approx \frac{1}{5} n_B n_B. \quad (26)
\]

In the presence of such a very weak field given by equation (24), this difference is close to about 20% and probably can be observed in experiments of the type reported in [4, 5].
We also note that if one integrates in equation (21) over photon emission directions, the term linear with respect to the field vanishes. But a quadratic term included in $W_0$ exists and represents a correction to the $W_{A\rightarrow A}^{(1)}$ transition probability, i.e., to the lifetime of the 2s level. This correction term reaches the magnitude of the radiative correction obtained in [12] in the field of the strength

$$D_1 = \frac{1}{\Delta} \sqrt{\frac{8\pi}{3} \frac{\delta \Gamma_{2s}}{W_{2p1s}}} \approx \sqrt{\frac{8\pi}{3} \frac{\delta \Gamma_{2s}}{\Gamma_{2s}}} D_{\max},$$

(27)

where the correction $\delta \Gamma_{2s}/\Gamma_{2s}$ was derived by Jentschura (see equation (36) in [12]). Though the correction in [12] is obtained for the process of the two-photon decay of 2s level, it also represents a correction to the lifetime of the 2s level. For the hydrogen atom $D_1 \sim 1.4 \times 10^{-7}$ V cm$^{-1}$. Since the experiments deal with differential cross sections, we compare also the linear term with the radiative correction. The linear term $\beta(D)$ reaches the magnitude of $\delta \Gamma_{2s}/\Gamma_{2s}$ at the field strength $7.5 \times 10^{-11}$ V cm$^{-1}$. It should be difficult to eliminate spurious fields of such magnitude in real experiments and, therefore, the comparison of the theoretical results in [12] with experimental ones requires some caution.

3. Transition probabilities in different forms and gauges

In this section different gauges in combination with different ‘forms’ for the one-photon transition probability are described. Atomic units $\hbar = e = m = 1$ will be used throughout this section.

The transition probability for the emission of a photon with definite angular momentum and parity can be described in the first order of QED perturbation theory within arbitrary gauge as

$$W_{A\rightarrow A}(\omega) = \sum_{kq} \left| |A'| a_{qkq} |A\rangle + \Phi_{qkq} |A\rangle \right|^2,$$

(28)

where $a_{qkq}$ and $\Phi_{qkq}$ denote the electric and magnetic vector potentials, respectively, and $\Phi_{qkq}$ corresponds to the scalar potential; $\omega$ is the photon frequency, $k, q$ are the total angular momentum of the emitted photon and its projection, respectively. The brackets $|A\rangle$ and $|A'|$ are stationary Dirac states (wavefunctions) with energies $E_A$ and $E_{A'}$ and $\omega$ is the Dirac matrices. In the momentum representation these potentials take the form

$$e_{A_{qkq}}(k) = \frac{4\pi^2 e^2 c^{3/2}}{\omega^{3/2}} \delta \left( k - \frac{\omega}{c} \right) \langle q | Y_{lq}(\mathbf{n}_k) + K | n_k Y_{lq}(\mathbf{n}_k) \rangle,$$

(29)

$$m_{A_{qkq}}(k) = \frac{4\pi^2 e^2 c^{3/2}}{\omega^{3/2}} \delta \left( k - \frac{\omega}{c} \right) m | n_k Y_{lq}(\mathbf{n}_k) \rangle,$$

(30)

$$\Phi_{qkq}(k) = \frac{4\pi^2 e^2 c^{3/2}}{\omega^{3/2}} \delta \left( k - \frac{\omega}{c} \right) K | n_k Y_{lq}(\mathbf{n}_k) \rangle.$$

(31)

Here $k$ denotes the variable in the momentum representation. Functions $e_{A_{qkq}}$ and $m_{A_{qkq}}$ are the vector spherical harmonics of electric and magnetic type, respectively, $Y_{lq}$ is the ordinary spherical harmonic, $c$ is the speed of light and $K$ denotes a gauge constant.

Usually two gauges are used: the so-called Coulomb gauge that corresponds to the vanishing longitudinal part of the vector potential and the scalar potential. This gauge is characterized by the choice of the gauge parameter $K = 0$. Another convenient gauge is defined by the following value of the parameter $K = -\sqrt{\frac{2\pi}{3}}$. Within this gauge the terms containing spherical functions $C_{s-0}^{(k)} = \frac{1}{\sqrt{2\pi}} Y_{k-0}$ vanish in the expression for the transition probability (28).

After some manipulations the expression for the probability of emission of an electric photon with the angular momentum $k$ can be cast into the form

$$W_{A\rightarrow A}^{E_k} = \frac{2(k + 1)\omega}{k(2k + 1)c} \times \sum_{q = -k}^k \left| \langle A'| e_{A_{qkq}}(k) + K | A\rangle \right|^2.$$

(32)

Here

$$e_{A_{qkq}}^{(k)} = -i \left[ k^{2k + 3/2} g_{k+1}(\omega r) | C_{s+1}^{(k+1)} \times a^{(1)}_{-q} \right],$$

(33)

$$m_{A_{qkq}}^{(k)} = i \left[ \sqrt{k(2k - 1)} g_{k-1}(\omega r) | C_{s-1}^{(k-1)} \times a^{(1)}_{-q} \right],$$

(34)

$$\Phi_{qkq}^{(k)} = 2k^{1/2} g_{k+1}(\omega r) C_{s+1}^{(k)}.$$

(35)

and $[a^{(s)} \times b^{(s')}]_{q}^{(s)}$ represents the tensor product of two irreducible spherical tensors of rank $s$ and $s'$ coupled to a spherical tensor of rank $s$ with components $q$. Here $C_{s}^{(k)} = \frac{2k^{3/2}}{\sqrt{\pi}} J_{s}^{(k)}$ should be understood as a spherical tensor of the rank $k$ with components $C_{s}^{(k)}$. The radial functions $g_{k}(\omega r)$ are related to Bessel functions $J_{\nu}(z)$ through $g_{k}(z) = (2\pi)^{3/2} \frac{1}{\sqrt{\pi}} J_{s}^{(k)}(z)$.

Using the following integral relation for the Dirac wavefunctions [42]:

$$i \int \psi_{A}^{*}(\alpha \psi_{A}) d^{3}r = \frac{\omega}{c} \int \psi_{A}^{*} \chi \psi_{A} d^{3}r,$$

(36)

where $\chi$ is an arbitrary function; one can establish another form for the $E_k$-transition probability (see [23]):

$$W_{A\rightarrow A}^{E_k} = \frac{2(k + 1)\omega^{3}}{k(2k + 1)c^{3}} \times \sum_{q = -k}^k \left| \langle A'| e_{A_{qkq}}^{(k)} + \frac{K}{\omega} \sqrt{k + 1} | O_{qkq}^{(k)} + \Phi_{qkq}^{(k)} \rangle | A\rangle \right|^2.$$

(37)
Deriving the nonrelativistic limit of equations (32) and (37) implies two distinct nonrelativistic forms for the one-photon transition probability with arbitrary gauge constant \( K \) (see [46]):

\[
W_{E_{A' \rightarrow A}}^{E} = \frac{2(k + 1)(2k + 1)\omega^{2k-1}}{k(2k + 1)!} \left| \sum_{q = -k}^{k} \left| (A') \left( Q^{(k)}_{q} + K \frac{k}{k + 1} \omega Q^{(k)}_{q} \right) \right|^{2} \right|
\]

and

\[
W_{E_{A' \rightarrow A}}^{E} = \frac{2(k + 1)(2k + 1)\omega^{2k+1}}{k(2k + 1)!} \sum_{q = -k}^{k} \left( \omega \frac{c}{k} \right)^{2k+1} \left| \sum_{q = -k}^{k} \left| (A') \left( Q^{(k)}_{q} + K \frac{k}{k + 1} \omega Q^{(k)}_{q} \right) \right|^{2} \right|.
\]

Here \( |A\rangle \) and \( (A') \) are nonrelativistic Schrödinger states (wavefunctions) together with operators

\[
Q^{(k)}_{q} = -r^{k} C^{(k)}_{q},
\]

\[
Q^{(k)}_{q} = -r^{-k-1} \left( k C^{(k)}_{q} \frac{\partial}{\partial r} + \frac{i}{r} \sqrt{k(k + 1)} \frac{1}{k} \omega Q^{(k)}_{q} \right).
\]

4. Application of the Coulomb Green function

In order to evaluate the transition probabilities for the processes \( 2p \rightarrow 2\gamma + 1s \) and \( 2\gamma \rightarrow 2\gamma + 1s \) in the hydrogen atom, we employ the nonrelativistic Coulomb Green function. The summations over the entire spectrum of the Schrödinger equation arise usually when perturbation theory is applied. The Green function approach allows one to express the intermediate summations in a closed analytic form. This is very useful for the analysis of and tests for numerical calculations.

