# Two-photon emission in the $3s \rightarrow 1s$ and $3d \rightarrow 1s$ transitions of hydrogenlike atoms

Viorica Florescu
*Faculty of Physics, University of Bucharest, P.O. Box 5211, Bucharest-Măgurele 76900, Romania*
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The results of an exact analytic calculation of the Kramers-Heisenberg matrix elements for the two-photon transitions $3s$-$1s$ and $3d$-$1s$ in hydrogenic atoms are presented. The formulas obtained are used for the study of two-photon emission in the $n=3 \rightarrow n=1$ transition. The numerical results are compared with the experimental data of Bannett and Freund concerning the $K$-shell vacancy filling by two-photon emission in Mo. Our hydrogenic calculation supports the experimental conclusion that in the Mo case the $K^{-1} \rightarrow M^{-1}$ transition is more probable than the $K^{-1} \rightarrow L^{-1}$ transition.

## I. INTRODUCTION

Various two-photon processes have been studied both theoretically and experimentally. Similar equations describe processes like Rayleigh and Raman scattering, two-photon emission from an excited state, and two-photon absorption. The variety of possible situations is far from being completely explored even for isolated atoms or ions.

This paper is concerned with the transition of a $n=3$ excited hydrogenic atom to the ground state by two-photon emission. It was initiated by the recent observation by Bannett and Freund[1] of two-photon emission in Mo following the creation of $K$-shell vacancies. Two peaks have been observed in the experiment, one at 17.1 keV, which corresponds to $K^{-1} \rightarrow L^{-1}$ two-photon transitions, and another one at 19.7 keV, corresponding to transitions from higher shells. The measured ratio of the intensities is about 2 in favor of the 19.7-keV peak. Whereas the $K^{-1} \rightarrow L^{-1}$ spectrum was found in agreement with the theoretical analysis, this was not the case for the transition from higher shells. The analysis of Bannett and Freund has also shown that the $K^{-1} \rightarrow L^{-1}$ transition can be approximately described by the theoretical predictions for hydrogenlike atoms. This fact suggests that the hydrogenic results for the $n=3 \rightarrow n=1$ transition with two-photon emission could be useful to understand the $K^{-1} \rightarrow M^{-1}$ spectrum in Mo. This information was not available when the experiment was analyzed.

From the theoretical point of view the hydrogenic case is unique, since exact calculations for two-photon processes are possible in the nonrelativistic dipole approximation. A variety of results have been obtained in the last 15 years. It is not our intention to review them here (see, however, the list of references in Ref. 2). The $n=3 \leftrightarrow n=1$ transition has been partially investigated (the $1s \rightarrow 3s$ absorption only[3]), but not on the basis of the simple analytic results that we shall establish here.

In Sec. II we present general formulas describing the two-photon spectrum dependence on the photon directions and polarizations. The formulas contain two invariant amplitudes which depend on the photon energies only. Their calculation is described in Sec. III; the final results, given in Eqs. (29) and (30), are rather simple compared with the intricacy of the calculation. In Sec. IV we consider the invariant amplitudes at some particular frequencies. In Sec. V we give some transition rates of experimental interest. Finally, in Sec. VI, we present the numerical results. We compare them with those for the $n=2 \rightarrow n=1$ two-photon transition and we find for the ratio of the transition probabilities, evaluated in the middle of the corresponding spectra, a value of about 6 in favor of the $n=3$ states. This result agrees with the experimental result of Bannett and Freund for Mo.[1]

## II. TWO-PHOTON EMISSION FROM $n=3$ STATES

Two-photon emission in an atomic transition from an initial state $i$ to a final $f$ is characterized by the dimensionless function

$$\gamma_{i,f} \equiv \frac{d^3\Gamma_{i,f}}{d\omega_1\, d\Omega_1\, d\Omega_2} , \tag{1}$$

where $d^3\Gamma_{i,f}$ is the probability-per-unity-of-time interval for the emission of one photon with frequency in the interval $d\omega_1$, and another one with the frequency given by the energy conservation law

$$\hbar\omega_1 + \hbar\omega_2 = E_i - E_f ,$$

the directions of the photons being in the solid-angle elements $d\Omega_1$ and $d\Omega_2$, respectively.

According to quantum electrodynamics the two-photon emission is a second-order process, for which $\gamma_{i,f}$ is given by

$$\gamma_{i,f} = \frac{r_0^2 \omega_1 \omega_2}{8\pi^3 c^2} \,|\mathscr{M}_{i,f}|^2 , \tag{2}$$

where in the nonrelativistic dipole approximation $\mathscr{M}_{i,f}$ is the Kramers-Heisenberg amplitude

$$\mathscr{M}_{i,f} = -\frac{1}{m_e}\big(\langle E_f \,|\, \vec{s}_2^{\,*}\cdot\vec{P}\,G(\Omega_1)\,\vec{s}_1^{\,*}\cdot\vec{P} + \vec{s}_1^{\,*}\cdot\vec{P}\,G(\Omega_2)\,\vec{s}_2^{\,*}\cdot\vec{P} \,|\, E_i\rangle\big) \tag{3}$$

 

with

$$G(\Omega)=\sum_n \frac{|E_n\rangle\langle E_n|}{E_n-\Omega} \tag{4}$$

the Coulomb resolvent operator, $\vec{P}$ the momentum operator, $\vec{s}_1$ and $\vec{s}_2$ the vectors describing the photon polarizations, $r_0$ the classical electron radius, and $m_e$ the electron mass. The parameters $\Omega_1$ and $\Omega_2$, given by

$$\Omega_\alpha=E_i-\hbar\omega_\alpha \quad (\alpha=1,2) \tag{5}$$

contain the dependence on the photon energies.

