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Two-photon decay of hydrogenic atoms

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The two-photon decay mode of hydrogenic atoms from an arbitrary state (n_1,l_1,m_1) to an arbitrary state (n_2,l_2,m_2) is studied within the framework of nonrelativistic quantum mechanics. In the dipole approximation, these decay rates, which involve infinite summation over intermediate states, are derived exactly via a general second-order matrix element obtained by Kelsey and Macek and an implicit technique introduced by Dalgarno and Lewis. The results are expressed in terms of hypergeometric functions. For transitions $n_1s \rightarrow n_2s$, our results reduce to those of Klarsfeld whose starting point is the Coulomb Green's function. For transitions to the ground state, an alternative expression involving a simple one-dimensional integral is presented. The decay rate of the $2s$ metastable state of atomic hydrogen is calculated as an illustration of the method. The result, $1/\tau=8.2284\ \mathrm{sec}^{-1}$, agrees with Klarsfeld. For transitions of $n_1s \rightarrow 1s$ and $n_1d \rightarrow 1s$ $(n_1 \geq 3)$, the transition rates exhibit interesting and unexpected structures. In particular, "zeros" are found in the two-photon emission spectrum indicating that two-photon emission is not possible at certain frequencies. Physically, these "zeros" are the result of destructive interference between the radiating dipole terms associated with the sum over intermediate states. In addition to the emission spectrum the expected coincidence signal between two detectors monitoring the two photons simultaneously emitted during a two-photon transition is calculated as a function of the angle between the detectors. The angular distribution for the $n_1d \rightarrow 1s$ transitions is shown to be significantly different from the $n_1s \rightarrow 1s$ transitions. Finally, a possible experiment is suggested to test the results presented in this paper.

I. INTRODUCTION

The possibility of a two-photon process, which proceeds via intermediate states, was first pointed out by Mayer[1] in 1931. Breit and Teller[2] applied this theory to the case of the $2s \rightarrow 1s$ transition in atomic hydrogen and found that double photon emission is the most probable radiative decay mode, and is therefore the principal cause of the decay mechanism of the interstellar $2s$ hydrogen atoms. They also found that the mean lifetime τ corresponding to this mode of decay can be bracketed by the relation $6.5 < 1/\tau < 8.7\ \mathrm{sec}^{-1}$. Later, more detailed calculations[3,4] were carried out which involved term-by-term numerical evaluation of the infinite summation over intermediate states in the second-order matrix elements responsible for the decay. In particular, Shapiro and Breit[4] found that the decay rate for the metastable $2s$ state of a hydrogenlike atom of atomic number Z, $1/\tau$, is equal to $8.226Z^6\ \mathrm{sec}^{-1}$, which corresponds to a lifetime of 1.9 msec for the case of He$^+$. However, these conclusions could be modified[5,6] due to the possible existence of a nuclear or electronic dipole moment which would produce a nonzero one-photon decay mode for the metastable hydrogenlike atom. Therefore, a careful study of the properties of this state is useful in the search for new fundamental interactions.

In connection with this interest and in view of experimental success in two-photon-absorption and ionization experiments, a series of theoretical papers[7–20] has appeared on how to perform exactly, within the framework of nonrelativistic quantum mechanics, the infinite sums in the second-order matrix elements responsible for various multiphoton processes. For the decay transition, the numerical result of the two-photon decay rate of metastable hydrogenic atoms, viz., $1/\tau=(8.2283\pm0.0001)Z^6\ \mathrm{sec}^{-1}$, obtained by Klarsfeld[14] is believed to be the most accurate one.[6,19] Recent calculations,[21,22] including all relativistic and retardation effects and all combinations of photon multipoles, give a very small correction in the case of low-Z hydrogenlike atoms. In addition, the two-photon decay rates of the singlet and triplet metastable states of heliumlike ions have also been calculated using variation procedures by Drake, Victor, and Dalgarno.[23]

In a recent paper[24] Kelsey and Macek used the implicit technique[7,8] to obtain a simple reformulation of a closed-form expression for a general second-order matrix element for hydrogen. While equivalent expressions have been derived[13,25,26] employing various representations[27–29] of the Coulomb Green's function, the mathematics involved is quite cumbersome. Although the work of Kelsey and Macek is very important and useful, it has not received enough attention. One of the purposes of this paper is to show that the elegant results of Kelsey and Macek and the powerful implicit technique can be employed to study the two-photon decay mode of a hydrogenlike atom from an arbitrary initial state (n_1,l_1,m_1) to an arbitrary final state (n_2,l_2,m_2). As a result, the two-photon transition rate is expressed in terms of repeated parametric differentiations of hypergeometric functions. The results we have obtained are equivalent to those of Gazeau,[19] but the starting points are quite different. Gazeau used powerful group-theoretical techniques whereas we have used simple algebra. However, as one proceeds to higher n_1, these calculations become impractical. For instance, in the case of the $3s \rightarrow 2s$ transition, there is only one investigation[17] reported so far and it required the evaluation of ten hypergeometric functions. Thus, another purpose of our paper is to derive an alternative expression involving only a simple one-dimensional integral for transitions to the final s state. This method is then applied to study the $n_1 s \rightarrow 1s$ and $n_1 d \rightarrow 1s$ transitions for n_1 up to 6. Atomic units will be used unless otherwise stated.