The Green function for the Schrödinger equation with the Hamiltonian \( \hat{H} \) is defined by the solution of the equation

\[
\hat{H} G(E; \mathbf{r}, \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}')
\]

and can always be represented in terms of a spectral decomposition

\[
G(E; \mathbf{r}, \mathbf{r}') = \sum_{N} \frac{\psi_{N}(\mathbf{r})\psi_{N}(\mathbf{r}')}{E_{N} - E}.
\]

In equation (44) the sum runs over the entire spectrum of the Hamiltonian (bound and continuous spectrum). The set of quantum numbers \( N \) may be specified as usual by the principal quantum number \( n \), orbital angular momentum number \( l \) and projection \( m \). In view of the spherical symmetry it is sufficient to derive a closed expression for the radial part \( g_{l}(E; \mathbf{r}, \mathbf{r}') \) of the Green function defined by the partial wave decomposition

\[
\Phi_{l, r}(r, r') = \sum_{\nu} \frac{\phi_{\nu, l}^{r}(r)\phi_{\nu, l}^{r'}(r')}{E_{\nu, l} - E}.
\]

In the particular case of an external Coulomb potential the Green function of equation (43) is called the Coulomb Green function (CGF). With the use of expansion (45) the radial integrals occurring in equations (39) and (40) for the transition probabilities can be calculated explicitly (see [47] for details).

For the radial part of the Coulomb Green function it is convenient to employ the Sturmian expansion [17], which is defined in the entire complex energy plane via

\[
\frac{1}{r^{r'}} g_{l}(E; \mathbf{r}, \mathbf{r}') = \sum_{n_{l} = 0}^{\infty} \frac{\Phi_{n_{l}, l}(r)\Phi_{n_{l}, l}(r')}{E_{n_{l}, l} - E},
\]

where \( \Phi_{n_{l}, l}(r) \) denote the Sturmian functions. The Sturmian expansion of the CGF can be represented in an alternative form by introducing radial functions,

\[
R_{n_{l}, l}(2
\nu \sqrt{\frac{Z}{\nu r}}) = \frac{1}{r} \sqrt{\frac{Z}{\nu r} (2l + 1)!} \Gamma(\nu_{l} + l + 1) \Gamma(\nu_{l} - l) M_{n_{l}, l, l}^{\nu_{l}}(2
\nu, l) ,
\]

which are related to Whittaker functions \( M_{n_{l}, l, l}^{\nu_{l}}(2
\nu, l) \), where \( \nu = Z/\sqrt{-2E} \). For integer values \( \nu = n \) these functions coincide with the normalized, radial hydrogenic wavefunctions

\[
\Phi_{n_{l}, l}(r) = \sqrt{\frac{\nu r}{Z}} R_{n_{l}}(2
\nu, l).
\]
Substitution of equation (48) into (46) yields
\[
\frac{1}{rr} g_{\ell}(v; r, r') = \frac{v^2}{2\pi} \sum_{n=0}^{\infty} \frac{n - v}{n - v} R_{nl} \left( 2r \right) R_{nl} \left( 2r' \right).
\]

(49)

Within this paper we apply the Green function method for the evaluation of the two-photon decay probability in the hydrogen atom.

In [48] the two-photon transition process \(2s \rightarrow \gamma(E1) + \gamma(E1) + 1s\) has been considered. The probability for the two-photon decay \(A \rightarrow \gamma(E1) + \gamma(E1) + A'\) with photon frequencies \(\omega_1\) and \(\omega_2\) within the nonrelativistic limit and dipole approximation is
\[
dW_{E1E1}^{A \rightarrow A'}(\omega_2) = \frac{8}{9\pi} \left( \frac{4\pi}{3} \right)^3 \sum_{M_l, M_s} \left| A_{l}^l | rY_{1M_l}(n_r) G(E_A) - \omega_1; r, r' \right|^2 \left| A_{l'}^l | r'Y_{1M_l}(n_r) G(E_A) - \omega_1; r, r' \right|^2 \left( \omega_1 \omega_2 \right)^2 d\omega_2.
\]

(50)

The energy conservation law implies \(\omega_1 = E_A - E_A' - \omega_2\). After the evaluation of angular matrix elements in equation (50) the remaining radial integrals have the form
\[
\int_0^\infty \int_0^\infty \int_0^\infty d\nu \, d\nu' \, dx (\nu x)^{3/2} (\nu' x)^{3/2} \times \exp\left( -\frac{1}{\nu} (x + 1) - (x + 1) \cos(x) \right) \times \left( \coth \left( \frac{x}{2} \right) \right)^{3/2} I_{2l+1} \left( \frac{2\sqrt{\nu\nu'}}{\nu} \sinh(x) \right),
\]

(51)

where \(n\) and \(n'\) are the principal quantum numbers of the initial and final states, respectively, together with the parameters \(\beta = \sqrt{\nu}/n, \beta' = \sqrt{\nu'}/n'\) and \(\nu = \sqrt{2(E_{nl} - \omega)}\). These integrals can be evaluated analytically after inserting the series expansion for the modified Bessel functions \(I_{2l+1}\). The integration over \(x\) should be done at the end. Assuming emission of two E1 photons, one can write the total probability for such a two-photon decay as
\[
W_{E1E1}^{A \rightarrow A'} = \int_0^{\omega_0} dW_{E1E1}^{A \rightarrow A'}(\omega)
\]

(52)

with \(\omega_0 = E_A - E_A'\). For the process \(2s \rightarrow 2\gamma(E1) + 1s\) in [48] the result of the evaluations was reported as
\[
W_{E1E1}^{2s1s} = 8.226 \text{ s}^{-1}
\]

(53)

with an accuracy of about 1%.

However, in further calculations it is convenient to use the other representation of the radial Coulomb Green function in terms of an expansion over Laguerre polynomials [17] (also employed in [48]):
\[
g_{\ell}(v; r, r') = \frac{4Z}{v} \left( \frac{4}{v^2} rr' \right)^{l} \exp\left( -\frac{r + r'}{v} \right) \times \sum_{n=0}^{\infty} \frac{n! L_{2l+1}^{2l+1}(\frac{r}{2}) L_{2l+1}^{2l+1}(\frac{r'}{2})}{(2l + 1 + n)!(n + l + 1 - v)}.
\]

(54)

Series (54) converges absolutely as \(n^{-3/2}\) for arguments \(r, r' > 0\) and \(\text{Im}(\nu) = 0\) [17]. The angular momentum quantum number \(l = 1\) for the intermediate states is fixed after the angular integration. Inserting the expansion (54) for \(l = 1\) into expression (50) yields
\[
dW_{E1E1}^{2s1s}(\omega) = \frac{2}{3} \left( \frac{\omega_1 \omega_2}{\pi} \right) I_1(\nu) I_1(\nu') \text{d}\omega,
\]

(55)

\[
I_1(\nu) = \frac{16\sqrt{2}}{\nu^3} \left( \frac{\nu}{2} \right)^{2l+1} \sum_{m=0}^{\infty} \frac{m!}{(m + 2)!} \int_0^\infty \mathrm{d}t r^4 e^{-t} \left( \frac{1 - \frac{v}{4}}{t} \right) L_m^3(t).
\]

(56)

These integrals can be evaluated analytically. After inserting this result into equation (52) the integration over \(\omega\) has to be performed in order to obtain the total transition probability for the E1E1 decay of the 2s state in the hydrogen atom. This is achieved numerically with the aid of the computer-algebra code MATHEMATICA. The final result is
\[
W_{E1E1}^{2s1s}(\omega) = \frac{1}{2} \int_0^{\omega_0} dW_{E1E1}^{2s1s}(\omega) = 0.001 318 23 (\alpha Z)^6 \text{ au}
\]

\[
= 8.229 31 \text{ s}^{-1} (Z = 1)
\]

(57)

with \(\omega_0 = E_{2s} - E_{1s}\). In equation (57) we indicated the \(Z\)-dependence of the \(W_{E1E1}^{2s1s}\) transition probability. The numerical value (57) coincides with most precise result [12] up to five digits. This will serve us as an accuracy estimate of our approach in the following calculations.

5. \(E1E2\) decay probability for the \(2p\) state

In this section we consider the E1E2 decay of the 2p state in the hydrogen atom. Again the set of quantum numbers \(nlm_j\) is employed as long as the total angular momentum \(j\) is not important in this calculation performed within the nonrelativistic approach. Nevertheless, in order to compare our results with those obtained from the relativistic evaluation (see [13, 14]), we shall perform the calculation within two different gauges according to equations (39)–(42). This will also elucidate the potential influence of relativistic effects associated with the contribution of the negative-energy Dirac spectrum.