In this paper we consider the transitions from $3s$ and $3d$ states to the ground state of hydrogen. The method we use goes back to the study of Rayleigh scattering from the $K$ shell of hydrogen.[4] It is based on the use of Schwinger integral representation for the Green's function (4) in momentum space and on the possibility of an analytic evaluation of the momentum integrals in (3). The only integral left finally, coming from the Green's-function integral representation, is absorbed in the definition of the integral representation of some hypergeometric functions. We write the amplitude (3) as

$$\mathscr{M}_{3lm,1s}=-\sum_{j,k}[\Pi_{jk;3lm,1s}(\Omega_1)+\Pi_{kj;3lm,1s}(\Omega_2)]s^*_{1j}s^*_{2k} , \tag{6}$$

where

$$\Pi_{jk;3lm,1s}(\Omega)=\frac{1}{m_e}\langle 1s\,|\,P_kG(\Omega)P_j\,|\,3lm\rangle . \tag{7}$$

It can be shown from rotation invariance arguments that the amplitudes $\Pi$ should have the following form:

$$\Pi_{jk;3s,1s}(\Omega)=a(\Omega)\delta_{jk} , \tag{8}$$

$$\Pi_{jk;32m,1s}(\Omega)=b(\Omega)C_{m,jk} , \tag{9}$$

where $a$ and $b$ are *invariant amplitudes,* and $C_{m,jk}$ are the coefficients of the harmonic polynomial $l=2,m$ [see Eq. (20) below].

In Sec. III we shall derive compact analytic expressions for the invariant amplitudes. Based on (8) and (9), Eq. (6) gives, respectively,

$$\mathscr{M}_{3s,1s}=-(a_1+a_2)\vec{s}^{\,*}_1\cdot\vec{s}^{\,*}_2 , \tag{10}$$

$$\mathscr{M}_{32m,1s}=-(b_1+b_2)\sum_{j,k}C_{m,jk}s^*_{1j}s^*_{2k} , \tag{11}$$

where the convenient notations

$$a_i\equiv a(\Omega_i),\quad b_i\equiv b(\Omega_i),\quad i=1,2 \tag{12}$$

have been adopted. The connection between the different *transition rates* and the amplitudes described here is presented in Sec. V.

## III. ANALYTIC EVALUATION OF THE INVARIANT AMPLITUDES

In Eq. (7) we use the Green's function in momentum space written as[4]

$$G(\vec{p}_2,\vec{p}_1;\Omega)=\frac{m_e}{2\pi^2X}\frac{ie^{i\pi\tau}}{2\sin\pi\tau}\times\int_1^{(0+)}\rho^{-\tau}\frac{d}{d\rho}\left[\frac{1-\rho^2}{\rho}\frac{1}{N^2}\right]d\rho ,$$

with

$$N\equiv(\vec{p}_2-\vec{p}_1)^2+\gamma(p_1^2+X^2)(p_2^2+X^2), \qquad \gamma=(1-\rho)^2/4\rho X^2 , \tag{13}$$

$$X=\sqrt{-2m_e\Omega}\quad(\mathrm{Re}X\geq 0), \qquad \tau=\lambda/X,\quad \lambda=\alpha Zm_ec , \tag{14}$$

and we obtain

$$\Pi_{jk;3lm,1s}(\Omega)=\frac{1}{2\pi^2X}\frac{ie^{i\pi\tau}}{2\sin\pi\tau}\int_1^{(0+)}\rho^{-\tau}\frac{d}{d\rho}\times\left[\frac{1-\rho^2}{\rho}R_{jk;3lm,1s}(X,\lambda;\rho)\right]d\rho , \tag{15}$$

where

$$R_{jk;3lm,1s}(X,\lambda;\rho)\equiv\int\int\frac{u_{100}(\vec{p}_1)p_{1k}p_{2j}u_{3lm}(\vec{p}_2)}{N^2}\times d\vec{p}_1d\vec{p}_2 . \tag{16}$$

The wave functions in momentum space are[5]

$$u_{nlm}(\vec{p})=F_{nl}(p)Y_{lm}(\vec{p}/p) . \tag{17}$$

The functions $F_{nl}(p)$ of interest for our case are given by (A1)–(A3).

In the 3s-1s case one gets easily

$$R_{jk;3s,1s}(X,\lambda;\rho)=R_s(X,\lambda;\rho)\delta_{jk} , \tag{18}$$

where

$$R_s(X,\lambda;\rho)=\frac{1}{12\pi}\int\int\frac{F_{10}(p_1)\vec{p}_1\cdot\vec{p}_2F_{30}(p_2)}{N^2}d\vec{p}_1d\vec{p}_2 . \tag{19}$$

In the 3d-1s case we express the spherical harmonics $Y_{2m}$ as

$$Y_{2m}(\vec{p}/p)=\frac{1}{\sqrt{4\pi}}\sum_{\alpha,\beta}C_{m,\alpha\beta}p_\alpha p_\beta/p^2 , \tag{20}$$

where the coefficients $C_{m,\alpha\beta}$ are complex numbers. Their properties are given in (A4)–(A8).

