Two-Photon Decay in Monovalent Atoms

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Abstract

Two-photon decay of excited states of atoms with a single valence electron is reexamined with an eye to a possible missing factor of 1/2 in Table 5 of Ref. [1]. Indeed, such a factor, presumably the result of integrating the singly differential rate over the full spectral range, was discovered and all calculations in reported in that table were redone.

Basic Equations

The differential two-photon transition rate is

$$\frac{dw}{d\omega_1} = \frac{8}{9\pi}\alpha^6\omega_1^3\omega_2^3 \sum_{m_1 m_2} |M_{m_1 m_2}|^2, \tag{1}$$

where,

$$M_{m_2,m_1} = \sum_N \left[D^N_{m_1 m_2} + E^N_{m_1 m_2}\right], \tag{2}$$

with

$$D^N_{m_1 m_2} = \frac{\langle F|Q_{m_2}(\omega_2)|N\rangle\langle N|Q_{m_1}(\omega_1)|I\rangle}{E_N + \omega_1 - E_I} \tag{3}$$

$$E^N_{m_1 m_2} = \frac{\langle F|Q_{m_1}(\omega_1)|N\rangle\langle N|Q_{m_2}(\omega_2)|I\rangle}{E_N + \omega_2 - E_I}. \tag{4}$$

In the above, we have assumed that $Q_m(\omega)$ is a retarded electric-dipole transition operator normalized to $Q_m(\omega) = er_m$ in the low-frequency limit.

After averaging over initial substates and summing over final substates, the sum in Eq. (1) reduces to

$$\sum_{m_1 m_2} |M_{m_1 m_2}|^2 \Rightarrow \frac{1}{2j_I+1}\left\{\sum_j \frac{1}{2j_j+1}\left[D^j D^j + E^j E^j\right]\right.$$
$$\left. + \sum_{j_1 j_2} (-1)^{j_1+j_2} \begin{Bmatrix} j_1 & j_F & 1 \\ j_2 & j_I & 1 \end{Bmatrix} \left[D^{j_1}E^{j_2} + D^{j_2}E^{j_1}\right]\right\}, \quad (5)$$

where n and j are the principal and angular quantum numbers of the intermediate state N. In the above,

$$D^j = \sum_n \frac{\langle F\|Q_1(\omega_2)\|nj\rangle\langle nj\|Q_1(\omega_1)\|I\rangle}{E_{nj}+\omega_1-E_I} \quad (6)$$

$$E^j = \sum_n \frac{\langle F\|Q_1(\omega_1)\|nj\rangle\langle nj\|Q_1(\omega_2)\|I\rangle}{E_{nj}+\omega_2-E_I}. \quad (7)$$

We consider the following three cases to check the calculations in Ref. [1]:

- $2s_{1/2} \to p_{1/2},\ np_{3/2} \to 1s_{1/2}$:

$$\sum_{m_1 m_2} |M_{m_1 m_2}|^2 \Rightarrow \frac{1}{4}\left[D^{1/2}D^{1/2}+E^{1/2}E^{1/2}\right] + \frac{1}{8}\left[D^{3/2}D^{3/2}+E^{3/2}E^{3/2}\right]$$
$$-\frac{1}{6}D^{1/2}E^{1/2} + \frac{1}{12}D^{3/2}E^{3/2} - \frac{1}{3}\left[D^{1/2}E^{3/2}+D^{3/2}E^{1/2}\right] \quad (8)$$

- $d_{5/2} \to np_{3/2} \to s_{1/2}$:

$$\sum_{m_1 m_2} |M_{m_1 m_2}|^2 \Rightarrow \frac{1}{24}\left[D^{3/2}D^{3/2}+E^{3/2}E^{3/2}\right] + \frac{1}{12}D^{3/2}E^{3/2} \quad (9)$$

- $d_{3/2} \to np_{1/2},\ np_{3/2} \to s_{1/2}$:

$$\sum_{m_1 m_2} |M_{m_1 m_2}|^2 \Rightarrow \frac{1}{8}\left[D^{1/2}D^{1/2}+E^{1/2}E^{1/2}\right] + \frac{1}{16}\left[D^{3/2}D^{3/2}+E^{3/2}E^{3/2}\right]$$
$$+\frac{1}{6}D^{1/2}E^{1/2} - \frac{1}{12}D^{3/2}E^{3/2} + \frac{1}{12}\sqrt{\frac{5}{2}}\left[D^{1/2}E^{3/2}+D^{3/2}E^{1/2}\right] \quad (10)$$

The formulas for the two-photon decay of d states agree precisely with those given in Ref. [1] and the formulas for decay of s states agree with those in [2] once numerators in the expressions for D^j and E^j are replaced by radial integrals.