II. THEORY

The probability per second for the spontaneous two-photon emission of a hydrogenic atom from an arbitrary state (n_1,l_1,m_1) to an arbitrary state (n_2,l_2,m_2) with one photon in the frequency range $d\nu'$ at ν' (with unit polarization vector $\hat{\epsilon}'$ and photon momentum $\vec{k}'$) is,[1,2,30] in the nonrelativistic dipole approximation,

$$A_{n_2l_2m_2,n_1l_1m_1}(\nu')d\nu' = \frac{2^{10}\pi^{b}\nu'^{3}\nu''^{3}}{c^6}\left[\left|\sum_n \left(\frac{\langle n_2,l_2,m_2|\hat{\epsilon}'\cdot\vec{r}|n\rangle\langle n|\hat{\epsilon}''\cdot\vec{r}|n_1,l_1,m_1\rangle}{E_n-E_{n_1}+E_{\nu'}} + \frac{\langle n_2,l_2,m_2|\hat{\epsilon}''\cdot\vec{r}|n\rangle\langle n|\hat{\epsilon}'\cdot\vec{r}|n_1,l_1,m_1\rangle}{E_n-E_{n_1}+E_{\nu''}}\right)\right|^2\right]_{\text{av}} d\nu' , \tag{1}$$

where ν'' is the frequency (with unit polarization vector $\hat{\epsilon}''$ and photon momentum $\vec{k}''$) of the second photon which is, in turn, related to ν' by

$$\nu'+\nu'' = \frac{(E_{n_1}-E_{n_2})}{2\pi} = \left[\frac{1}{n_2^2}-\frac{1}{n_1^2}\right]\Big/ 4\pi . \tag{2}$$

The "av" in Eq. (1) is the average of the relative angle of $\hat{\epsilon}'$ and $\hat{\epsilon}''$ over all orientations if the polarization is not detected. Because of the well-known dipole selection rule, $A(\nu')$ is nonvanishing only for $\Delta l = l_2 - l_1 = 0$ and ± 2. The total transition rate is obtained by integrating the spectral distribution $A(\nu')$ of the two photons over all possible frequencies. Thus,

$$\begin{aligned} A^T_{n_2l_2m_2,n_1l_1m_1} &= \frac{1}{\tau} = \frac{1}{2}\int_0^{(E_{n_2}-E_{n_1})/2\pi} A_{n_2l_2m_2,n_1l_1m_1}(\nu')d\nu' \\ &= \frac{1}{2^5\pi c^6}\left[\frac{1}{n_2^2}-\frac{1}{n_1^2}\right]^7 \int_0^1 x^3(1-x^3)(P^1_{n_2l_2m_2,n_1l_1m_1}+P^2_{n_2l_2m_2,n_1l_1m_1})^2 dx \end{aligned} \tag{3}$$

with

$$P^1_{n_2l_2m_2,n_1l_1m_1} = \sum_n \frac{\langle n_2,l_2,m_2|\hat{\epsilon}'\cdot\vec{r}|n\rangle\langle n|\hat{\epsilon}''\cdot\vec{r}|n_1,l_1,m_1\rangle}{E_n-E_{n_1}+E_{\nu'}} \tag{4}$$

and

$$P^2_{n_2l_2m_2,n_1l_1m_1} = \sum_n \frac{\langle n_2,l_2,m_2|\hat{\epsilon}''\cdot\vec{r}|n\rangle\langle n|\hat{\epsilon}'\cdot\vec{r}|n_1,l_1,m_1\rangle}{E_n-E_{n_1}+E_{\nu''}} . \tag{5}$$

In Eq. (3) we have used a new variable

$$x = 4\pi\nu' \Big/ \left[\frac{1}{n_2^2}-\frac{1}{n_1^2}\right] .$$

The sums over n in Eqs. (1), (4), and (5) run over all hydrogen wave functions, including both continuum and bound states. We now proceed to derive analytic expressions for P with E_ν representing $E_{\nu'}$ or $E_{\nu''}$, respectively.

A. General case: state (n_1,l_1,m_1) to state (n_2,l_2,m_2)

We rewrite Eqs. (4) and (5) as

$$P_{n_2l_2m_2,n_1l_1m_1} = \left[\left[\hat{\epsilon}'\cdot\frac{\partial}{\partial\vec{k}'}\right]\left[\hat{\epsilon}''\cdot\frac{\partial}{\partial\vec{k}''}\right]\sum_n \frac{\langle n_2,l_2,m_2|e^{i\vec{k}'\cdot\vec{r}}|n\rangle\langle n|e^{i\vec{k}''\cdot\vec{r}}|n_1,l_1,m_1\rangle}{E-E_n}\right]_{\vec{k}'=0,\ \vec{k}''=0} , \tag{6}$$

where

$$E=E_{n_1}-E_\nu<0\ . \tag{7}$$

The initial and final bound-state wave functions can be written as

$$\phi_{nlm}=\mathscr{D}(\mu,\vec{a})e^{-\mu r+i\vec{a}\cdot\vec{r}}\Big|_{\mu=1/n,\ \vec{a}=0}\ . \tag{8}$$

Here $\mathscr{D}(\mu,\vec{a})$ is the differential operator which generates the corresponding wave functions when operating on the exponential in Eq. (8) above. Thus

$$P_{n_2l_2m_2,n_1l_1m_1}=\left[\left[\hat{\epsilon}'\cdot\frac{\partial}{\partial\vec{k}'}\right]\left[\hat{\epsilon}''\cdot\frac{\partial}{\partial\vec{k}''}\right]\mathscr{D}_2(\mu_2,\vec{a}_2)\mathscr{D}_1(\mu_1,\vec{a}_1)\mathscr{M}\right]_{\substack{\mu_1=1/n_1,\ \mu_2=1/n_2,\\ \vec{a}_1=\vec{a}_2=0,\\ \vec{k}'_1=\vec{k}''_2=0}}, \tag{9}$$

where we define

$$\mathscr{M}=\sum_n\frac{\langle e^{-\mu_2 r}|e^{i\vec{p}_2\cdot\vec{r}}|n\rangle\langle n|e^{i\vec{p}_1\cdot\vec{r}}|e^{-\mu_1 r}\rangle}{E-E_n} \tag{10}$$