Owing to the symmetry properties of the integral (16) in the $3d$ case, one gets

$$R_{jk;32m,1s}(X,\lambda;\rho)=R_d(X,\lambda;\rho)C_{m,jk} , \tag{21}$$

where

$$R_d(X,\lambda;\rho)=\frac{1}{30\pi}\int\int\frac{F_{10}(p_1)\vec{p}_1\cdot\vec{p}_2F_{32}(p_2)}{N^2}d\vec{p}_1d\vec{p}_2 . \tag{22}$$

With Eqs. (18), (21), and (15) one gets the structures (8) and (9) for the quantities $\Pi_{jk;3lm,1s}(\Omega)$ and the first expressions of the invariant amplitudes. The function $a$ is

$$a(\Omega)=\frac{1}{2\pi^2 X}\frac{ie^{i\pi\tau}}{2\sin\pi\tau}\times\int_1^{(0+)}\rho^{-\tau}\frac{d}{d\rho}\left[\frac{1-\rho^2}{\rho}R_s(X,\lambda;\rho)\right]d\rho \tag{23}$$

and the amplitude $b$ is given by a similar expression with $R_s\to R_d$.

The integrals $R_s$ and $R_d$ can be expressed with the help of the following integrals:

$$I_{i,j}\equiv\int\int\frac{d\vec{p}_1 d\vec{p}_2}{N_1^i N N_2^j}, \qquad i,j=1,2,3,4$$
$$J_{i,j}\equiv\int\int\frac{d\vec{p}_1 d\vec{p}_2}{N_1^i N^2 N_2^j}, \tag{24}$$

where

$$N_1\equiv p_1^2+\lambda^2,\ N_2\equiv p_2^2+\mu^2,\ \mu=\lambda/3\ . \tag{25}$$

Explicitly, one has

$$R_s=-\frac{4\lambda^5}{27\sqrt{3}\pi^2}[3I_{22}-16\mu^2(I_{23}-\mu^2 I_{24})-3\gamma J_{11}+(16\gamma\mu^2-3\delta_2)J_{12}-3\delta_1 J_{21}+(3\delta_3+16\delta_1\mu^2)J_{22}$$
$$+16\mu^2(\delta_2-\gamma\mu^2)J_{13}-16\mu^2(\delta_3+\delta_1\mu^2)J_{23}-16\mu^4\delta_2 J_{14}+16\delta_3\mu^4 J_{24}]\ ,$$

$$R_d=-\frac{2^6\lambda^7}{3^5 5\pi^2}\left[\frac{2}{15}\right]^{1/2}[I_{23}-\mu^2 I_{24}-\gamma J_{12}-\delta_1 J_{22}+(\gamma\mu^2-\delta_2)J_{13}+(\delta_1\mu^2+\delta_3)J_{23}+\delta_2\mu^2 J_{14}-\delta_3\mu^2 J_{24}]$$

with

$$\delta_1=1+\gamma(X^2-\lambda^2),\ \delta_2=1+\gamma(X^2-\mu^2)\ ,$$
$$\delta_3=\lambda^2+\mu^2-\gamma(X^2-\lambda^2)(X^2-\mu^2)\ .$$

The integrals $I_{ij}$ can be obtained taking as many derivatives as necessary with respect to $\lambda$ and $\mu$ of the integral $I(\lambda,\mu;\rho)$ given by (B1), while the integrals $J_{ij}$ can be obtained in the same way from the integral $J(\lambda,\mu;\rho)$ given by (B2). These two basic integrals $I$ and $J$ have been calculated a long time ago in connection with Rayleigh scattering from the $K$ shell.[4] We shall not reproduce the integrals $I_{ij}$ and $J_{ij}$ here. We have checked their analytic expressions by the requirement that for $\mu=\lambda$ they reduce to integrals previously evaluated in the study of Rayleigh scattering from $n=3$ states.[6]

After long calculations we find the expressions

$$R_s=-\frac{128\pi^2 X^4\lambda^5}{27\sqrt{3}}\frac{\rho^3}{1-\rho^2}\frac{c_0+c_1\rho+c_2\rho^2+c_3\rho^3}{(X+\lambda)^2(X+\mu)^4 d^5}\ , \tag{26}$$

$$R_d=-\frac{1024\pi^2 X^5}{81}\left[\frac{2}{15}\right]^{1/2}\lambda^6\frac{\rho^3}{1-\rho^2}\frac{\tilde{c}_0+\tilde{c}_1\rho+\tilde{c}_2\rho^2+\tilde{c}_3\rho^3}{(X+\lambda)^2(X+\mu)^4 d^5} \tag{27}$$

with

$$c_0=(X+\lambda)^3(X+\mu)^3(-9X^2+22\mu X-9\mu^2),\ \tilde{c}_0=-5(X+\lambda)^3(X+\mu)^3,$$
$$c_1=(X+\lambda)^2(X-\lambda)(X-\mu)(21X^2+2X\mu+21\mu^2),\ \tilde{c}_1=5(X+\lambda)^2(X+\mu)^2(X-\lambda)(X-\mu)\ ,$$
$$c_2=-5(X+\lambda)(X+\mu)(X-\lambda)^2(3X^4+10\mu^2X^2+3\mu^4),\ \tilde{c}_2=10\mu X(X+\lambda)(X+\mu)(X-\lambda)^2\ ,$$
$$c_3=(X-\lambda)^3(X-\mu)(3X^4+10\mu^2X^2+3\mu^4),\ \tilde{c}_3=-2\mu X(X-\lambda)^3(X-\mu)\ ,$$

and

$$d=(X+\lambda)(X+\mu)-\rho(X-\lambda)(X-\mu)\ .$$

When the results (26) and (27) are introduced in the expression (23) of the invariant amplitudes, the integrals over $\rho$ lead to hypergeometric Gauss functions. Thus, we get