As a test for the method the gauge constant \(K = -\sqrt{\frac{4\pi}{3}}\) is chosen in expression (39) for the transition probability, which corresponds to the nonrelativistic ‘length’ form as mentioned above. This would be equivalent to the choice \(K = 0\) together with form (40). Inspection of equations (39) and (41) reveals that the emission of electric photons (E\(k\)) is described by the potentials
\[
V_{Ek} = \sqrt{\frac{k + 1}{k}} \frac{2\omega^{1/2}}{(2k + 1)!!} r^k Y_{k-lq}.
\]

(58)

Accordingly, the two electric photon decay rate of the atomic state \(A\) can be written as
\[\frac{dW_{\text{EIE2}}^{\text{EEK}}}{d\omega} = \sum_{q_{q,m},m_{q},m_{q'}} \sum_{N} \left| A(N|N|V_{\text{EIE2}}^{\text{EEK}}|A) \right|^2 \right|_{E_N - E_A + \omega} \times \delta(\omega + \omega' - E_A + E_A') \frac{d\omega d\omega'}{d\omega d\omega'}. \]  

(59)

Here the labels \(A, A'\) and \(N\) abbreviate the set of nonrelativistic quantum numbers (principal quantum number \(n\), orbital momentum \(l\) and projection \(m_l\)) for indicating the state of the atomic electron as the initial (\(A\)), intermediate (\(N\)) and final (\(A'\)). The photons will be characterized by the angular momentum and its projection \((kq)\) as well as by the type of the photon (electric or magnetic). Equation (59) also implies the summation over degenerate substates of the final atomic state \(A'\) and the average over the degenerate substates of the initial atomic state \(A\) as well as summations over the angular momentum projections of both emitted photons. The frequencies of the two photons \(\omega\) and \(\omega'\) are related by the energy conservation law \(\omega' = \omega_0 - \omega\), where \(\omega_0 = E_A - E_A'\).

Employing the eigenmode decomposition of the Coulomb Green function (45) the probability of the two-photon decay process takes the form

\[dW_{\text{EIE2}}^{\text{EEK}} = \frac{2\pi}{2\lambda + 1} \sum_{q_{q,m},m_{q'}} \sum_{l,m} \left( \int dr_1 dr_2 R_{n_l,m} n_l(r_1) \times Y_{l,m,l}(n_l) V_{\text{EIE2}}^{\text{EEK}}(r_1) r_{l,m,l}(r_2) Y_{l,m,l}(n_l) \right) \times Y_{l,m,l}(n_l) V_{\text{EIE2}}^{\text{EEK}}(r_2) r_{l,m,l}(r_1) \times Y_{l,m,l}(n_l) V_{\text{EIE2}}^{\text{EEK}}(r_1) r_{l,m,l}(r_2) Y_{l,m,l}(n_l) \left( \int dr_1 dr_2 R_{n_l,m} n_l(r_1) \times Y_{l,m,l}(n_l) V_{\text{EIE2}}^{\text{EEK}}(r_1) r_{l,m,l}(r_2) Y_{l,m,l}(n_l) \right) \right) \right|_{E_N - E_A + \omega} \times \delta(\omega + \omega' - E_A + E_A') \frac{d\omega d\omega'}{d\omega d\omega'}. \]  

(60)

where \(V_{\text{EIE2}}^{\text{EEK}}(r)\) is the potential (58) written in the gauge \(K = -\frac{2\pi}{4\sqrt{2}}\) and compatible with the form (39), together with parameters \(v = Z/\sqrt{-2(\omega_0 + \omega)}\), \(v' = Z/\sqrt{-2(\omega_0 + \omega')}\) and frequency \(\omega' = E_A - E_A' - \omega\).

Specifying equation (60) for the transition between levels \(A = 2p, A' = 1s\) and taking into account that in this case the angular momentum of the photon can take values \(k = 1, 2\), we obtain four different terms contributing in equation (60). Unfortunately, in the previous paper [24] an error in the summation over projections of the Clebsch–Gordan coefficients occurred (see expression (41) in [24]). Here we correct this mistake and give the proper expression for the probability. After angular integration and summation over projections we find

\[dW_{\text{EIE2}}^{\text{EEK}}(\omega) = \frac{24\omega\omega'\omega^2}{3\sqrt{32\pi}} - \omega^2|I_1(\omega)|^2 + I_2(\omega)^2 \right|_{E_1 - E_2} \times \frac{d\omega}{d\omega'} + \frac{1}{\sqrt{6}} \int_0^\infty dr_1 \int_0^\infty dr_2 r_1^2 r_2^2 e^{-r_1 - r_2} g_1(E_A - \omega; r_1, r_2) \int_0^\infty dr_3 \int_0^\infty dr_4 r_3^2 r_4^2 e^{-r_3 - r_4} g_2(E_A - \omega; r_1, r_2). \]  

(61)

and

\[I_2(\omega) = \frac{1}{8\sqrt{6}} \int_0^\infty dr_1 \int_0^\infty dr_2 r_1^2 r_2^2 e^{-r_1 - r_2} g_1(E_A - \omega; r_1, r_2) \right|_{E_1 - E_2} \times \frac{d\omega}{d\omega'} \]  

respectively. Inserting again the representation (54) for the CGF with \(l = 1\) leads to radial integrals that can be evaluated analytically.

Substituting the integrals (62) and (63) into (61) and integrating over frequencies \(\omega\) yields

\[W_{\text{EIE2}}^{\text{EEK}} = \frac{1}{2} \int_0^{\infty} dW_{\text{EIE2}}^{\text{EEK}} = 1.98896 \times 10^{-5} (\alpha Z)^8 \text{ au} \]  

\[= 6.61197 \times 10^{-6} s^{-1} (Z = 1) \]  

(64)

with \(\omega_0 = E_{2p} - E_{1s}\). In equation (64) we indicated the Z-dependence of the \(W_{\text{EIE2}}^{\text{EEK}}\) transition probability. Compared with the relativistic result in the ‘length’ gauge (see [14]) the relative discrepancy is about 0.1%.

The calculation of the E12 two-photon decay with the nonrelativistic ‘velocity’ form is more involved. Now the gauge constant should be chosen as either \(K = -\frac{\sqrt{2}}{4\sqrt{2}}\) for the form (40) or \(K = 0\) for the form (39). We choose \(K = 0\) together with the form (39). The potential in this case reads

\[V_{\text{EIE2}}^{\text{EEK}}(r) = \frac{4\omega\omega'}{(2k + 1)!} \left( \frac{k + 1}{k(2k + 1)} \right)^{k-1} \left[ Y_{k}(k\omega r) \frac{\partial}{\partial r} \right] \]  

\[+ \frac{i}{r} \sqrt{k(k + 1)} |Y_{k}(k\omega r)| \text{ } \text{d} \omega' \]  

(65)

The formula for \(dW_{\text{EIE2}}^{\text{EEK}}\) follows again from equation (60). Performing angular integrations and summations over projections as discussed in previous cases now yields

\[dW_{\text{EIE2}}^{\text{EEK}}(\omega) = \frac{24\omega\omega'\omega^2}{3\sqrt{32\pi}} - \omega^2|I_1(\omega)|^2 + I_2(\omega)^2 \right|_{E_1 - E_2} \times \frac{d\omega}{d\omega'} + \frac{1}{\sqrt{6}} \int_0^\infty dr_1 \int_0^\infty dr_2 r_1^3 r_2^3 e^{-r_1 - r_2} g_1(E_A - \omega; r_1, r_2) \int_0^\infty dr_3 \int_0^\infty dr_4 r_3^2 r_4^2 e^{-r_3 - r_4} g_2(E_A - \omega; r_1, r_2). \]  

(66)

with radial integrals of the type

\[I_1(\omega) = \frac{1}{\sqrt{6}} \int_0^\infty dr_1 \int_0^\infty dr_2 r_1^3 r_2^3 e^{-r_1 - r_2} \left[ 1 - 9i r_2 r_2 \frac{1}{2} \right] \]  

\times \left[ \frac{\partial}{\partial r_1} - \frac{2i}{r_1} \right] g_1(E_A - \omega; r_1, r_2) \]  

(67)

and

\[I_2(\omega) = \frac{1}{\sqrt{6}} \int_0^\infty dr_1 \int_0^\infty dr_2 r_1^3 r_2^3 e^{-r_1 - r_2} \left[ 1 - 9i r_2 r_2 \frac{1}{2} \right] \]  