with

$$\vec{p}_1=\vec{k}''+\vec{a}_1 \tag{11}$$

and

$$\vec{p}_2=\vec{k}'-\vec{a}_2\ . \tag{12}$$

In order to evaluate $\mathscr{M}$ which involves an infinite sum over intermediate states, Kelsey and Macek[24] first introduced an auxiliary function

$$x(\vec{p}_1\cdot\vec{r})=\sum_n\frac{\langle\vec{r}|n\rangle\langle n|e^{i\vec{p}_1\cdot\vec{r}}|e^{-\mu_1 r}\rangle}{E-E_n} \tag{13}$$

which in turn is a solution of the inhomogeneous differential equation

$$(H-\epsilon)x(\vec{p}_1\cdot\vec{r})=-e^{i\vec{p}_1\cdot\vec{r}}e^{-\mu_1 r}\ , \tag{14}$$

where H is the nonrelativistic Hamiltonian for hydrogen. Since the inhomogeneous term singles out direction $\vec{p}_1$ in space, Kelsey and Macek wrote the Hamiltonian in parabolic coordinates and found the solution with the series-expansion method. Thus,

$$\begin{aligned}\mathscr{M}&=\langle e^{-\mu_2 r}|e^{i\vec{p}_2\cdot\vec{r}}|x(\vec{p}_1\cdot\vec{r})\rangle\\&=-2^4\pi X\frac{\partial}{\partial\mu_1}\frac{\partial}{\partial\mu_2}\int_0^1 d\rho\frac{\rho^{-\xi}}{D_1D_2-2(E_1E_2-4X^2\vec{p}_1\cdot\vec{p}_2)\rho+F_1F_2\rho^2}\ ,\end{aligned} \tag{15}$$

where

$$X=\sqrt{-2\epsilon}=\left[\frac{1}{n_1^2}+2E_\nu\right]^{1/2},$$

$$D_i=(X+\mu_i)^2+P_i^2\ ,$$

$$E_i=X^2-\mu_i^2-P_i^2\ ,$$

$$F_i=(X-\mu_i)^2+P_i^2\ ,$$

$$\xi=1/X\ .$$

Equation (15) is actually Eq. (25) in Ref. 24 using the following substitution:[27]

$$\int_0^1 d\rho\,\rho^{-\xi}(\cdots)\rightarrow\frac{i}{2\sin\pi\xi}e^{\pi i\xi}\int_C d\rho\,\rho^{-\xi}(\cdots)\ .$$

Defining

$$\beta=(E_1E_2-4X^2\vec{p}_1\cdot\vec{p}_2)/D_1D_2\ ,$$

$$\gamma^2=F_1F_2/D_1D_2\ ,$$

$$u_1=\beta+(\beta^2-\gamma^2)^{1/2}\ ,$$

$$u_2=\beta-(\beta^2-\gamma^2)^{1/2}\ ,$$

Eq. (15) becomes

$$\mathscr{M}=-2^4\pi X\frac{\partial}{\partial\mu_1}\frac{\partial}{\partial\mu_2}\times\left[\frac{1}{D_1D_2(u_1-u_2)}\int_0^1 d\rho\,\rho^{-\xi-1}\times\left[\frac{1}{1-u_1\rho}-\frac{1}{1-u_2\rho}\right]\right]\ . \tag{16}$$

The integral over ρ may be done immediately via[31]

$$ {}_2F_1(a,b;c;x)=\frac{\Gamma(c)}{\Gamma(b)\Gamma(c-b)} \times\int_0^1 dt\, t^{b-1}(1-t)^{c-b-1}(1-tx)^{-a} \,. \qquad (17)$$

We finally obtain

$$\mathscr{M}=2^4\pi X^2\frac{\partial}{\partial\mu_1}\frac{\partial}{\partial\mu_2} \times\left[\frac{1}{D_1D_2(u_1-u_2)}[\,{}_2F_1(1,-\xi;1-\xi'';u_1) -{}_2F_1(1,-\xi;1-\xi;u_2)]\right] . \qquad (18)$$

Thus we have shown that $\mathscr{M}$, its derivatives, and hence $P_{n_2l_2m_2,n_1l_1m_1}$ in Eq. (9) may be expressed in terms of Gaussian hypergeometric functions. Equations (9) and (18) are equivalent to Eqs. (3.4) and (3.10) in Ref. 19.

B. Special case: state (n_1s) to state (n_2s)

For s states ($\vec{a}_1=0$, $\vec{a}_2=0$, $\vec{p}_1=\vec{k}''$, $\vec{p}_2=\vec{k}'$), all expressions in Sec. II A could be further simplified. First, taking into account the rotational symmetry and transversality of the photon, one has[13]

$$\left[\hat{\epsilon}'\cdot\frac{\partial}{\partial\vec{k}'}\right]\left[\hat{\epsilon}''\cdot\frac{\partial}{\partial\vec{k}''}\right] =\hat{\epsilon}'\cdot\hat{\epsilon}''\frac{\partial}{\partial(\vec{k}'\cdot\vec{k}'')}+(\hat{\epsilon}'\cdot\vec{k}')(\hat{\epsilon}''\cdot\vec{k}'')\frac{\partial^2}{\partial(\vec{k}'\cdot\vec{k}'')^2} \,; \qquad (19)$$

here the second term is vanishing in the long-wavelength dipole approximation. Then we carry out the derivative with respect to $(\vec{k}'\cdot\vec{k}'')$ in Eqs. (10) and (15), namely,

$$\left[\frac{\partial}{\partial(\vec{k}'\cdot\vec{k}'')}\int_0^1 d\rho\frac{\rho^{-\xi}}{D_1D_2-2(E_1E_2-4X^2\vec{k}'\cdot\vec{k}'')\rho+F_1F_2\rho}\right]_{\vec{k}'=\vec{k}''=\vec{0}} =-8X^2\frac{1}{D_1^2D_2^2}\int_0^1 d\rho\frac{\rho^{1-\xi}}{(1-\bar{\gamma}\rho)^4} \,, \qquad (20)$$

where

$$D_i=(X+\mu_i)^2=\xi^{-2}(\mu_i\xi+1)^2 \,,$$

$$\tilde{\gamma}=\frac{(X-\mu_1)(X-\mu_2)}{(X+\mu_1)(X+\mu_2)}=\frac{(\mu_1\xi-1)(\mu_2\xi-1)}{(\mu_1\xi+1)(\mu_2\xi+1)} \,.$$