$$a(\Omega)=384\sqrt{3}\frac{\tau^5}{(1+\tau)^6(3+\tau)^6}[(1+\tau)^2(27-22\tau+3\tau^2)F(2)-6(1-\tau^2)(9-\tau^2)F(3)+(1-\tau)^2(27+22\tau+3\tau^2)F(4)]\ ,$$

$$b(\Omega)=3072\left[\frac{6}{5}\right]^{1/2}\frac{\tau^6}{(1+\tau)^6(3+\tau)^4}[(1+\tau)^2F(2)-(1-\tau)^2F(4)]$$

with the notation

$$F(j)\equiv\frac{1}{j-\tau}\,{}_2F_1(j-\tau,6,j-\tau+1;\zeta)\ .$$

The variable $\zeta$ of the hypergeometric functions is

$$\zeta=\frac{(1-\tau)(3-\tau)}{(1+\tau)(3+\tau)}\ . \tag{28}$$

We have found it convenient to express the results in terms of only $F(3)$, by the recurrence relation[7,8]

$$F(j)=\frac{1}{j-\tau}[-(5-j+\tau)\zeta F(j+1)+(1-\zeta)^{-5}]\ ,$$

and then use the well-known relation[9]

$${}_2F_1(a,b,c;z)=(1-z)^{c-a-b}\,{}_2F_1(c-a,c-b,c;z)\ .$$

We obtain thus

$$a(\Omega)=\frac{3\sqrt{3}}{64(4-\tau^2)(9-\tau^2)}\times[81-68\tau^2+11\tau^4-5(1-\tau)(27-7\tau^2)\times{}_2F_1(1,-2-\tau,4-\tau;\zeta)]\ , \tag{29}$$

$$b(\Omega)=\frac{3\sqrt{3}\tau^2}{8\sqrt{10}(4-\tau^2)(9-\tau^2)}\times[7-\tau^2-(1-\tau)\,{}_2F_1(1,-2-\tau,4-\tau;\zeta)]\ . \tag{30}$$

Equations (10), (11), (29), and (30) contain our final analytic results. The parameter $\tau$ is defined in Eq. (3) and contains the dependence on $\Omega$, with $\Omega_1$ and $\Omega_2$ given by Eq. (5).

We mention that on the basis of Eqs. (29) and (30) we can also study other second-order processes connecting the $n=1$ and 3 states: two-photon absorption, Raman, and anti-Stokes scattering. All we have to do is to change the meaning of $\Omega_1$ and $\Omega_2$ (and, consequently, of $\tau_1$ and $\tau_2$) and then to evaluate the appropriate rates and cross sections. This task will be carried out in a subsequent paper.[10]

## IV. PROPERTIES OF THE AMPLITUDES *a* AND *b*

The invariant amplitudes $a(\Omega)$ and $b(\Omega)$ depend in fact only on $\tau$. Introducing

$$k_\alpha\equiv\frac{\hbar\omega_\alpha}{\lambda^2/2m_e}\quad(\alpha=1,2) \tag{31}$$

i.e., the photon energies measured in $Z^2x$ Rydberg units, one has

$$k_1+k_2=\tfrac{8}{9} \tag{32}$$

and

$$\tau_1=1/(\tfrac{1}{9}+k_1)^{1/2},\quad \tau_2=1/(1-k_1)^{1/2}\ . \tag{33}$$

As $0\le k_1\le\frac{8}{9}$ the parameter $\tau_1$ decreases monotonically from 3 to 1, while $\tau_2$ increases from 1 to 3. The amplitudes $a$ and $b$ take real values. The sums $a_1+a_2$ and $b_1+b_2$ determine in fact the amplitudes of the transitions, according to Eqs. (10) and (11). These sums are both symmetric with respect to the middle of the spectrum which is located at $k_1=\frac{4}{9}$.

For $\tau=3$ the apparent singularity in the expressions (29) and (30) of $a$ and $b$ can be removed. A simple calculation yields

$$a\,|_{\tau=3}=\frac{33\sqrt{3}}{64},\quad b\,|_{\tau=3}=-\frac{21\sqrt{6}}{64\sqrt{5}}\ .$$

For $\tau=1$ we get the simple results

$$a\,|_{\tau=1}=\frac{3\sqrt{3}}{64},\quad b\,|_{\tau=1}=\frac{3\sqrt{6}}{64\sqrt{5}}\ .$$

Consequently,

$$a_1+a_2\,|_{k_1=0}=\frac{9\sqrt{3}}{16}\simeq0.974\,28\ , \tag{34}$$

$$b_1+b_2\,|_{k_1=0}=-\frac{9\sqrt{6}}{32\sqrt{5}}\simeq-0.308\,09\ . \tag{35}$$

For $\tau=2$ the amplitudes $a$ and $b$ become infinite. At $k_1=\frac{5}{36}$ the parameter $\tau_2$ equals 2 and, consequently, $a_1$ becomes infinite, while at $k_1=\frac{3}{4}$ the parameter $\tau_2$ equals 2 and $a_2$ becomes infinite. This is due to the pole of the Green's function (4) at $\Omega=E_2$, the only pole that occurs in the process studied here. At $k_1=\frac{5}{36}$ one has $\hbar\omega_1=E_3-E_2$ and $\hbar\omega_2=E_2-E_1$. The role of the energies is changed at $k_1=\frac{3}{4}$. These energies are resonant energies for the hydrogenic atom. If the natural widths of the energy levels are included, the value of the amplitude will be large, but not infinite.