\times \left[ \frac{\partial}{\partial r_1} - \frac{3i}{r_1} \right] g_2(E_A - \omega; r_1, r_2) \]  

(68)

together with parameters \(v = Z/\sqrt{-2(\omega_0 + \omega)}\) and \(v' = Z/\sqrt{-2(\omega_0 + \omega')}\), respectively. The integrations over \(r_1\) and \(r_2\) lead to a rather lengthy analytical expression containing various combinations of integrals similar to those in equations (62) and (63). The numerical evaluation yields finally

\[W_{\text{EIE2}}^{\text{EEK}} = \frac{1}{2} \int_0^{\infty} dW_{\text{EIE2}}^{\text{EEK}}(\omega) = 3.6896 \times 10^{-6} (\alpha Z)^8 \text{ au} \]  

\[\simeq 1.227 \times 10^{-6} s^{-1} (Z = 1), \]  

(69)
6. E1M1 two-photon decay

For the mixed E1M1 two-photon transition probability expression (59) should be replaced by

\[
\text{d}W_{\text{E1M1}}^{(2p)} = \sum_{A \rightarrow A'} \left[ \sum_{m,n,m,m'} \left( \frac{\langle A'|V^{E1}(\omega)\rangle N(N|V^{M1}(\omega')|A)}{E_N - E_A + \omega} \right)^2 + \frac{\langle A'|V^{M1}(\omega')|N(N|V^{E1}(\omega)|A)}{E_N - E_A + \omega'} \right]^2 d\omega.
\]

(70)

Here \(V^{E1}(\omega)\) is the spherical tensor of rank 1 with the spherical components \(Y^1_{M}\), \(V^{M1}(\omega)\) is the magnetic photon includes total angular momentum and the spin operator (spherical tensors of rank 1) of the electron, respectively. This expression corresponds to the nonrelativistic ‘length’ form for describing the emission of the electron photons. Since the potential for the magnetic photon includes total angular momentum and spin operator, coupled wavefunction calculations with the set of quantum numbers \(N = (nls\ell m)\) should be used, i.e.

\[
\phi_{nljm} = \sum_{m,m} c^{\ell m}_{lm,m} \phi_{nljm}(r) \chi_{lm,m},
\]

where \(\phi_{nljm}(r)\) is the solution of the radial Schrödinger equation and \(\chi_{lm,m}\) is the spin function. The magnetic potentials in equation (70) do not depend on radial variables. Thus, only the intermediate state with \(nl = nA\) or \(nl = nA'\) will contribute to the probability in equation (70). After performing angular integrations and summations over all projections one arrives at the expressions

\[
\text{d}W_{\text{E1M1}}^{(2p)}(\omega) = \frac{2\pi}{\alpha_s^2} \left( \frac{2}{3} \right)^{12} \omega\omega^3 d\omega.
\]

(72)

As the final result we obtain

\[
W_{\text{E1M1}}^{2p} = \frac{2^5}{\pi} \left( \frac{2}{3} \right)^{12} \frac{243}{655360} (\alpha Z)^8 \text{au} = \frac{1}{\pi} \frac{1}{10935} (\alpha Z)^8 \text{au} = 9.6769 \times 10^{-6} \text{s}^{-1} (Z = 1).
\]

(74)

Again the Z-dependence of the \(W_{\text{E1M1}}^{2p}\) transition probability is indicated. Comparison with the result of a fully relativistic calculation now reveals a discrepancy of about 0.1%.

7. E1E2 and E1M1 transition probabilities for the 2p hydrogenic state expressed through photon momentum and polarization

In this section we are going to derive expressions which allow for the analysis of the dependence of the directions and polarization degrees of freedom of the emitted photons. For this purpose we turn back to the generic S-matrix formulation employing the set of quantum numbers defined by the polarization vector \(e\) and wave vector \(k\). Relativistic units are used throughout this section.

The S-matrix element of the two-photon decay process \(A \rightarrow A' + 2\gamma\) is represented by

\[
S_{AA'}^{(2\gamma)} = (-i)^2 e^2 \int \text{d}x_1 \text{d}x_2 (\hat{\psi}_{A}(x_1)\gamma^{\mu}A^{\alpha\beta}_A(x_1)S(x_1, x_2)\gamma^\nu A^{\alpha\beta}_A(x_2)),
\]

(75)

where \(x_1 = (r_1, t_1)\) and \(x_2 = (r_2, t_2)\) are 4-vectors. Also

\[
S(x_1, x_2) = \frac{1}{2\pi i} \int_{-\infty}^{\infty} \text{d}\omega_1 \text{e}^{i\omega(t_1 - t_2)} \sum_n \psi_n(x_1)\bar{\psi}_n(x_2)
\]

(76)

is the electron propagator where the sum runs over the Dirac spectrum for the electron in the field of the nucleus, \(\psi_n(x)\) is the electron Dirac wavefunction, \(E_n\) is the electron energy,

\[
A^{\mu\nu}_n(x) = \sqrt{\frac{2\pi}{\alpha_\gamma}} e^{i\omega_n} \text{e}^{i(kr_n - \omega t)}
\]

(77)

is the wavefunction of the photon characterized by the momentum \(k\) and polarization vector \(e^{\mu}_n(\mu, \lambda = 1, 2, 3, 4, x \equiv (r, t))\). For the real transverse photons instead of equation (77) we use

\[
A(x) = \sqrt{\frac{2\pi}{\alpha_\gamma}} \text{e}^{i(kr_n - \omega t)} \equiv \sqrt{\frac{2\pi}{\alpha_\gamma}} A_{e,k}(r) \text{e}^{-i\omega t}.
\]

(78)

Inserting equations (76)–(78) in equation (75), integrating over time and frequency variables and introducing the amplitude \(U_{AA}\) as

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

(79)

we obtain

\[
U_{AA'}^{(2\gamma)} = \frac{2\pi e^2}{\sqrt{\omega_1 \omega_2}} \sum_n \frac{(\alpha e_{nA})\gamma_{\mu}(\alpha e_{nA'})\gamma_{\nu}}{E_n - E_A^{\mu\nu}},
\]

(80)

where \(e\) is the electron charge.

Taking into account photon permutation symmetry we define the transition probability as

\[
\text{d}W_{AA'} = 2\pi \delta(E_A - E_A' - \omega - \omega') \times |U_{AA'}^{(2\gamma)} + U_{AA'}^{(2\gamma)}|^2 d\omega d\omega' (2\pi)^3 (2\pi)^3.
\]

(81)
Taking $dk = \omega^2 \, d\omega$ and integrating over $\omega$ yields
\[
dW^{(2)}_{AA}(\omega', n_k, n_{k'}, e, e') = e^{i\omega'(E_A - E_A' - \omega')/(2\pi)^3} \times \sum_{m_{A},m'_{A}} \frac{1}{m_{A} + 1} \sum_{n} \sum_{A} \frac{(\alpha_{e}^{A}_{e'})_{A} (\alpha_{e}^{A}_{e'})_{A'} E_{n} - E_{A} + \omega'}{E_{n} - E_{A} + \omega'} \\
+ \sum_{n} \frac{(\alpha_{e}^{A}_{e'})_{A} (\alpha_{e}^{A}_{e'})_{A'} E_{n} - E_{A} + \omega'}{E_{n} - E_{A} + \omega'} \, d n_k \, d n_{k'} \, d \omega'. 
\tag{82}
\]
Here the summation over $n$ abbreviates the summation over the whole set of quantum numbers $n_{jl} \ell_{m}$ of intermediate states. 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 (82) are also included.

In the Pauli approximation (see equation (8)) the (82) expression can be rewritten as
\[
dW^{(2)}_{AA'} = e^{i\omega'(E_A - E_{A'} - \omega')/(2\pi)^3} \times \sum_{m_{A},m'_{A}} \frac{1}{m_{A} + 1} \sum_{n} \sum_{A} \frac{U_{A n}^{P} (e, k) U_{A'n}^{P} (e', k')}{E_{n} - E_{A} + \omega'} \\
+ \sum_{n} \frac{U_{A n}^{P} (e', k') U_{A'n}^{P} (e, k)}{E_{n} - E_{A} + \omega'} \, d n_k \, d n_{k'} \, d \omega'. 
\tag{83}
\]

where $U_{A n}^{P} (e, k)$ is defined by equation (8).