Therefore we obtain

$$P_{n_2s,n_1s}=(\hat{\epsilon}'\cdot\hat{\epsilon}'')[\mathscr{D}_2(\mu_2)\mathscr{D}_1(\mu_1)M_{n_2s,n_1s}]_{\mu_2=1/n_2,\ \mu_1=1/n_1} \,, \qquad (21)$$

where we define M_{n_2s,n_1s} via

$$M_{n_2s,n_1s}=\frac{\partial}{\partial(\vec{k}'\cdot\vec{k}'')}\mathscr{M}$$

$$=2^7\pi\xi^5\frac{\partial}{\partial\mu_1}\frac{\partial}{\partial\mu_2}\left[(\mu_1\xi+1)^{-4}(\mu_2\xi+1)^{-4}\int_0^1 d\rho\,\rho^{1-\xi}(1-\tilde{\gamma}\rho)^{-4}\right] \qquad (22)$$

$$=2^7\pi\xi^5(2-\xi)^{-1}\frac{\partial}{\partial\mu_1}\frac{\partial}{\partial\mu_2}[(\mu_1\xi+1)^{-4}(\mu_2\xi+1)^{-4}{}_2F_1(4,2-\xi;3-\xi;\tilde{\gamma})] \,. \qquad (23)$$

We note that M^K, defined by Klarsfeld in Ref. 13 as

$$M^K=\sum_n\frac{\langle e^{-\mu_2r}/r\,|\,e^{i\vec{p}_2\cdot\vec{r}}\,|\,n\rangle\langle n\,|\,e^{i\vec{p}_1\cdot\vec{r}}\,|\,e^{-\mu_1r}/r\rangle}{E-E_n} \,, \qquad (24)$$

is related to our M_{n_2s,n_1s} [Eq. (11)] via

$$M_{n_2s,n_1s}=\frac{\partial}{\partial\mu_1}\frac{\partial}{\partial\mu_2}M^K \,. \qquad (25)$$

Thus our Eqs. (21) and (22) are exactly the same as Eqs. (3), (4), and (18) in Ref. 13, which were used to calculate the two-photon decay rate reported in Ref. 14. However, the starting point in Klarsfeld's approach is the Coulomb Green's function, not the implicit technique.

C. An alternative expression for state (n_1l_1) to state $(1s)$

If the final state is the ground state, then $A_{n_1l_1,1s}(\nu')$ via

$$A_{1s,n_1l_1}(\nu')d\nu'=\frac{2^{10}\pi^6\nu'^3\nu''^3}{c^6}\frac{1}{2l_1+1}\sum_{m_1}\left[\left|\sum_n\left[\frac{\langle 1s|\hat{\epsilon}'\cdot\vec{\mathrm{r}}|n\rangle\langle n|\hat{\epsilon}''\cdot\vec{\mathrm{r}}|n_1,l_1,m_1\rangle}{E_n-E_{n_1}+E_{\nu'}}+\frac{\langle 1s|\hat{\epsilon}'\cdot\vec{\mathrm{r}}|n\rangle\langle n|\vec{\epsilon}''\cdot\vec{\mathrm{r}}|n_1,l_1,m_1\rangle}{E_n-E_{n_1}+E_{\nu''}}\right]\right|^2\right]_{\mathrm{av}}d\nu' \tag{26}$$

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is nonvanishing only for $l_1=0$ (s state) and $l_1=2$ (d state). After calculating the angular parts in Eq. (26), we have

$$A_{1s,n_1l_1}(\nu')d\nu'=C_{l_1}\frac{2^{10}\pi^6\nu'^3\nu''^3}{c^6}\times[P_{l_1,1}(\nu')+P_{l_1,2}(\nu'')]^2d\nu' , \tag{27}$$

with

$$C_{l_1}=\frac{1}{2l_1+1}\sum_{m_1}\left[\left|\sum_{l,m}\langle Y_{00}|\hat{\epsilon}'\cdot\hat{r}|Y_{lm}\rangle\times\langle Y_{lm}|\hat{\epsilon}''\cdot\hat{r}|Y_{l_1m_1}\rangle\right|^2\right]_{\mathrm{av}}$$

$$=\begin{cases}\frac{1}{72}\int_0^{\pi}(1+\cos^2\theta)(\sin\theta)d\theta=\frac{1}{27},\quad l_1=0 & (28\mathrm{a})\\ \frac{13}{1800}\int_0^{\pi}(1+\frac{1}{13}\cos^2\theta)(\sin\theta)d\theta=\frac{2}{135},\quad l_1=2 & (28\mathrm{b})\end{cases}$$

and

$$P_{l_1,1}=\sum_n\frac{\langle R_{10}|r|R_{n1}\rangle\langle R_{n1}|r|R_{n_1l_1}\rangle}{E_n-E_{n_1}+E_{\nu'}} , \tag{29}$$

$$P_{l_1,2}=\sum_n\frac{\langle R_{10}|r|R_{n1}\rangle\langle R_{n1}|r|R_{n_1l_1}\rangle}{E_n-E_{n_1}+E_{\nu''}} . \tag{30}$$