In the vicinity of $\tau_1=2$ one finds the approximate behavior of the invariant amplitudes $a_1$ and $b_1$:

$$a_1\simeq-\frac{2^{10}\sqrt{3}}{3^3\,5^5}\frac{1}{k_1-\frac{5}{36}}\ , \tag{36}$$

$$b_1\simeq\frac{2^{14}\sqrt{6}}{3^3\,5^6\sqrt{5}}\frac{1}{k_1-\frac{5}{36}}\ . \tag{37}$$

These approximate results can also be obtained from the initial formulas (3) and (4) by using the one-pole approximation, i.e., by retaining only the contribution of the $2p$ states in the sum over intermediate states (4); they are the terms which contain the pole of the Green's function relevant for the two-photon emission we study. As a *check* of Eqs. (29) and (30) we have performed this approximate calculation also, and we have rederived the results (36) and (37).

## V. EMISSION RATES

The emission rate (1) corresponds to photons of given energies, directions, and polarizations, and to a well-defined atomic $(3lm)$ initial state. If the different $3d$ states are equally populated, one is interested in the quantity

$$\gamma_{3d,1s} \equiv \frac{1}{5} \sum_m \gamma_{32m,1s} \; . \tag{38}$$

Using Eqs. (2), (11), and (A7) we can sum over the quantum number $m$. We obtain

$$\gamma_{3d,1s} = \frac{r_0^2 \omega_1 \omega_2}{8\pi^3 c^2} \frac{1}{4} | b_1 + b_2 |^2 (3 - 2 | \vec{s}_1 \cdot \vec{s}_2 |^2 + 3 | \vec{s}_1 \cdot \vec{s}_2^{\,*} |^2) \; .$$

Using Eqs. (2) and (10) we rewrite the function $\gamma_{3s,1s}$ as

$$\gamma_{3s,1s} = \frac{\alpha^6 Z^4}{16\pi^2} S(k_1) | \vec{s}_1 \cdot \vec{s}_2 |^2 \; , \tag{39}$$

while

$$\gamma_{3d,1s} = \frac{\alpha^6 Z^4}{16\pi^2} D(k_1)(3 - 2 | \vec{s}_1 \cdot \vec{s}_2 |^2 + 3 | \vec{s}_1 \cdot \vec{s}_2^{\,*} |^2) \tag{40}$$

with

$$S(k_1) \equiv \frac{k_1 k_2}{2\pi} | a_1 + a_2 |^2 \; , \tag{41}$$

$$D(k_1) \equiv \frac{k_1 k_2}{8\pi} | b_1 + b_2 |^2 \; . \tag{42}$$

If the photon polarizations are not observed, one is interested in the functions

$$\tilde{\gamma}_{3l,1s} = \sum_{\vec{s}_1, \vec{s}_2} \gamma_{3l,1s} \quad (l = 0,2) \; , \tag{43}$$

which depend on the photon energies and on the angle $\theta$ between their directions as

$$\tilde{\gamma}_{3s,1s} = \frac{\alpha^6 Z^4}{16\pi^2} (1 + \cos^2\theta) S(k_1) \; , \tag{44}$$

$$\tilde{\gamma}_{3d,1s} = \frac{\alpha^6 Z^4}{16\pi^2} (13 + \cos^2\theta) D(k_1) \; . \tag{45}$$

The functions $S$ and $D$ are symmetric with respect to the middle of the spectrum ($k_1 = \frac{4}{9}$).

A total emission rate can be calculated for each transition

$$A_{3l,1s}^{2E1} = \frac{1}{2} \int_0^{\omega_{\max}} \int_{\vec{k}_1 / k_1} \int_{\vec{k}_2 / k_2} \tilde{\gamma}_{3l,1s} d\Omega_1 d\Omega_2 d\omega_1, \quad l = 0,2 \tag{46}$$

which represents the total probability for deexcitation by two-photon emission. Of course $\hbar\omega_{\max} = E_3 - E_1$. The integrals over the two photon directions give

$$A_{3s,1s}^{2E1} = \frac{1}{3} \alpha^8 Z^6 \frac{m_e c^2}{\hbar} S_t \; , \tag{47}$$

$$A_{3d,1s}^{2E1} = \frac{10}{3} \alpha^8 Z^6 \frac{m_e c^2}{\hbar} D_t \; , \tag{48}$$

where

$$S_t \equiv \int_0^{8/9} S(k_1) dk_1 \tag{49}$$

and $D_t$ is defined in the same way. The functions $S_t$ and $D_t$ are finite only if the finite width of the intermediate $2p$ level is taken into account.

## VI. NUMERICAL RESULTS AND DISCUSSION

The dependence on the photon energies of the emission rates for $3s \rightarrow 1s, 3d \rightarrow 1s$ two-photon transitions are contained in the functions $S$ and $D$ [Eqs. (41) and (42)]; they depend only on the variable $k_1$ given by Eq. (31). We have evaluated the functions $S$ and $D$ using the analytic expressions (29) and (30) for the invariant amplitudes $a$ and $b$, respectively.

Because $1s$-$3s$ absorption was already studied by Quattroppani *et al.*,[3] it is useful to give the connection between the quantity $D_1^3$ studied by these authors and the sum $a_1 + a_2$. Analyzing the expression of $D_1^{d,3}(J_0)$ given in Eq. (3a) of Ref. 3, we derive the equality

$$a_1 + a_2 = -\frac{k_1 + k_2}{3} D_1^3 \; .$$

Agreement was found between our numbers and those given in Ref. 3, obtained by a completely different procedure, which represents a valuable check of our analytic expression, Eq. (29).