Within the Pauli approximation we have to take into account the two terms of the exponent expansion in the expression for the emission operator (in relativistic units)
\[
A^{P} (e, k) = \langle (e' \hat{p}) + i(e'[k \times \hat{s}]) \rangle e^{-i k r} \\
\approx i[\hat{H}, e' \hat{r}] + \frac{1}{2} [\hat{H}, (e' \hat{r}) k r] \\
+ \frac{1}{2} (e'[k \times ((r \times \hat{p}) + 2\hat{s})]), \\
\langle A^{P} (e, k) \rangle_{A A'} = U_{A n}^{P} (e, k). 
\tag{84}
\]

The first term in this expression corresponds to the electric dipole moment of electron, the second one is the electric quadrupole moment and the last term in equation (84) represents the magnetic dipole moment of the electron. For the beginning we evaluate the two-photon E12 decay rate. The probability of this process can be written as
\[
dW^{(E12)}_{AA} (\omega') = e^{i\omega'(E_A - E_{A'} - \omega')/(2\pi)^3} \times \sum_{m_{A},m'_{A}} \frac{1}{m_{A} + 1} \sum_{n} \sum_{A} \frac{U_{A n}^{P(E1)} (e, k) U_{A'n}^{P(E2)} (e', k')}{E_{n} - E_{A} + \omega'} \\
+ \sum_{n} \frac{U_{A n}^{P(E1)} (e', k') U_{A'n}^{P(E2)} (e, k)}{E_{n} - E_{A} + \omega'} \, d n_k \, d n_{k'} \, d \omega'. 
\tag{85}
\]

the notations $U_{A n}^{P(E1)}$ and $U_{A n}^{P(E2)}$ for the dipole and quadrupole photons are used in accordance with decomposition (84). The Hamiltonian $\hat{H}$ in equation (84) acts on its eigenfunctions and, therefore, we can rewrite expression (85) in the form
\[
dW^{(E12)}_{AA} (\omega') = e^{i\omega'(E_A - E_{A'} - \omega')/(2\pi)^3} \times \sum_{m_{A},m'_{A}} \frac{1}{m_{A} + 1} \sum_{n} \frac{U_{A n}^{P(E1)} (e, k) U_{A'n}^{P(E2)} (e', k')}{E_{n} - E_{A} + \omega'} \\
+ \sum_{n} \frac{U_{A n}^{P(E1)} (e', k') U_{A'n}^{P(E2)} (e, k)}{E_{n} - E_{A} + \omega'} \, d n_k \, d n_{k'} \, d \omega'. 
\tag{86}
\]

where the relation $\omega = E_A - E_{A'} - \omega'$ holds.

For the summation over polarizations we use again equation (12) and for integrating over the directions of the emitted photons we employ the formulae
\[
\int d n_{n1} = \int d n_{n1} n_{n1} = 0, \quad \int d n_{n1} n_{n1} = \frac{4\pi}{3} \delta_{n1}, \\
\int d n_{n1} n_{n1} = \frac{4\pi}{15} \left( \delta_{n1} + \delta_{n2} + \delta_{n3} \right). 
\tag{87}
\]

The formula
\[
\sum_{e' e} \left| \langle e e' \rangle \right|^2 = 1 + [n_k \times n_{k'}]^2 
\tag{88}
\]

is also useful for calculations. We should stress that in our paper [14] an unfortunate misprint does exist: equation (51) should contain a vector product.

For the evaluation of the quadrupole matrix elements in equation (86) it is convenient to make use of the identity
\[
Y_{l_{m1}} (n) Y_{l_{m2}} (n) = \sum_{LM} \sqrt{\frac{(2L+1)(2j_{1}+1)}{4\pi (2L+1)}} C_{LM}^{1,0} C_{LM}^{1,0} Y_{LM} (n). 
\tag{89}
\]

Therefore,
\[
Y_{l_{m1}} (n) Y_{l_{m2}} (n) = \sqrt{\frac{2}{3}} \sqrt{\frac{4\pi}{5}} \sum_{l_{2},p_{2},M} (-1)^{p_{1}p_{2}} C_{LM}^{1,1} (l_{1} l_{2}, p_{1} p_{2}) \times C_{p_{1} l_{1}, p_{2} l_{2}}^{2 M} \, e_{e'} (n_{k}) P_{l_{2}} Y_{LM} (n_{k}), 
\tag{90}
\]

where $M = -M$. In this case the integration over angles can be provided by the standard relations (see [38])
\[
\int_{4\pi} d n_{l_{m1}} (n) Y_{l_{m2}} (n) = \delta_{l_{1} l_{2}} \delta_{m_{1} m_{2}}, 
\tag{91}
\]

\[
\int_{4\pi} d n_{l_{m1}} (n) Y_{l_{m2}} (n) Y_{l_{m3}} (n) = \sqrt{\frac{(2L+1)(2j_{1}+1)}{4\pi (2L+1)}} C_{LM}^{1,0} C_{LM}^{1,0} C_{LM}^{1,0} 
\tag{92}
\]
Finally, integrating equation (86) over angles and summing over all projections of the angular momenta, we receive
\[
dW_{2p|1s}^{(1E1)}(\omega') = e^4 \frac{\omega^3}{(2\pi)^2 S^2 \omega^3} \int d\kappa \int d\kappa' \sum_{\epsilon \epsilon'} |\epsilon \epsilon'|^2
\]
\[
\times \left[ \omega^2 I_1(\omega') + I_2(\omega') \right]^2 + \omega^2 \left[ I_1(\omega) + I_2(\omega') \right]^2 d\omega', \tag{93}
\]
where \( I_1(\omega), I_2(\omega) \) are defined by equations (62), (63). After the summation over polarizations and integrating over photon directions the previous results equations (61) and (64) are recovered.

The next step is the evaluation of E1M1 two-photon transition 2p \( \rightarrow \) 1s + \gamma (M1) + \gamma (E1) with the set of quantum numbers of \( e \) and \( k \). Formula (85) can be cast into the form
\[
dW_{2p|1s}^{(E1)}(\omega') = e^4 \frac{\omega^3}{(2\pi)^2 S^2 \omega^3} \sum_{m \neq m'} \sum_{n \neq n'} \frac{1}{2j_A + 1}
\]
\[
\times \left| U_{nA}^{(P1)}(e, k)U_{nA}^{(P1)}(e', k') \right|^2 E_n - E_{A' + \omega'}
\]
\[
+ \left| U_{A'n}^{(P1)}(e, k)U_{A'n}^{(P1)}(e', k') \right|^2 E_n - E_{A' - \omega'}
\]
\[
+ \left| U_{nA}^{(P1)}(e, k)U_{nA}^{(P1)}(e', k') \right|^2 E_n - E_{A' + \omega'}
\]
\[
\times \frac{d\kappa d\kappa'}{d\omega'}
\]
\[
(94)
\]

and, according to equation (84),
\[
dW_{2p|1s}^{(E1)}(\omega') = e^4 \frac{\omega^3}{(2\pi)^2 S^2 \omega^3} \sum_{m \neq m'} \sum_{n \neq n'} \frac{1}{2j_A + 1}
\]
\[
\times \left| U_{nA}^{(P1)}(e, k)U_{nA}^{(P1)}(e', k') \right|^2 E_n - E_{A' + \omega'}
\]
\[
+ \left| U_{A'n}^{(P1)}(e, k)U_{A'n}^{(P1)}(e', k') \right|^2 E_n - E_{A' - \omega'}
\]
\[
+ \left| U_{nA}^{(P1)}(e, k)U_{nA}^{(P1)}(e', k') \right|^2 E_n - E_{A' + \omega'}
\]
\[
\times \frac{d\kappa d\kappa'}{d\omega'}
\]
\[
(95)
\]

where \( \hat{1} = [r \times \hat{p}] \).

All the matrix elements can be easily evaluated. For the total probability, we arrive again at equations (72)–(74). Thus, in this section we have calculated two-photon transition probabilities, E1E2 and E1M1, for the process of 2p state decay in the hydrogen atom. In contrast to [24], calculations were based on the other set of quantum numbers. Comparison of both calculations serves as an additional check of the results obtained. The analytic results are in good agreement with corresponding relativistic values (discrepancy is not more than 0.1%). Recently the two-photon emission probabilities were evaluated by fully numerical methods in [49]. The corresponding results are in perfect agreement with ours. The method applied in sections 5 and 6 is more traditional and somewhat easier. However, the method applied in this section simplifies the determination of the dependence on directions of the emitted photons in the two-photon transition probability when the external field is present.