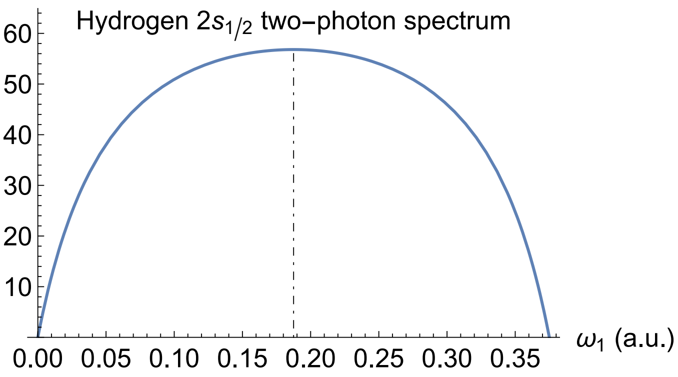

Figure 1: The differential decay rate $dw/d\omega_1$ times 4πRy c for two-photon decay of the $2s_{1/2}$ state of hydrogen is shown in the blue curve. Integrating from 0 to $(E_I - E_F)/2$ leads to $w = 8.22913$ sec^{-1} for the final decay rate of the $2s_{1/2}$ state.

Decay of the $2\mathrm{s}_{1/2}$ state of hydrogen

We carry out the sums over n in Eqs. (6,7) using a hydrogenic B-spline basis to obtain D^j and E^j as functions of ω_1 for intermediate np_j states with $j = 1/2$ and $j = 3/2$. For simplicity, we have omitted retardation in the dipole matrix elements $Q_m(\omega)$. The sum in Eq. (8) is multiplied by

$$\frac{8}{9\pi}\omega_1^3\omega_2^3 \times 4\pi\mathrm{Ry}\ \mathrm{c} \tag{11}$$

to form the differential decay rate $dw/d\omega_1$ in units (sec^{-1}/a.u.) shown in Fig. 1. To obtain the final decay rate w, we integrate the differential rate from $\omega_1 = 0$ to $(E_I - E_F)/2$. Owing to the sharp rise in the rate near the endpoints of the spectrum, care must be taken in integrating the differential rate over ω_1. Here, we use the NIntegrate routine in Mathematica to obtain a value $w = 8.22913$ s^{-1} for the two-photon decay rate of the $2s_{1/2}$ state of H, in close agreement with the value obtained in Ref. [2].

Decay of $nd_{3/2}$ and $nd_{5/2}$ states in Ca$^+$, Sr$^+$ and Ba$^+$

We carry out both Dirac-Fock (DF) and all-order single-double (SD) calculations of $5d \rightarrow 6s$ two-photon transitions rates in alkaline earth ions with an eye validating the results in Table 5 of [1].

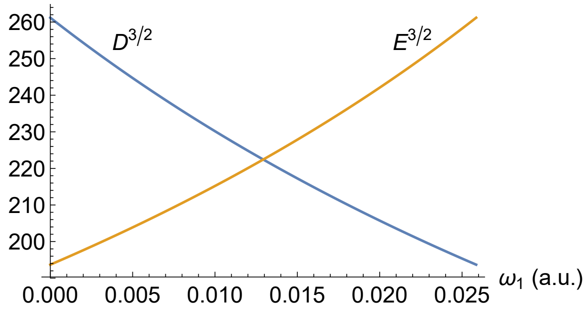

Figure 2: The SD functions $D^{3/2}(\omega_1)$ and $E^{3/2}(\omega_2)$ in Eq.(9) for the $5d_{5/2} \to 6s_{1/2}$ transition in Ba$^+$ are plotted against ω_1.