In Fig. 1 we represent the dependence of the function $-(a_1 + a_2)$ on the photon energy $k_1$ for half of the spectrum, i.e., for $0 \leq k_1 \leq \frac{4}{9}$, while in Fig. 2 we present the graph of $-(b_1 + b_2)$. In Table I we tabulate the functions $S$ and $D$ for the same energy range. For easy reading, the

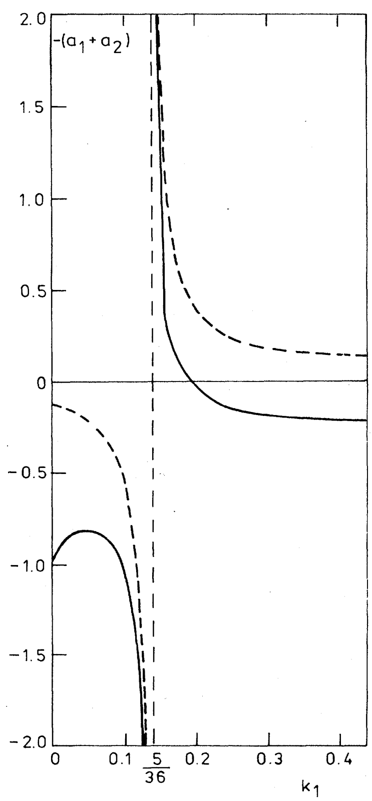


FIG. 1. Energy dependence of the function $-(a_1 + a_2)$. Dashed curves represent the approximate result of Eq. (52).

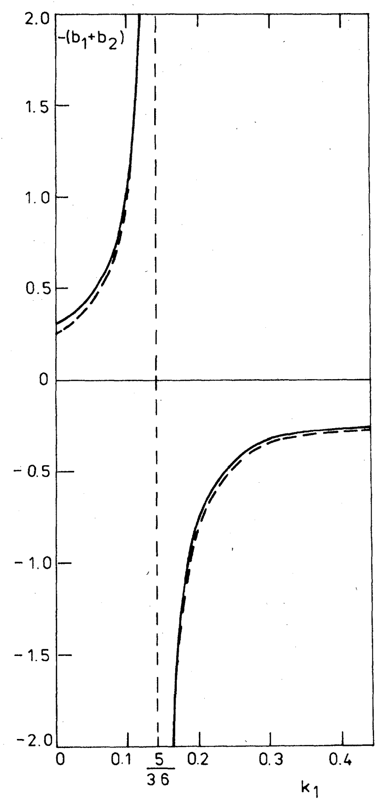


FIG. 2. Energy dependence of the function $-(b_1+b_2)$. Dashed curves represent the approximate result of Eq. (53).

corresponding values of $k_2=\frac{8}{9}-k_1$ are also given. As mentioned in Sec. IV, there is a resonance at $k_1=\frac{5}{36}$ due to the intermediate $2p$ states.

However, the interest in the present calculation relates to the case when the process takes place in a many-electron atom, in which vacancies have been created in the $K$ shell. In this case formulas similar to (3) and (4) can be written,[11] using the wave functions of the many-electron atom. In the independent electron approximation, in which one has adopted a common central self-consistent potential for all atomic electrons, these formulas reduce precisely to Eqs. (3) and (4), for the optically active electron.

Before we comment on the validity of the hydrogenic results for a many-electron atom, we shall use them in order to show the predictions of a model that ignores the electron interaction in an atom with a filled $M$ shell and a vacancy in the $K$ shell. The quantity (1) characterizing the contribution of a filled $M$ shell at the emission of unpolarized photons is

$$\tilde{\gamma}_{3,1}=\tilde{\gamma}_{3s,1s}+5\tilde{\gamma}_{3d,1s} .$$

Using Eqs. (44), (45), (41), and (42), the result at $\theta=\pi/2$ can be written in a manner similar to Eq. (2) as

$$\tilde{\gamma}_{3,1}=\frac{r_0^2\omega_1\omega_2}{8\pi^3c^2}\,|M_{\mathrm{ef}}|^2 \qquad (50)$$

with an "effective" amplitude $M_{\mathrm{ef}}$ given by

TABLE I. The values of the functions $S(k_1)$ and $D(k_1)$ [Eqs. (41) and (42)] for $0\le k_1\le\frac{4}{9}$. Quantities in parentheses denote powers of 10 by which the numbers are to be multiplied.