8. Two-photon decay of the 2s and 2p hydrogenic states in an external electric field

In this section we evaluate the two-photon 2s-1s transition probability for the hydrogenic atoms in the presence of an external electric field. As in the case of one-photon decay we take into account only the mixing of the 2s and 2p states. Such level mixing leads to additional E1E2 and E1M1 two-photon decays besides the dominant ‘pure’ E1E1 two-photon transition. As it was shown in previous sections the E1E2 and E1M1 two-photon transition probabilities are about \((\alpha Z)^2\) times smaller than E1E1 transition probability. However, a consideration must be given to the rapidly increasing accuracy of spectroscopic experiments. Therefore, E1E2 and E1M1 two-photon transition rates should be taken into account as a correction to E1E1 decay. Moreover, we will show that in the presence of the external electric field, terms that are linear in the field will add to E1E1 transition probability; these are the interference terms. Most, if not all, spectroscopical experiments (see most accurate experiments [4, 5]) are performed in an external electric field, so analysis of two-photon decay transitions in an external electric field is indeed required.

In order to evaluate the two-photon \( \bar{2}s \rightarrow 1s + 2\gamma \) transition probability in an external electric field we should turn to equation (83) and use the decomposition (84). The mixing of the 2s and 2p states is described by equation (15). According to equation (19), the two-photon transition probability in an external weak electric field can be introduced in the form
\[
dW^{(2s|1s)}(\omega', \kappa, \kappa', e, e') = e^4 \frac{\omega^3}{(2\pi)^2 S^2 \omega^3} \sum_{\mu \mu'} \sum_{\mu'' \mu'''} \frac{1}{2j_A + 1}
\]
\[
\times \left| \sum_n \left( S_{\mu | \mu'} | A^p(e, k) \rangle \langle n | A^p(e', k') \right| 2s_{\mu''} \right|^2 E_n - E_{A' + \omega'}
\]
\[
- \sum_n \left( S_{\mu | \mu'} | A^p(e, k) \rangle \langle n | A^p(e', k') \right| 2s_{\mu''} \right|^2 E_n - E_{A' - \omega'}
\]
\[
\times \frac{d\kappa d\kappa'}{d\omega'}
\]
\[
(96)
\]

where \( A^p(e, k) \) is defined by equation (84).

The decomposition (84) of the \( A^p(e, k) \) operator shows that the first and third terms in equation (96) correspond to the E1E1 two-photon decay rate of the 2s electron level. Other terms in equation (96) represent the admixed E1E2 and E1M1 amplitudes of the 2p state two-photon decay probability. Application of the expansion (84) to the second term in equation (96) leads to the expression
\[
\sum_n \frac{\langle 1s\mu | A^p (e, k) | n \rangle \langle n | A^p (e', k') | 2p\mu \rangle}{E_n - E_A + \omega'} = -i\omega \sum_n \frac{\langle 1s\mu | e \bar{r} \rangle | n \rangle \langle n | | e' \bar{r} \rangle (n_k r) | 2p\mu \rangle}{E_n - E_A + \omega'} + \omega \sum_n \frac{\langle 1s\mu | e \bar{r} \rangle | n \rangle \langle n | | e' \bar{r} \rangle (n_k r) | 2p\mu \rangle}{E_n - E_A + \omega'} - i\omega \sum_n \frac{\langle 1s\mu | 1/2 (| e \times n_k (\bar{r} + \bar{2s}) \rangle n \rangle \langle n | | e' \bar{r} \rangle | 2p\mu \rangle}{E_n - E_A + \omega'} + \omega \sum_n \frac{\langle 1s\mu | 1/2 (| e \times n_k (\bar{r} + \bar{2s}) \rangle n \rangle \langle n | | e' \bar{r} \rangle | 2p\mu \rangle}{E_n - E_A + \omega'}
\]
\]

(97)

In order to perform the summation over intermediate states in this expression we employ the Coulomb Green function method. We should note that in terms involving a magnetic dipole photon the application of the Coulomb Green function is not necessary due to the orthogonality of the radial functions.

Summing over all angular momenta projections in expression (96) we obtain

\[
dW_{\pi s}^{(2p)} (\omega) = e^2 \frac{\alpha Z}{2(2\pi)^3} \left[ \frac{2}{9} g_\omega \omega' |(e\bar{r})| \left( I_1^{2s1s}(\omega) + I_1^{2p1s}(\omega) \right)^2 \right]
\]

+ \omega g_\omega \omega' \left[ \frac{2}{3} \frac{\sqrt{\beta}}{\Delta^2} \left( I_1^{2s1s}(\omega) + I_1^{2p1s}(\omega) \right) \right]

\times \omega_1^{2p1s}(\omega) (eDnk) + \omega I_1^{2p1s}(\omega) (eDnk)

+ \omega g_\omega \omega' \left[ \frac{2}{3} \frac{\sqrt{\beta}}{\Delta^2} \left( I_1^{2s1s}(\omega) + I_1^{2p1s}(\omega) \right) \right]

\times \omega \left( \omega' (eD \times [e' \times n_k]) \right) + \omega' \left( \omega' (eD \times [e \times n_k]) \right) \right] (e\bar{r})^*

+ \omega g_\omega \omega' \left[ \frac{2}{3} \frac{\sqrt{\beta}}{\Delta^2} \left( I_1^{2s1s}(\omega) + I_1^{2p1s}(\omega) \right) \right]

\times \omega \left( \omega' (eD \times [e' \times n_k]) \right) + \omega' \left( \omega' (eD \times [e \times n_k]) \right) \right] (e\bar{r})^*

+ \omega g_\omega \omega' \left[ \frac{2}{3} \frac{\sqrt{\beta}}{\Delta^2} \left( I_1^{2s1s}(\omega) + I_1^{2p1s}(\omega) \right) \right]

\times \omega \left( \omega' (eD \times [e' \times n_k]) \right) + \omega' \left( \omega' (eD \times [e \times n_k]) \right) \right] (e\bar{r})^*

+ \omega g_\omega \omega' \left[ \frac{2}{3} \frac{\sqrt{\beta}}{\Delta^2} \left( I_1^{2s1s}(\omega) + I_1^{2p1s}(\omega) \right) \right]

\times \omega \left( \omega' (eD \times [e' \times n_k]) \right) + \omega' \left( \omega' (eD \times [e \times n_k]) \right) \right] (e\bar{r})^*

+ \omega g_\omega \omega' \left[ \frac{2}{3} \frac{\sqrt{\beta}}{\Delta^2} \left( I_1^{2s1s}(\omega) + I_1^{2p1s}(\omega) \right) \right]

\times \omega \left( \omega' (eD \times [e' \times n_k]) \right) + \omega' \left( \omega' (eD \times [e \times n_k]) \right) \right] (e\bar{r})^*

+ \omega g_\omega \omega' \left[ \frac{2}{3} \frac{\sqrt{\beta}}{\Delta^2} \left( I_1^{2s1s}(\omega) + I_1^{2p1s}(\omega) \right) \right]

\times \omega \left( \omega' (eD \times [e' \times n_k]) \right) + \omega' \left( \omega' (eD \times [e \times n_k]) \right) \right] (e\bar{r})^*

\right] \times d\mu d\nu d\omega'.

(98)

where \( I_1^{2s1s}(\omega) \) is defined by equation (55) and equation (56) for the 2s-1s transition, and \( I_1^{2p1s}(\omega), I_2^{2p1s}(\omega) \) are defined by equations (62), (63), correspondingly.

The summation over polarizations is provided by equations (12) and (88). The radial integration can be performed analytically as well. Finally, the integration over \( \omega' \) is carried out with MATHEMATICA code. The result is

\[
dW_{\pi s}^{(2p)}(\omega) = \frac{0.00131822 (\alpha Z)^6 - 0.000230135 \epsilon \Gamma_{2p} \Delta^2 |D_{nk}|}{\pi^3} \times (|D_{nk}| + |D_{nk}|) (1 + (n_k n_k))(\alpha Z)^7 + 0.00175961 \Delta^2 (\alpha Z)^8.
\]

(99)

The first term in this expression is the differential E1E1 2s-1s transition probability. The second and third terms represent interference terms for the mixed 2s and 2p two-photon transition probabilities (the second term corresponds to the E1E1-E1E2 interference and the third one represents E1E1-E1M1 interference). The last term is related to the sum of the E1E2 and E1M1 two-photon probabilities.

Rewriting equation (99) in a form similar to equation (21) yields

\[
dW_{\pi s}^{(2p)}(\omega) = \frac{0.000230135 (\alpha Z)^7 |e| \Gamma_{2p}}{\omega_0 \pi^3} \Delta^2.
\]

\[
\beta_1(D) = \frac{0.000230135 (\alpha Z)^7 |e| \Gamma_{2p}}{\omega_0 \pi^3} \Delta^2.
\]

The maximum value for \( \beta_1 \) (or \( \beta_2 \)) is achieved at the field strength

\[
D_{\text{max}} = \frac{W_{\pi s}^{(2p)} \Delta}{|e|} \approx \pm 0.000018 \text{au} \approx \pm 57 \text{ kV cm}^{-1},
\]

where the (−) and (+) signs in equation (103) correspond to the H and H\( \text{\textasciitilde} \) atoms, respectively.

