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2010 J. Phys. B: At. Mol. Opt. Phys. 43 074014

(http://iopscience.iop.org/0953-4075/43/7/074014)

J. Phys. B: At. Mol. Opt. Phys. **43** (2010) 074014 (5pp) doi:10.1088/0953-4075/43/7/074014

Two-photon transitions in Ca^+, Sr^+ and Ba^+ ions

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Received 6 August 2009, in final form 15 September 2009
Published 19 March 2010
Online at stacks.iop.org/JPhysB/43/074014

Abstract
Two-photon (2E1) decay rates are calculated for metastable $3d_j$ states in Ca^+, $4d_j$ states in Sr^+ and $5d_j$ states in Ba^+ to evaluate contributions of these transitions to the corresponding lifetimes. The calculations are carried out using the relativistic single-double method, where single and double excitations of Dirac–Fock wavefunctions are included to all orders of perturbation theory. We find that lowest-order calculations of the two-photon rates are strongly modified when correlation corrections are included.

1. Introduction

Recent advances in high-precision theoretical and experimental methodologies have led to significant improvements in determining lifetimes of long-lived metastable nd states in Ca^+, Sr^+ and Ba^+. These ions are of particular interest for developing optical frequency standards [1–3] and quantum information processing [4] owing to the extremely long lifetimes of nd states. High-precision calculations and measurements of these lifetimes are reported in many publications. One of the first many-body calculations of nd_j state lifetimes in Ca^+, Sr^+ and Ba^+ was published by Guet and Johnson [5]. Theoretical and experimental studies of these lifetimes were presented in [6–21] for the $3d$ states of Ca^+, in [22–25] for $4d$ states of Sr^+ and in [26–35] for $5d$ states of Ba^+. Theoretical results for all three ions, together with the review of previous theoretical calculations and available experimental measurements, were presented by Sahoo *et al* [36].

The most recent theoretical and experimental values of these lifetimes are summarized in tables 1 and 2. Experimental values of Ba^+ $5d$ lifetimes have the largest uncertainties (5–15%) since these lifetimes are by far longer than the corresponding lifetimes in the other two ions, leading to complications in experimental measurements. From the theoretical standpoint, the expected precision is similar in all three systems. The lifetimes of the nd states in Ca^+ and Sr^+ were recently determined experimentally with uncertainty smaller than 1%. A high-precision result (0.4%) for the lifetime of the $4d_{5/2}$ level in Sr^+ was presented by Letchumanan *et al* [25]. Uncertainties of 0.6% and 0.7% were quoted for the lifetime of the $3d_{5/2}$ level in Ca^+ by Barton *et al* [17] and Kreuter *et al* [21], respectively. The uncertainties of the theoretical $3d_{5/2}$ lifetimes in Ca^+ calculated by Kreuter *et al* [21] and by Sahoo *et al* [36] were estimated to be 0.9% and 0.8%, respectively. Theoretical and experimental values of the $3d_{3/2}$ and $3d_{5/2}$ lifetimes in Ca^+ from [21] are in agreement within the uncertainty bounds. However, the theoretical coupled-cluster value of the $3d_{5/2}$ lifetime in Ca^+ given by Sahoo *et al* [36] differs from the experimental value [21] by 4.3%. The difference between the theoretical value of the $4d_{5/2}$ lifetime in Sr^+ presented by Sahoo *et al* [36] and the experimental value determined by Letchumanan *et al* [25] is 5.1%. All-order theoretical Sr^+ lifetimes [37] are in agreement with experimental values.

We note that the theoretical uncertainties in the lifetimes include only the estimated uncertainties of the primary $(n+1)s$–nd E2 transitions. Significant discrepancies in the theoretical lifetimes of the upper $5d_{5/2}$ level in Ba^+ were later explained by the contribution of the $5d_{5/2}$–$5d_{3/2}$ M1 transition [38]; contributions to the $nd_{5/2}$ decay rates from M1 transitions for Ca^+ and Sr^+ were found to be negligible [36]. In light of the improved precision of theory and experiment, as well as the remaining discrepancies between various calculations seen

Table 1. Lifetimes τ of the $nd_{3/2}$ states in Ca^+, Sr^+ and Ba^+ in seconds.

Ion	State	Theory	Experiment
Ca^+	$3d_{3/2}$	0.98 [6]	1.111 ± 0.046 [11]
		1.271 [5]	1.17 ± 0.05 [15]
		1.16 [8]	1.20 ± 0.01 [17]
		1.080 [9]	1.176 ± 0.011 [21]
		1.196 ± 0.011 [21]	
		1.185 ± 0.007 [36]	
Sr^+	$4d_{3/2}$	0.454 [5]	0.435 ± 0.004 [23]
		0.422 [24]	0.435 ± 0.004 [24]
		0.426 ± 0.007 [36]	0.455 ± 0.029 [24]
		0.441 ± 0.003 [37]	
Ba^+	$5d_{3/2}$	83.7 [5]	79.8 ± 4.6 [30]
		81.5 [32]	89.4 ± 15.6 [34]
		81.4 [33]	
		80.086 ± 0.714 [36]	
		82.0 [34]	
		81.5 ± 1.2 [35]	

Table 2. Lifetimes τ of the $nd_{5/2}$ states in Ca^+, Sr^+ and Ba^+ in seconds.