| $k_1$ | $S$ | $D$ | $k_2=\frac{8}{9}-k_1$ |
|---|---|---|---|
| 0 | 0 | 0 | 0.888 889 |
| 0.000 01 | 1.3426(−6) | 3.3574(−8) | 0.888 879 |
| 0.000 1 | 1.3406(−5) | 3.3598(−7) | 0.888 79 |
| 0.000 5 | 6.6581(−5) | 1.6852(−6) | 0.888 39 |
| 0.001 | 1.3206(−4) | 3.3840(−6) | 0.887 89 |
| 0.002 | 2.5987(−4) | 6.8243(−6) | 0.886 89 |
| 0.002 89 | 3.7014(−4) | 9.9328(−6) | 0.886 |
| 0.005 | 6.2049(−4) | 1.7523(−5) | 0.883 89 |
| 0.01 | 1.1590(−3) | 3.6855(−5) | 0.878 89 |
| 0.015 | 1.6383(−3) | 5.8532(−5) | 0.873 89 |
| 0.02 | 2.0753(−3) | 8.3155(−5) | 0.868 89 |
| 0.025 | 2.4825(−3) | 1.1143(−4) | 0.863 89 |
| 0.03 | 2.8701(−3) | 1.4423(−4) | 0.858 89 |
| 0.035 | 3.2469(−3) | 1.8260(−4) | 0.853 89 |
| 0.045 | 3.9991(−3) | 2.8182(−4) | 0.843 89 |
| 0.05 | 4.3899(−3) | 3.4662(−4) | 0.838 89 |
| 0.075 | 6.8998(−3) | 9.8251(−4) | 0.813 89 |
| 0.09 | 9.5960(−3) | 2.0031(−3) | 0.798 89 |
| 0.1 | 1.2812(−2) | 3.5159(−3) | 0.788 89 |
| 0.11 | 1.9076(−2) | 7.0192(−3) | 0.778 89 |
| 0.115 | 2.4994(−2) | 1.0747(−2) | 0.773 89 |
| 0.12 | 3.5503(−2) | 1.7972(−2) | 0.768 89 |
| 0.125 | 5.7752(−2) | 3.4706(−2) | 0.763 89 |
| 0.13 | 1.2265(−1) | 8.8358(−2) | 0.758 89 |
| 0.132 | 1.9248(−1) | 1.4955(−1) | 0.756 89 |
| 0.134 | 3.5947(−1) | 3.0180(−1) | 0.754 89 |
| 0.136 | 9.6615(−1) | 8.7839(−1) | 0.752 89 |
| 0.137 | 2.1874(0) | 2.0712(0) | 0.751 89 |
| 0.138 | 9.5546(0) | 9.4273(0) | 0.750 89 |
| 0.138 2 | 1.5801(1) | 1.5721(1) | 0.750 69 |
| 0.138 4 | 3.1163(1) | 3.1264(1) | 0.750 49 |
| 0.138 6 | 8.8644(1) | 8.9679(1) | 0.750 29 |
| 0.138 8 | 9.2996(2) | 9.4873(2) | 0.750 09 |
| 0.138 89 | resonance | | 0.75 |
| 0.139 | 5.9112(2) | 6.0815(2) | 0.749 89 |
| 0.139 05 | 2.8086(2) | 2.8955(2) | 0.749 839 |
| 0.139 1 | 1.6326(2) | 1.6867(2) | 0.749 79 |
| 0.139 2 | 7.4884(1) | 7.7692(1) | 0.749 69 |
| 0.139 4 | 2.7555(1) | 2.8831(1) | 0.749 49 |
| 0.139 5 | 1.9211(1) | 2.0186(1) | 0.749 39 |
| 0.139 6 | 1.4137(1) | 1.4918(1) | 0.749 29 |
| 0.14 | 5.7108(0) | 6.1298(0) | 0.748 89 |
| 0.142 | 6.7840(−1) | 7.9419(−1) | 0.746 89 |
| 0.145 | 1.5716(−1) | 2.1066(−1) | 0.743 89 |
| 0.15 | 3.8777(−2) | 6.6194(−2) | 0.738 89 |
| 0.16 | 6.5873(−3) | 1.9739(−2) | 0.728 89 |
| 0.17 | 1.5710(−3) | 9.7574(−3) | 0.718 89 |
| 0.18 | 3.3142(−4) | 5.9851(−3) | 0.708 89 |
| 0.19 | 2.5964(−5) | 4.1391(−3) | 0.698 89 |
| 0.2 | 1.4152(−5) | 3.0896(−3) | 0.688 89 |
| 0.22 | 2.2419(−4) | 1.9886(−3) | 0.668 89 |
| 0.25 | 5.8690(−4) | 1.2695(−3) | 0.638 89 |
| 0.3 | 1.0110(−3) | 8.0657(−4) | 0.588 89 |
| 0.35 | 1.2518(−3) | 6.2571(−4) | 0.538 89 |
| 0.375 | 1.3248(−3) | 5.7877(−4) | 0.513 89 |
| 0.4 | 1.3730(−3) | 5.4953(−4) | 0.488 89 |
| 0.42 | 1.3956(−3) | 5.3626(−4) | 0.468 89 |
| 0.44 | 1.4049(−3) | 5.3086(−4) | 0.448 89 |
| 0.444 44 | 1.4052(−3) | 5.3068(−4) | 0.444 44 |

$$|M_{\rm ef}|^2=|a_1+a_2|^2+\tfrac{65}{4}|b_1+b_2|^2 . \quad (51)$$

In the middle of the spectrum ($k_1=\frac{4}{9}$) the result is $|M_{\rm ef}(\frac{4}{9})|\approx 1.14$. This is to be compared with the contribution of the $L$ shell (at $k_1=\frac{3}{8}$) which, according to Ref. 12, has the value of 0.5522. With these numbers we find at $\theta=\pi/2$

$$\tilde{\gamma}_{3,1}(\tfrac{4}{9})/\tilde{\gamma}_{2,1}(\tfrac{3}{8})\simeq 6 .$$

The experimental results[1] lead to $|M_{\rm ef}|\geq 0.6$ and to a ratio of about 2 in favor of the intensity of the 19.7-keV peak, due to higher than $L$ shells, compared to the 17.1-keV peak, which is due to the $L$ shell. The theoretical predictions for hydrogen are manifestly higher than the data for the real atom. Although they cannot describe quantitatively the experimental results, our predictions support the experimental observation.