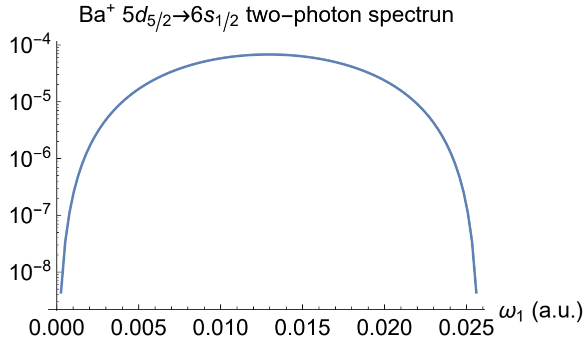

Figure 3: The SD differential decay rate $dw/d\omega_1$ times 4πRy c for two-photon decay of the $5d_{5/2}$ state to the $6s_{1/2}$ ground state of Ba$^+$ is shown in the blue curve. Integrating from 0 to $(E_I - E_F)/2$ leads to the final two-photon decay rate of $w = 4.039 \times 10^{-7}$ sec^{-1} for the $5d_{5/2}$ state.

Dirac-Fock calculation

Sums over n in Eqs. (6,7) are carried out using a Dirac-Fock B-spline basis to obtain D^j and E^j as functions of ω_1 for intermediate np_j states with $j = 1/2$ and $j = 3/2$. The sums in Eqs. (9) and (10) are multiplied by the expression in Eq.(11) to obtain differential rates $dw/d\omega_1$ in units (sec^{-1}/a.u.) plotted in the left-hand panels of Fig. 4. Total DF rates in sec^{-1} are listed in the column labeled Dirac-Fock in Table 1. These rates are half of the corresponding DF rates given in Table 5 of Ref. [1].

Table 1: Two-photon decay rates (sec^{-1}) of $(n-1)d_{3/2}$ and $(n-1)d_{5/2}$ states to $ns_{1/2}$ states in Ca$^+$ (n=4), Sr$^+$ (n=5) and Ba$^+$ (n=8) ions in the lowest-order DF approximation and in the all-order SD approximation. Numbers in brackets are powers of 10

Ion	Transition	Dirac-Fock	SD
Ca$^+$	$3d_{5/2} \rightarrow 4s$	3.404[-3]	9.959[-5]
Ca$^+$	$3d_{3/2} \rightarrow 4s$	3.458[-3]	9.798[-5]
Sr$^+$	$4d_{5/2} \rightarrow 5s$	2,718[-3]	3.807[-4]
Sr$^+$	$4d_{3/2} \rightarrow 5s$	2.777[-3]	3.526[-4]
Ba$^+$	$5d_{5/2} \rightarrow 6s$	1.013[-5]	4.039[-7]
Ba$^+$	$5d_{3/2} \rightarrow 6s$	7.384[-6]	1.537[-7]

All-order calculation of the $5d_{5/2} \rightarrow 6s_{1/2}$ transition in Ba$^+$

The sum over states converges rapidly in the functions $D^{3/2}(\omega_1)$ and $E^{3/2}(\omega_2)$ in Eq. (9), so we can limit the sum over n in Eqs. (6) amd(7) to the first 3 or 4 excited $np_{1/2}$ and $np_{3/2}$ states. We make use of SD reduced matrix elements for the states listed in Table 3 of Ref. [1] and corresponding energies from the NIST database [3] for the $6s_{1/2}$, $5d_{5/2}$ and $np_{3/2}$ $(n = 6 - 9)$ states of Ba$^+$ to evaluate $D^{3/2}(\omega_1)$ and $E^{3/2}(\omega_2)$. The resulting functions are plotted against ω_1 in Fig. 4. These functions are combined according to Eqs.(9) and (10) to obtain the differential decay rate $dw/d\omega_1$ illustrated in Fig. 2. This figure is essentially identical to Fig. 1 of [1]. Integrating the differential rate from 0 to $(E_I - E_F)/2$ leads to $w = 4.039 \times 10^{-7}$ sec^{-1}, which is half of the rate for this transition listed in Table 5 of Ref. [1]. It is obvious that the differential rate in [1] was incorrectly integrated over the entire range of photon energies $E_I - E_F$.