In Eqs. (28) θ is the angle between the photon momenta. Thus

$$A^T_{1s,n_1l_1}=\frac{1}{\tau}=\frac{1}{2}\int_0^{(E_{n_1}-E_1)/2\pi}A_{1s,n_1l_1}(\nu')d\nu'$$

$$=\frac{1}{2}\int_0^1A_{1s,n_1l_1}(x)dx \tag{31}$$

with

$$x=4\pi n_1^2\nu'/(n_1^2-1) \tag{31$'$}$$

and

$$A_{1s,n_1l_1}(x)=C_{l_1}\frac{(n_1^2-1)^7}{2^4\pi n_1^{14}c^6}x^3(1-x)^3(P_{l_1,1}+P_{l_1,2})^2 . \tag{31$''$}$$

The transition rate $A(x)$ is also called spectral function in the literature. Like Eq. (14), we define another auxiliary function $U(r,\nu)$,

$$U(r,\nu)=\sum_n\frac{rR_{n1}(r)\langle R_{n1}|r|R_{n_1l_1}\rangle}{E_n-E_{n_1}+E_\nu} \tag{32}$$

with E_ν representing $E_{\nu'}$ or $E_{\nu''}$. Notice

$$P_{l_1}=\int_0^{\infty}R_{10}(r)U(r,\nu)r^2dr . \tag{33}$$

Using the radial Schrödinger equation with the orthonormal and the closure conditions for $rR_{n1}(r)$, we obtain for U the following inhomogeneous differential equation:

$$\left[E_\nu-E_{n_1}-\frac{1}{2}\frac{d^2}{dr^2}-\left[\frac{1}{r}-\frac{1}{r^2}\right]\right]U(r,\nu)=r^2R_{n_1l_1}(r) . \tag{34}$$

Instead of using the series-expansion method, we now introduce the Laplace transform of U,

$$S(p,\nu)=\int_0^{\infty}U(r,\nu)e^{-pr}dr , \tag{35}$$

which in turn satisfies the following first-order inhomogeneous differential equation:

$$\left[-\frac{p^2}{2}-E_{n_1}+E_\nu\right]\frac{d}{dp}\left[\frac{dS}{dp}\right]-(2p-1)\left[\frac{dS}{dp}\right]=\int_0^{\infty}R_{n_1l_1}(r)r^4e^{-pr}dr . \tag{36}$$

From Eqs. (33)–(35), one sees that

$$P_{l_1}=2\left[\frac{d^2S}{dp^2}\right]_{p=1}=2\left[\frac{dY}{dp}\right]_{p=1} , \tag{37}$$

where Y is the solution of the following equation:

$$\left[p^2-p_0^2\right]\frac{dY}{dp}+2(2p-1)Y=2F_{n_1l_1}(p) \tag{38}$$

with

$$p_0^2=2(-E_{n_1}+E_\nu)$$

and

$$F_{n_1l_1}(p)=-\int_0^\infty R_{n_1l_1}(r)r^4e^{-pr}dr$$

$$=\begin{cases} -2\left[\dfrac{1}{n_1^3}\right]^{1/2}\displaystyle\sum_{j=0}^{n_1-1}\frac{(-n_1+1)_j}{(2)_j}\left[\frac{2}{n_1}\right]^j\frac{(j+1)(j+2)(j+3)(j+4)}{(p+1/n_1)^{j+5}} & \text{for } l_1=0 \qquad (39)\\ -2\left[\dfrac{1}{n_1^3}\right]^{1/2}\dfrac{[(n_1^2-4)(n_1^2-1)]^{1/2}}{30n_1^2} & \\ \times\displaystyle\sum_{j=0}^{n_1-3}\frac{(-n_1+3)_j}{(6)_j}\left[\frac{2}{n_1}\right]^j\frac{(j+3)(j+4)(j+5)(j+6)}{(p+1/n_1)^{j+7}} & \text{for } l_1=2\ . \qquad (40)\end{cases}$$

In Eqs. (39) and (40) $(a)_j$ is the usual Pockhammer symbol.[32]

The whole problem is reduced to solving Eq. (38) and finding the values of $Y(p)$ at $P=1$. P_{l_1} can be obtained immediately via Eqs. (37) and (38):

$$P_{l_1}=\frac{4}{1-p_0^2}[F_{n_1l_1}(1)-Y(1)]\ . \qquad (41)$$

We choose p_1 in the neighborhood of p_0 with $1>p_1>p_0$. The value of $Y(p)$ can be obtained via Taylor-series expansion and Eq. (38); thus,

$$Y(p_1)=Y(p_0)+\sum_{k=1}^{\infty}\frac{1}{k!}Y^{(k)}(p_0)(p_1-p_0)^k \qquad (42)$$

with

$$Y(p_0)=\frac{F_{n_1l_1}(p_0)}{2p_0-1} \qquad (43)$$

and

$$Y^{(k)}(p_0)=\frac{2F^{(k)}_{n_1l_1}(p_0)-(k^2+3k)Y^{(k-1)}(p_0)}{2[(k+2)p_0-1]}\ . \qquad (44)$$

Equation (38) has, then, no regular singular point for $p>p_1$. By using the integrating factor method,[33,10] the solution of Eq. (38) can be shown to be

$$Y(1)=\left[\frac{1-p_0}{1+p_0}\right]^{1/p_0}\frac{1}{(1-p_0^2)^2}$$
$$\times\left[\int_{p_1}^{1}2F_{n_1l_1}(p)(p^2-p_0^2)\left[\frac{p+p_0}{p-p_0}\right]^{1/p_0}dp+(p_1^2-p_0^2)^2\left[\frac{p_1+p_0}{p_1-p_0}\right]^{1/p_0}Y(p_0)\right]\ . \qquad (45)$$

The integrals in Eqs. (45) and (31) can be numerically evaluated by employing the usual Gauss-Legendre quadrature method.