The qualitative usefulness of hydrogenic results for two-photon processes in many-electron atoms have been already discussed[13,14] and tested[14] in other special cases. One of the reasons for the semiquantitative agreement should be found in the $Z$ independence of the results, except for the factor of $Z^4$ in the spectrum. Some screening corrections could be possible, leading to a $Z$-dependent ratio $\tilde{\gamma}_{3,1}/\tilde{\gamma}_{2,1}$.

In order to better understand the results, we have separately evaluated the contribution of the $2p$ states—the intermediate states which are responsible for the resonance at $k_1=\frac{5}{36}$. The contribution of the $2p$ states to the invariant amplitudes is given by

$$(a_1+a_2)_{2p}=-\frac{2^{10}\sqrt{3}}{3^3 5^5}\left[\frac{1}{k_1-\frac{5}{36}}+\frac{1}{\frac{3}{4}-k_1}\right] , \quad (52)$$

$$(b_1+b_2)_{2p}=-\frac{2^4}{5}\left[\frac{2}{5}\right]^{1/2}(a_1+a_2)_{2p} . \quad (53)$$

The expressions of $a_1$ and $b_1$ have been already given in Eqs. (36) and (37). In Figs. 1 and 2 the contribution of the $2p$ states is represented by the dashed lines. One notices that the $3d$-$1s$ transition is dominated by the contribution of these states.

We have also calculated total rates [Eqs. (47) and (48)], but only for $Z=1$. The calculation was done with the approximations (36) and (37) for the invariant amplitudes, in which $k_1$ was replaced by $k_1-\frac{1}{2}i\Delta$, with $\Delta=2m\hbar/\lambda^2\tau_{2p}=2^9\alpha^3/3^8$, where $\tau_{2p}$ is the lifetime of the $2p$ states.[5] Therefore our calculation includes the width of the $2p$ level, but neglects the width of the $3s$ or $3d$ levels. In this way we find $A^{2E1}_{3s,1s}\simeq 0.63\times 10^9$/sec, $A^{2E1}_{3d,1s}\simeq 0.65\times 10^8$/sec. The numbers coincide with the total rates for one-photon emission $A^{E1}_{3s,2p}$ and $A^{E1}_{3d,2p}$, respectively, showing that there is practically no change in the lifetime of these states due to the nonresonant two-photon emission.

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## APPENDIX A: DETAILS ON THE WAVE FUNCTIONS

For $n=1$ and 3 the functions $F_{nl}(p)$ in Eq. (17) are[5]

$$F_{10}(p)=4\left[\frac{2}{\pi}\right]^{1/2}\frac{\lambda^{5/2}}{(p^2+\lambda^2)^2} , \quad (A1)$$

$$F_{30}(p)=4\left[\frac{2}{\pi}\right]^{1/2}\frac{\mu^{5/2}(3p^4-10\mu^2p^2+3\mu^4)}{(p^2+\mu^2)^4} , \quad (A2)$$

$$F_{32}(p)=\frac{64}{\sqrt{5\pi}}\frac{\mu^{9/2}p^2}{(p^2+\mu^2)^4} \quad (A3)$$

with $\lambda$ and $\mu$ given by (14) and (25), respectively.

The coefficients $C_{m,\alpha\beta}$ defined by Eq. (20) have the following properties:

$$C_{m,\alpha\beta}=C_{m,\beta\alpha} , \quad (A4)$$

$$\sum_{\alpha}C_{m,\alpha\alpha}=0 , \quad (A5)$$

$$\sum_{\alpha,\beta}C_{m,\alpha\beta}C^*_{m',\alpha\beta}=\tfrac{15}{2}\delta_{mm'} , \quad (A6)$$

$$\sum_{m}C_{m,\alpha\beta}C^*_{m,\gamma\delta}=\tfrac{5}{4}[-2\delta_{\alpha\beta}\delta_{\gamma\delta}+3(\delta_{\alpha\gamma}\delta_{\beta\delta}+\delta_{\alpha\delta}\delta_{\beta\gamma})] , \quad (A7)$$

$$C^*_{m,\alpha\beta}=(-1)^m C_{-m,\alpha\beta} . \quad (A8)$$

## APPENDIX B: MOMENTUM INTEGRALS

We have obtained the integrals $I_{ij}$ of Eq. (24), required by the evaluation of $R_s$ and $R_d$, from the integral $I_{11}$, which is simply

$$I_{11}=8\pi^2X^2I(\lambda,\mu;X^2) ,$$

where $I(\lambda,\mu;X^2)$ is the integral evaluated in Ref. 4. Consequently, one has

$$I_{11}=4\pi^4\ln\frac{(\lambda+\beta X)(\mu+\beta X)}{X^2+\beta X(\lambda+\mu)+\lambda\mu} \quad (B1)$$

with $\beta=(1+\rho)/(1-\rho)$.

In a similar manner we have

$$J_{11}=8\pi^2X^4J(\lambda,\mu;X^2)$$

with the integral $J(\lambda,\mu;X^2)$ given by Eq. (44) of Ref. 4. Explicitly,

$$J_{11}=\frac{2\pi^4X^2}{\alpha^2\beta(1+\beta)}\frac{1}{(X+\lambda)(X+\mu)[X^2+\beta X(\lambda+\mu)+\lambda\mu]} \quad (B2)$$

with $\alpha=(1-\rho)^2/4\rho$. The integrals $J_{ij}$ of Eq. (24) are obtained from $J_{11}$ by taking the adequate derivatives with respect to $\lambda$ and $\mu$. The expressions of $I_{ij}$ and $J_{ij}$, which are rather cumbersome, are not reproduced here.

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