Then the corresponding maximum value of the transition rate \( dW_{\pi s}^{(2p)}(\omega) \) is obtained via

\[
\frac{dW_{\pi s}^{(2p)}}{d\omega} = \frac{W_0 (D_{\text{max}})}{1 \pm 0.00024397 |n_k n_k + n_k n_k|} \times (1 + (n_k n_k))(\epsilon_0 000036 14|n_k n_k + n_k n_k|)
\]

\[\times (1 + (n_k n_k)).
\]

(103)

Integration over the directions of the emitted photons \( n_k \) and \( n_k \) leads to the value (57) for the E1E1 two-photon decay rate of the 2s-state, because the interference terms give a zero result (see equation (87)). But for the differential transition probability (100) the interference terms clearly demonstrate the linear dependence on the external electric field \( D \). Thus, the total two-photon \( W_{\pi s}^{(2p)} \) transition probability integrated over photon directions is

\[
W_{\pi s}^{(2p)}(D_{\text{max}}) = W_0 (D_{\text{max}}) = \frac{W_{\pi s}^{(2p)} \epsilon_0 000036 14|D_{\text{max}}|}{\Delta^2} \approx 3.98116 \times 10^{-16} \text{ au} \approx 16.4585 \text{ s}^{-1},
\]

(104)

i.e. twice as large as the zero field value (53).
In principle, the dependence on the external electric field in the transition probability $W^{(2\gamma)}_{2p\,1s}\ (104)$ can be considered as a correction which does not vanish after integration over the photons’ emission directions. If we return to the radiative correction considered in [12], then it is easy to see that the radiative correction (equation (36) in [12])

$$
\delta \Gamma_{2\gamma}/\Gamma_{2\gamma} = 2.020536\frac{\sigma(Z)^2}{(\alpha Z)^2} \ln\left[\frac{(\alpha Z)^2}{(\alpha Z)^2 - 2}\right] = -2.4594 \times 10^{-6}
$$

corresponds to the magnitude of the field $|d\varepsilon| \approx D_{\max}\sqrt{\Delta \Gamma_{2\gamma}/\Gamma_{2\gamma}} \approx 2.8 \times 10^{-8} \text{ au} \approx 90 \text{ V cm}^{-1}$. Such fields are often used in spectroscopic experiments; therefore, this effect should also be included in this context.

The linear over field corrections $\beta_1(D)$ and $\beta_2(D)$ in equation (100) reach the magnitude of the radiative correction at the fields of approximately the same order. Unlike the correction discussed earlier in section 2, this is the correction directly to the same process, as the radiative correction [12].

As was mentioned above, the formal T-noninvariance of the factor $nDnk$ in equation (20) and in equation (100) ($nDnk$ are T-odd and T-even vectors, respectively) is compensated for by the dependence on $\Gamma_{2\gamma}$; this is the limitation of T-noninvariance in unstable systems, as predicted by Zeldovich [44].

The relative difference for the decay rates in $H$ and $\bar{H}$ atoms at the maximum value $D_{\max}$ equals

$$
\frac{dW^{(2\gamma)}_{2p\,1s}(H)}{W_0(D_{\max})} = \frac{dW^{(2\gamma)}_{2p\,1s}(\bar{H})}{W_0(D_{\max})} = 2\beta_1(D_{\max})[(1 + (nDnk)(1 + (nDnk)^2)] + 2\beta_2(D_{\max})[(1 + (nDnk)(1 + (nDnk)^2)]
$$

$$
- (nDnk + nDnk)(0.000 280 111 + 0.000 243 97(nDnk)) + 0.000 036 1414 nDnk).
$$

This ratio is close to 0.028% and represents the difference between matter and anti-matter, a tiny effect even at maximum field strength $D_{\max}$.

For completeness the $2p \rightarrow 1s + 2\gamma$ two-photon transition probability should be considered as well. It can be evaluated similarly to $2s \rightarrow 1s + 2\gamma$ two-photon decay rate with the use of the wavefunction $|2p\mu\gamma\rangle = |2p\mu\rangle - \eta \sum \mu (2s\mu\gamma) e D_{\mu}(2p\mu)|2s\mu\rangle$.

In this case the two-photon transition without an external electric field will be provided by the sum of the E1E2 and E1M1 decays, and the interference terms will be the same as in equation (98).

The result can be presented in the form

$$
dW^{(2\gamma)}_{2p\,1s} = \left[ dW^{E1E2}_{2p\,1s} + dW^{E1M1}_{2p\,1s} + \frac{9\epsilon^2 D^2}{\Delta^2} dW^{E1E1}_{2s\,1s} \right]
$$

$$
+ \left[ \frac{0.000 230 135}{\pi^3} \Gamma_2 \frac{(eDnk + eDnk)[(nDnk)^2]}{(1 + (nDnk))^2}\right.\left(\alpha Z)^7 \right.
$$

$$
+ \left. \frac{0.000 034 091}{\pi^3} \Gamma_2 \frac{(eDnk + eDnk)[(nDnk)^2]}{(1 + (nDnk))^2}\right)\times nDnk\,dnk.
$$

$$
dW^{(2\gamma)}_{2p\,1s} = W_0[1 \mp \beta_1(D)(nDnk + nDnk)(1 + (nDnk)^2] + \beta_2(D)(nDnk + nDnk)(1 + (nDnk)^2)]
$$

where $W_0 = W^{E1E2}_{2p\,1s} + W^{E1M1}_{2p\,1s} + 9\epsilon^2 D^2/W^{E1E1}_{2s\,1s}/\Delta^2$ and the functions $\beta_1(D)$, $\beta_2(D)$ are defined again by equation (101).

Then the maximum of the $\beta_1$ (or $\beta_2$) is achieved at

$$
|D_{\max}| = \frac{\Delta}{3|\epsilon|W^{2\gamma}} \approx 7.1 \times 10^{-11} \text{ au} \approx 0.23 \text{ V cm}^{-1}.
$$

The corresponding maximum value of $dW^{(2\gamma)}_{2p\,1s}$ is

$$
dW^{(2\gamma)}_{2p\,1s} = W_0(D_{\max})[1 \mp 0.000 486 13(nDnk + nDnk)]
$$

$$
\times (1 + (nDnk)^2) \mp 0.000 720 147(nDnk + nDnk)
$$

$$
\times (1 + (nDnk)^2)]
$$

After integration over $nDnk$ and $nDnk$ in equation (107) the term quadratic in the external electric field for the correction to the two-photon transition probability $2p\,1s$ still remains

$$
W^{(2\gamma)}_{2p\,1s}(D_{\max}) = W^{E1E2}_{2p\,1s} + W^{E1M1}_{2p\,1s} + \frac{9\epsilon^2 D^2}{\Delta^2} W^{E1E1}_{2s\,1s}
$$

$$
\approx 4.09 \times 10^{-22} \text{ au} \approx 1.69 \times 10^{-3} \text{ s}^{-1}.
$$

Finally, the (+) and (−) signs in equation (110) correspond to the $H$ and $\bar{H}$ atoms, respectively. The relative difference for the decay rates in $H$ and $\bar{H}$ atoms at the maximum value $D_{\max}$

$$
\frac{dW^{(2\gamma)}_{2p\,1s}}{W_0(D_{\max})} = \frac{dW^{(2\gamma)}_{2p\,1s}}{W_0(D_{\max})} = 2\beta_1(D_{\max})(nDnk + nDnk)(1 + (nDnk)^2)
$$

$$
+ 2\beta_2(D_{\max})(nDnk + nDnk)(1 + (nDnk)^2)
$$

$$
= (nDnk + nDnk)(0.011 1629 + 0.009 7226(nDnk)^2 + 0.001 440 29 nDnk).
$$

This ratio turns out to be close to 1%. However, any direct observation of this difference is difficult due to the huge background from the one-photon transition $2p \rightarrow 1s + \gamma$.

### 9. Three-photon decay rate for the $2p$ state of hydrogen-like light atomic systems

In this last section we present the calculation of the E1E1E1 transition probability for the $2p$ hydrogenic state decay. A parametric estimate can be easily obtained in the usual way and is $a(\alpha Z)^8$ au. Therefore, one can expect a numerical result for the E1E1E1 decay rate which is comparable with values obtained for the E1E2 and E1M1 transitions.

The evaluation of the multiphoton transition probabilities in the nonrelativistic (dipole) approximation is well known [17, 28, 37].