III. RESULTS AND DISCUSSION

In Sec. II A we have shown that the probability per second for the spontaneous two-photon emission of a hydrogenic atom from an arbitrary state (n_1,l_1,m_1) to an arbitrary state (n_2,l_2,m_2) can be expressed in terms of repeated parametric differentiations of hypergeometric functions. The resulting expressions are rather complicated for arbitrary (n_1,l_1,m_1) and (n_2,l_2,m_2). For n_1s-n_2s transitions, all the theoretical results in Sec. II B are quite compact in terms of hypergeometric functions. Nevertheless, for large n, this gives rise to a huge number of hypergeometric functions, resulting from differentiations, making calculations very cumbersome.

In Sec. II C we have presented an approach which is simpler to carry out and less prone to numerical error. If the final state is the ground state, one is able to evaluate the angular parts first. Using the implicit technique, the evaluation of infinite summations involving radial matrix elements is replaced by the solution of an inhomogeneous differential equation. The solution, easily found with the use of Laplace transforms, is expressed as a one-dimensional integral representation involving simple functions. Since $F_{n_1l_1}$ is rather simple [see Eqs. (41) and (42)], all the computations are also rather simple. To demonstrate the simplicity and utility of this approach, we have considered the two-photon decay of a metastable hydrogenic atom ($n_1=2$, $l_1=0$). For this case, Eq. (41) reduces to

$$F_{20}(p)=-12\sqrt{2}\frac{p-2}{(p+0.5)^6}\ .$$

The integrals in Eqs. (47) and (31) are calculated, using a 20-point Gaussian quadrature, in less than 0.25 sec on the AMDAHL 470 V5 computer at the University of Arkansas. Our result, $1/\tau=8.2284\ \text{sec}^{-1}$, agrees with the work of Klarsfeld,[14] who used expressions identical to Sec. II B involving hypergeometric functions.

Figure 1 shows a plot of the spectral distribution function $A_{1s,2s}(x)$ as a function of x. The variable x was defined in Eq. (3) and is proportional to the emission frequency ν'. This curve is also in agreement with that previously reported.[6,14] In particular, $A_{1s,2s}(x)$ goes to zero, as expected, when either of the emitted photon frequencies goes to zero (ν' or $\nu''=0$) and is a maximum when the two emitted photons have the same frequency ($\nu'=\nu''$). In Fig. 2(a), however, we present a new result. In this figure the spectral distribution function $A_{1s,3s}(x)$ is plotted as a function of x. Obviously, there are several interesting features present in the plot of $A_{1s,3s}(x)$ which were not

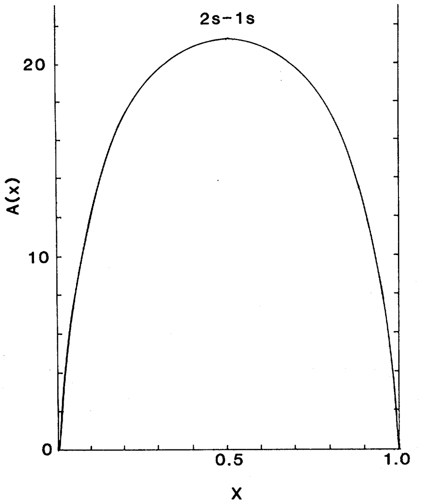

FIG. 1. Spectral distribution function $A_{1s,2s}(x)$ as a function of x. The variable x is the single-photon frequency ν' relative to the two-photon $1s$ to $2s$ transition frequency. The units of $A_{1s,2s}(x)$ are $\sec^{-1}$ and physically the transition rate per unit frequency where the unit frequency is taken to be the two-photon $2s$ to $1s$ transition frequency.

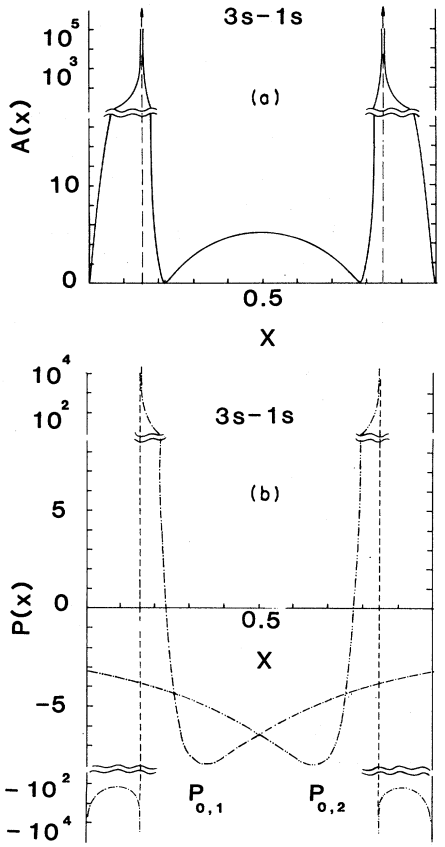

FIG. 2. (a) Spectral distribution function $A_{1s,3s}(x)$ as a function of x. The variable x is the single-photon frequency ν' relative to the two-photon $1s$ to $3s$ transition frequency. The units of $A_{1s,3s}(x)$ are $\sec^{-1}$ and physically the transition rate per unit frequency where the unit frequency is taken relative to the two-photon $3s$ to $1s$ transition frequency. (b) Functions $P_{0,1}(x)$ and $P_{0,2}(x)$, defined in Eq. (31), as a function of x.