SD calculation of $(n-1)d \rightarrow ns$ rates Ca$^+$, Sr$^+$ and Ba$^+$

We repeat the calculations of the previous subsection for $3d_{3/2,5/2} \rightarrow 4s_{1/2}$ transitions in Ca$^+$, $4d_{3/2,5/2} \rightarrow 5s_{1/2}$ transitions in Sr$^+$ and $5d_{3/2,5/2} \rightarrow 6s_{1/2}$ transitions in Ba$^+$. The differential rates are presented in the right-hand panels of Fig. 4. The amplitudes of the SD differential rates are one or more orders of magnitude smaller than the corresponding DF amplitudes. Integrating the SD differential rates from 0 to the midpoint of the spectrum leads to the final SD rates tabulated in the fourth column of Table 1.

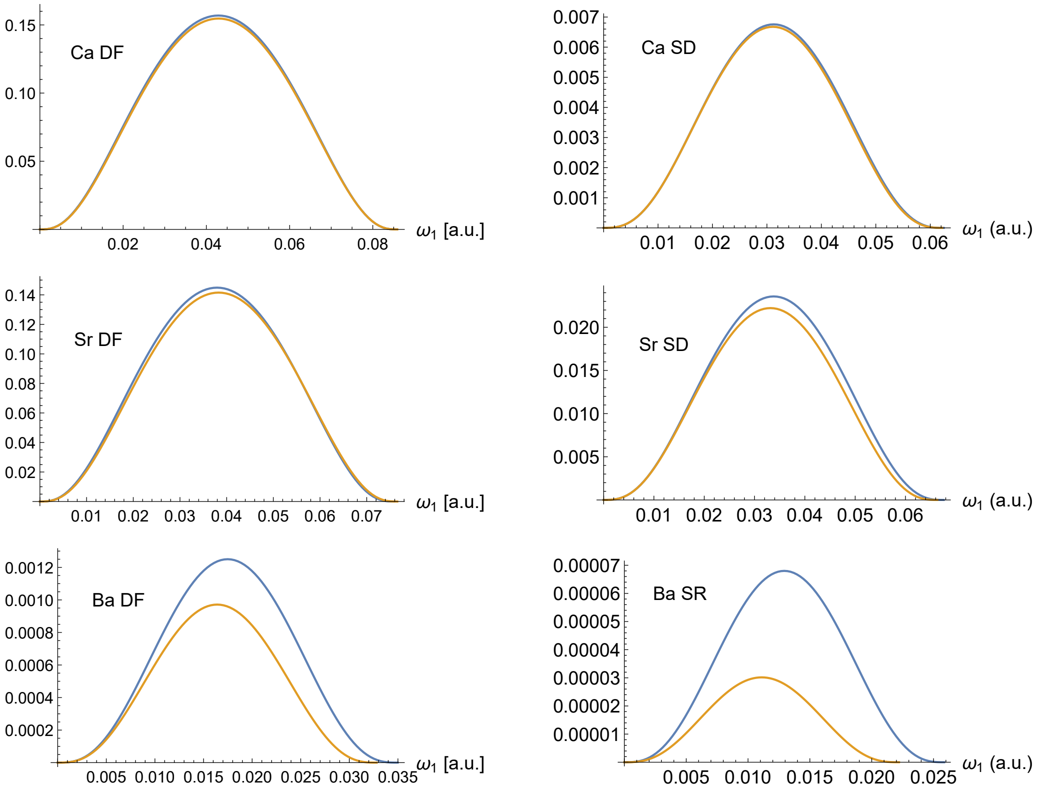

Figure 4: Left panels:Lowest-order Dirac-Fock two-photon differential rates $dw/d\omega_1$ in units (sec^{-1}/a..u.) for $(n-1)d_{5/2} \to s_{1/2}$ transitions (blue curves) and $(n-1)d_{3/2} \to ns_{1/2}$ transitions (orange curves) for Ca$^+$ (n=4), Sr$^+$ (n=5) and Ba$^+$ (n=6). Right panels: All-order SD rates for cases shown in left panels.

References

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[2] W. R. Johnson, Phys. Rev. Letts. **29**, 1123 (1972).

[3] A. Kramida, Yu. Ralchenko, J. Reader, and and NIST ASD Team, NIST Atomic Spectra Database (ver. 5.3), [Online]. Available: `http://physics.nist.gov/asd` [2017, July 18]. National Institute of Standards and Technology, Gaithersburg, MD. (2015).