The probability of the three-photon emission process is

$$
dW^{(3)}_{\chi\chi\chi} = 2\pi |U_{\chi\chi\chi}|^2 \delta(E_{\chi} + \omega_1 + \omega_2 + \omega_3 - E_A) \frac{dk_1dk_2dk_3}{(2\pi)^9}.
$$

Here $\omega_1$, $\omega_2$, $\omega_3$ are the frequencies (energies) of the emitted photons. The total probability can be obtained from equation (113) by the summation over photon polarizations $e_1, e_2, e_3$. 


and integration over all the photon-emission directions $k_1, k_2, k_3$ and frequencies $\omega_1, \omega_2, \omega_3$. For the summation over polarizations and integration over photon directions it is convenient to use the relations (12), (87), (88).

After averaging over angular momentum projections of the initial state and summing over final ones, the probability of the three-photon emission process results as (in relativistic units)

$$dW_{A'A}(\omega_1, \omega_2, \omega_3) = \frac{1}{2\Lambda + 1} \sum_{q_1, q_2, q_3} (-1)^{\delta(q_1, q_2, q_3)} U_{A'A}^{(3)}(q_1, q_2, q_3).$$

where the expression for the amplitude $U_{A'A}^{(3)}(q_1, q_2, q_3)$ in spherical representation is given by

$$U_{A'A}^{(3)}(q_1, q_2, q_3) = \sum_{s_1, s_2, s_3} \frac{(r_1, q_1)_{s_1}(r_2, q_2)_{s_2}(r_3, q_3)_{s_3}}{(E_{s_1} - E + \omega_1 + \omega_2)(E_{s_2} - E + \omega_1 + \omega_3)(E_{s_3} - E + \omega_2 + \omega_3)}$$

$$+ \sum_{s_1, s_2} \frac{(r_1, q_1)_{s_1}(r_2, q_2)_{s_2}(r_3, q_3)_{s_3}}{(E_{s_1} + \omega_1 + \omega_2)(E_{s_2} - E + \omega_1 + \omega_3)(E_{s_3} - E + \omega_2 + \omega_3)}$$

$$+ \sum_{s_1, s_2, s_3} \frac{(r_1, q_1)_{s_1}(r_2, q_2)_{s_2}(r_3, q_3)_{s_3}}{(E_{s_1} - E + \omega_1 + \omega_3)(E_{s_2} - E + \omega_1 + \omega_2)(E_{s_3} - E + \omega_2 + \omega_3)}$$

$$+ \sum_{s_1, s_2, s_3} \frac{(r_1, q_1)_{s_1}(r_2, q_2)_{s_2}(r_3, q_3)_{s_3}}{(E_{s_1} - E + \omega_1 + \omega_2)(E_{s_2} - E + \omega_1 + \omega_3)(E_{s_3} - E + \omega_2 + \omega_3)} + \sum_{s_1, s_2, s_3} \frac{(r_1, q_1)_{s_1}(r_2, q_2)_{s_2}(r_3, q_3)_{s_3}}{(E_{s_1} - E + \omega_1 + \omega_2 + \omega_3)(E_{s_2} - E + \omega_1 + \omega_3)(E_{s_3} - E + \omega_2 + \omega_3)}.$$

Here the summation over $s_i$ extends over all intermediate Schrödinger states with positive energy, $E_i$ are the Schrödinger energies for an atomic electron. In order to calculate the transition probabilities for the process $2p \rightarrow 3\gamma(E1) + 1s$ in the hydrogen atom the nonrelativistic Coulomb Green function method is employed. Inserting the Green function in the form (45) in (115) and representing the vector component $(r)_q$ like

$$q = \sqrt{\gamma} r_{1q},$$

we can perform the angular integration, which gives

$$U_{A'A}^{(3)}(q_1, q_2, q_3) = \frac{2\Lambda + 1}{2\Lambda + 1} \sum_{l_{m_1}, l_{m_2}} C_{l_{m_1}l_{m_2}}^{l_{l_{m_1}}} C_{l_{m_1}l_{m_1}}^{l_{l_{m_1}}} C_{l_{m_1}l_{m_1}}^{l_{l_{m_1}}}$$

$$\times \{ F_{12}(q_1, q_2, q_3) \left[ C_{l_{m_1}l_{m_1}}^{l_{l_{m_1}}} C_{l_{m_1}l_{m_1}}^{l_{l_{m_1}}} C_{l_{m_1}l_{m_1}}^{l_{l_{m_1}}} \right] + F_{13}(q_1, q_2, q_3) \left[ C_{l_{m_1}l_{m_1}}^{l_{l_{m_1}}} C_{l_{m_1}l_{m_1}}^{l_{l_{m_1}}} C_{l_{m_1}l_{m_1}}^{l_{l_{m_1}}} \right] + C_{l_{m_1}l_{m_1}}^{l_{l_{m_1}}} C_{l_{m_1}l_{m_1}}^{l_{l_{m_1}}} C_{l_{m_1}l_{m_1}}^{l_{l_{m_1}}} + C_{l_{m_1}l_{m_1}}^{l_{l_{m_1}}} C_{l_{m_1}l_{m_1}}^{l_{l_{m_1}}} C_{l_{m_1}l_{m_1}}^{l_{l_{m_1}}} \}.$$
Table 1. Electric (E1) and magnetic (M1) multiphoton transition rates between 2s, 2p and 1s levels are presented for hydrogen-like ions in relativistic units (r.u.) and for hydrogen in units s\(^{-1}\), respectively. Letters \(m\) and \(Z\) denote the electron mass and nuclear charge number.

| Transition (type) | Transition rates |
|-------------------|------------------|
| \(2p \rightarrow 1s\) (E1) | \(3.902 \times 10^{-2} ma(\alpha Z)^4\) r.u. \(6.25 \times 10^8 s^{-1}\) |
| \(2s \rightarrow 1s\) (E1E1) | \(1.317 \times 10^{-3} ma(\alpha Z)^2\) r.u. \(8.229 s^{-1}\) |
| \(2p \rightarrow 1s\) (E1E1E1) | \(2.635 \times 10^{-5} ma(\alpha Z)^8\) r.u. \(6.39 \times 10^{-8} s^{-1}\) |
| \(2s \rightarrow 1s\) (M1) | \(\frac{1}{2\pi} ma(\alpha Z)^3\) r.u. \(2.5 \times 10^{-6} s^{-1}\) |
| \(2p \rightarrow 1s\) (E1M1) | \(2.911 \times 10^{-5} ma(\alpha Z)^8\) r.u. \(9.68 \times 10^{-8} s^{-1}\) |
| \(2p \rightarrow 1s\) (E1E2) | \(1.989 \times 10^{-5} ma(\alpha Z)^3\) r.u. \(6.612 \times 10^{-6} s^{-1}\) |

10. Conclusions

In this paper analytical results for 2s, 2p level decays for the hydrogen-like atomic systems with one-, two- and three-photon emission have been presented. All calculations were performed within Pauli approximation utilizing the Coulomb Green function. The emission processes were also calculated in the presence of an external electric field. For the two-photon decays in the absence of an external electric field the obtained results are in good agreement with those of other calculations.

The two-photon decays E1E2 and E1M1 were evaluated with different sets of quantum numbers (representations) for the emitted photon, namely parity and momentum or polarization vector \(e\) and wave vector \(k\). Moreover, we have employed different forms in combination with different gauges. The results do not differ in magnitude by more than 0.1% from fully relativistic values which were obtained earlier. Recently a paper [49] appeared where, in particular, 2p-1s E1M1 and E1E2 transition rates were evaluated for the H-like ions in the wide range of \(Z\) values. For \(Z = 1\) the results of [49] are in agreement with ours in [13, 14]. This is an important check of the validity of the earlier results.

We have also evaluated the two-photon decay probabilities E1E2 and E1M1 with the set of quantum numbers \(e, k\) to investigate the probability dependence on directions of the photons’ emission. It allowed us to obtain the two-photon emission processes in the presence of the external electric field. In particular, we have demonstrated that interference terms in the E1E1 and E1E2, E1M1 transitions appear, which depend linearly on the external electric field.

The important result of our calculations is the prediction of a characteristic difference in transition probabilities (spectra) between H and He atoms in the presence of an external electric field, caused by the terms linear in the electric field. This effect was not yet discussed in the literature. The observation of this effect would also contribute to the understanding of fundamental symmetries in nature, i.e. the CPT-symmetry: any deviation from this result would provide a hint for CPT-violation from a low-energy physics scenario, i.e. atoms in an external electric field.

We have compared the radiative correction evaluated in [12] with the electric field correction and determined the magnitude of the electric field strength, when both corrections become of the same order.

Finally, we estimated the role, which the three-photon E1E1E1 processes could play in the cosmological recombination.

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