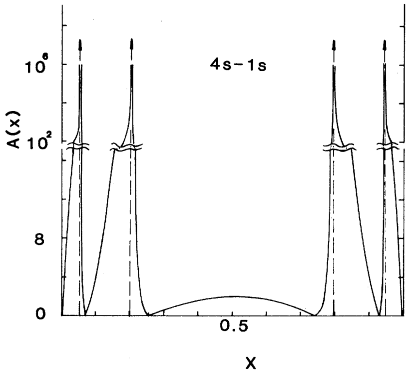

FIG. 3. Spectral distribution function $A_{1s,4s}(x)$ as a function of x. The variable x is the single-photon frequency ν' relative to the two-photon $1s$ to $4s$ transition frequency. The units of $A_{1s,4s}(x)$ are $\sec^{-1}$ and physically the transition rate per unit frequency where the unit frequency is taken to be the two-photon $4s$ to $1s$ transition frequency.

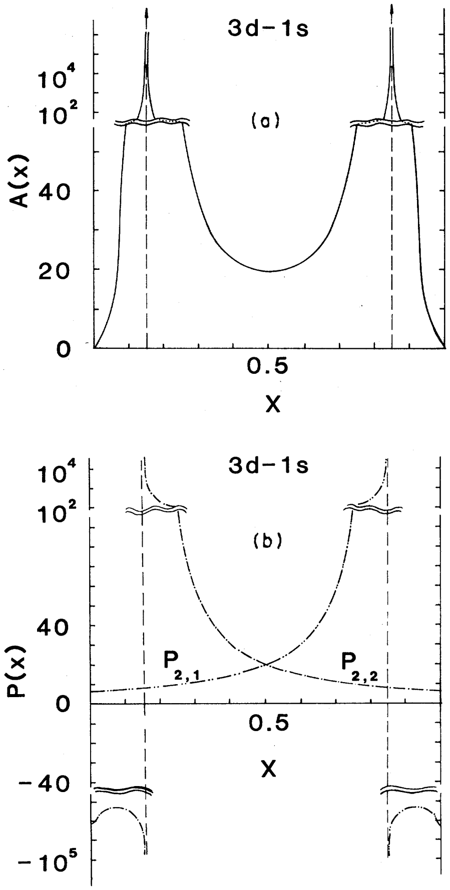

FIG. 4. (a) Spectral distribution function $A_{1s,3d}(x)$ as a function of x. The variable x is the single-photon frequency ν' relative to the two-photon $1s$ to $3d$ transition frequency. The units of $A_{1s,3d}(x)$ are $\sec^{-1}$ and physically the transition rate per unit frequency where the unit frequency is taken to be the two-photon $3d$ to $1s$ transition frequency. (b) Functions $P_{2,1}(x)$ and $P_{2,2}(x)$, defined in Eq. (31), as a function of x.

TABLE I. Positions of the first minimum on the high- and low-frequency side of $x=\frac{1}{2}$ (or $\nu'=\nu''$) for the $n_1s \rightarrow 1s$ transitions. Quantities in parentheses are powers of 10 by which the numbers are multiplied.

	Low-frequency side		High-frequency side	
Transition	x	ν' (sec^{-1})	x	ν' (sec^{-1})
$3s \rightarrow 1s$	0.2197	6.421(14)	0.7803	2.281(15)
$4s \rightarrow 1s$	0.2627	8.089(14)	0.7373	2.273(15)
$5s \rightarrow 1s$	0.2807	8.861(14)	0.7193	2.271(15)
$6s \rightarrow 1s$	0.2902	9.227(14)	0.7098	2.269(15)

present in the corresponding plot of $A_{1s,2s}(x)$ in Fig. 1. In particular, $A_{1s,3s}(x)$ exhibits an infinity or resonant behavior at $x=0.15625$ and 0.84375. Physically, this behavior is due to a resonance between a photon with the frequency corresponding to the $3s$ to $2p$ transition and another photon at the frequency corresponding to the $2p$ to $1s$ transition.

In addition to this resonant behavior, we note a second interesting feature, which is the zero behavior at $x=0.21970$ and 0.78030. Two-photon decay is not possible at these frequencies. In order to gain further insight into this unusual prediction, we have plotted $P_{0,1}$ and $P_{0,2}$ [see Eq. (31)] separately. As can be seen in Fig. 2(b), $A_{1s,3s}(x)$ goes to zero because the value of $P_{0,1}(x)$ exactly cancels $P_{0,2}(x)$ when $x=0.21970$ and 0.78030. Physically, the phase change in the radiation terms associated with the intermediate resonance makes this destructive interference possible. Similar behavior is seen in $A_{1s,4s}(x)$, which is plotted in Fig. 3. The additional zeros, however, are now made possible by the phase difference between the resonant dipole terms. For example, the phase difference between the resonant dipole terms at $x=0.05185$ and 0.20000 make possible the destructive interference at $x=0.07000$. Such minima have been predicted and observed in two-photon absorption spectra[34] where they have been referred to as "transparencies." Similar results have been found for $A_{1s,5s}(x)$ and $A_{1s,6s}(x)$. The first zero observed to the high- and low-frequency side of $x=\frac{1}{2}$ (or $\nu'=\nu''$) is listed in Table I. On the other hand, only the infinity or resonant behavior is observed in $A_{1s,3d}(x)$, which is plotted in Fig. 4(a). In this case, $P_{2,1}(x)$ and $P_{2,2}(x)$, shown in Fig. 4(b), do not cancel despite the phase change which occurs in the resonant terms. The possibility of zeros in $A_{1s,3d}(x)$ exists on the low-frequency side of the resonance at $x=0.15025$ and on the high-frequency side of the resonance at $x=0.84375$ but are prevented from occurring by the resonance terms at $x=0$ and $x=1$.

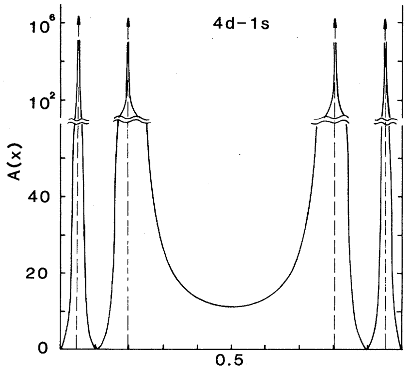

FIG. 5. Spectral distribution function $A_{1s,4d}(x)$ as a function of x. The variable x is the single-photon frequency ν' relative to the two-photon $1s$ to $4d$ transition frequency. The units of $A_{1s,4d}(x)$ are sec^{-1} and physically the transition rate per unit frequency where the unit frequency is taken to be the two-photon $4d$ to $1s$ transition frequency.

Although the zero behavior is not observed in $A_{1s,3d}(x)$, this is not a characteristic of $d \rightarrow s$ transitions. For example, $A_{1s,4d}(x)$ does exhibit zero behavior, as seen in Fig. 5. In this case the zero is made possible by the phase difference associated with the resonant dipole terms. For example, the phase difference between the resonant dipole terms at $x=0.05185$ and 0.20000 make possible the destructive interference at $x=0.10600$.

It is interesting to note that even though both $n_1s \rightarrow 1s$ and $n_1d \rightarrow 1s$ transitions display zero behavior in their emission spectrum they do not coincide in frequency. This can be seen directly, for example, from a comparison of Fig. 3 with Fig. 5. Since similar results are expected in the two-photon absorption spectrum,[35] in principle, it is possible in an experiment to choose ν' and ν'' such that the $1s \rightarrow n_1d$ transition is preferentially excited over the $1s \rightarrow n_1s$ transition or vice versa (see Tables II and III). For example, if we choose in an experiment $\nu' \simeq 0.64214 \times 10^{15}$ sec^{-1} and $\nu'' \simeq 2.2807 \times 10^{15}$ sec^{-1} or the corresponding wavelengths $\nu' \simeq 4671.9$ Å and $\nu'' \simeq 1315.4$ Å, then $A_{3s,1s}(x)$ will be zero while $A_{3d,1s}(x)$ will be nonzero. As a result, the $3d$ level will be preferentially pumped.

TABLE II. Transition rate for $n_1s \rightarrow 1s$ at $x=0.5$ or $\nu'=\nu''$. Quantities in parentheses are powers of 10 by which the numbers are multiplied.

Transition	$\nu=\nu'=\nu''$ (sec^{-1})	$\lambda=\lambda'=\lambda''$ (Å)	$A(\nu)$ (sec^{-1}GHz^{-1})
$2s \rightarrow 1s$	1.2330(15)	2431	8.638(−6)
$3s \rightarrow 1s$	1.4614(15)	2051	1.779(−6)
$4s \rightarrow 1s$	1.5413(15)	1945	6.410(−7)
$5s \rightarrow 1s$	1.5783(15)	1899	3.026(−7)
$6s \rightarrow 1s$	1.5984(15)	1876	1.672(−7)

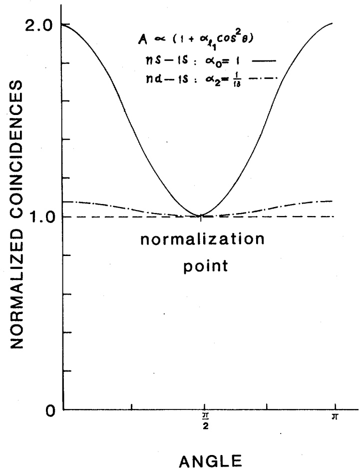

FIG. 6. Angular distribution function as a function of the angle between the two simultaneously emitted photons. The curve indicates the expected coincidence signal between two detectors monitoring ν' and ν'', respectively, as a function of the angle between the detectors. Interestingly, the expected coincidence signal for the $n_1d \rightarrow 1s$ transitions is shown to be significantly different from the more well-known result for the $n_1s \rightarrow 1s$ transitions.

TABLE III. Transition rate for $n_1d \rightarrow 1s$ at $x = 0.5$ or $\nu' = \nu''$. Quantities in parentheses are powers of 10 by which the numbers are multiplied.

Transition	$\nu = \nu' = \nu''$ (sec^{-1})	$\lambda = \lambda' = \lambda''$ (Å)	$A(\nu)$ (sec^{-1} GHz^{-1})
$3d \rightarrow 1s$	1.4614(15)	2051	6.717(−6)
$4d \rightarrow 1s$	1.5413(15)	1945	3.685(−6)
$5d \rightarrow 1s$	1.5783(15)	1899	2.084(−6)
$6d \rightarrow 1s$	1.5984(15)	1876	1.268(−6)

In addition to the emission spectra, we also report on the angular distribution expected between the two photons resulting from a two-photon transition. That is, we have calculated the expected coincidence signal between two detectors monitoring ν' and ν'', respectively, as a function of the angle between the detectors. The result is predicted by Eq. (28b) and plotted in Fig. 6. The predicted result for $n_1s \rightarrow 1s$ transitions is in agreement with that expected by others,[6,14,36] however, we have also presented a new result shown in Fig. 6. In particular, the angular distribution for $n_1d \rightarrow 1s$ transitions is plotted and shown to be significantly different from the $n_1s \rightarrow 1s$ result. Although our result is new, it is in agreement with the more general result of Yang[37] which predicts an angular correlation of the form $1 + \alpha \cos^2\theta$ for dipole-dipole transitions. As seen in Eq. (28), the parameter $\alpha = 1$ for $n_1s \rightarrow 1s$ transitions but $\alpha = \frac{1}{13}$ for $n_1d \rightarrow 1s$ transitions.

In conclusion, we have presented several new results which will be interesting to test experimentally either in emission or in absorption experiments. Unfortunately, two-photon absorption experiments will require tunable vacuum ultraviolet photons which are presently difficult to obtain with the large flux needed to excite a sufficient number of hydrogen atoms for detection. However, excimer lasers may make such experiments more feasible in the future.

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