Ion	State	Theory	Experiment
Ca^+	$3d_{5/2}$	0.95 [6]	0.994 ± 0.038 [11]
		1.236 [5]	1.064 ± 0.017 [13]
		1.14 [8]	0.969 ± 0.021 [14]
		1.045 [9]	1.09 ± 0.05 [15]
		1.165 ± 0.011 [21]	1.100 ± 0.018 [16]
		1.110 ± 0.009 [36]	1.168 ± 0.007 [17]
Sr^+	$4d_{5/2}$	0.405 [5]	0.372 ± 0.025 [22]
		0.384 [24]	0.408 ± 0.022 [24]
		0.357 ± 0.012 [36]	0.3908 ± 0.0016 [25]
		0.394 ± 0.003 [37]	
Ba^+	$5d_{5/2}$	37.2 [5]	32 ± 5 [27]
		30.3 [32]	34.5 ± 3.5 [28]
		36.5 [33]	32.0 ± 4.6 [34]
		29.856 ± 0.296 [36]	
		31.6 [34]	
		30.4 ± 0.4 [35]	

in tables 1 and 2, it is important to consider the possibility that other processes may contribute to the lifetimes of the nd metastable levels. This is particularly important in Ba^+, since the lifetimes are so long, especially for the $5d_{3/2}$ state which has a lifetime greater than 80 s.

In the present work, we consider two-photon $(n+1)s-nd$ decays in Ca^+ ($n = 3$), Sr^+ ($n = 4$) and Ba^+ ($n = 5$) ions via two E1 dipole transitions involving $n'p_j$ intermediate states. The singly ionized Ca, Sr and Ba atoms are monovalent systems with a single valence electron outside of a closed core. Two-photon transitions in monovalent and divalent ions are widely studied, both theoretically and experimentally (see [39–58]). The 2E1 two-photon transition gives the dominant contribution to the lifetime of the $2s$ metastable state in H-like ions. With increasing nuclear charge Z, the importance of the one-photon magnetic-dipole (M1) transition increases as $\sim Z^4$ and it becomes dominant (70%) for Sn^{49+}.

To the best of our knowledge, no estimates of two-photon decay rates of nd metastable levels of monovalent ions have been carried out prior to this work. In the present paper, we evaluate the two-photon decay rates by explicitly summing over intermediate np_j states. The evaluation of the required reduced electric-dipole matrix elements is performed using the relativistic single-double (SD) all-order method, where single and double excitations of Dirac–Fock wavefunctions are included to all orders of perturbation theory. Final results for the two-photon 2E1 transition rates are calculated for the $3d_j$ states in Ca^+, $4d_j$ states in Sr^+ and $5d_j$ states in Ba^+.

2. Method

The 2E1 decay of the excited state w to the ground state v in an atom with one valence electron is given by the expression [59]

$$\frac{dW}{d\omega_1} = \frac{8}{9\pi}\alpha^6\omega_1^3\omega_2^3\sum_{q_1q_2}|M_{q_1q_2}|^2, \tag{1}$$

where the photon frequencies are related by energy conservation, $\omega_1 + \omega_2 = E_w - E_v$. The two-photon matrix element $M_{q_1q_2}$ is given by

$$M_{q_1q_2} = \sum_n \left[\frac{\langle w|D_{q2}|n\rangle\langle n|D_{q1}|v\rangle}{E_n + \omega_2 - E_w} + \frac{\langle w|D_{q1}|n\rangle\langle n|D_{q2}|v\rangle}{E_n + \omega_1 - E_w}\right]. \tag{2}$$

In this equation, n designates intermediate states and D_q is the qth component of the dipole operator in a spherical basis. It is convenient to consider the two terms in equation (2) separately, $M_{q_1q_2} = C_{q_1q_2} + E_{q_1q_2}$, when performing the angular reduction:

$$C_{q_1q_2} = \sum_{nj} D^{nj}(\omega_2)\sum_{m_n}(-1)^{j_w-m_v}\begin{pmatrix} j_w & 1 & j_n \\ -m_w & q_2 & m_n\end{pmatrix} \times (-1)^{j_n-m_n}\begin{pmatrix} j_n & 1 & j_v \\ -m_n & q_1 & m_v\end{pmatrix} \tag{3}$$

$$E_{q_1q_2} = \sum_{nj} D^{nj}(\omega_1)\sum_{m_n}(-1)^{j_w-m_w}\begin{pmatrix} j_w & 1 & j_n \\ -m_w & q_1 & m_n\end{pmatrix} \times (-1)^{j_n-m_n}\begin{pmatrix} j_n & 1 & j_v \\ -m_n & q_2 & m_v\end{pmatrix}, \tag{4}$$

where

$$D^{nj}(\omega) = \frac{\langle w\|D\|nj\rangle\langle nj\|D\|v\rangle}{E_{nj} + \omega - E_w} \tag{5}$$

and $\langle w\|D\|nj\rangle$, $\langle nj\|D\|v\rangle$ are the reduced electric-dipole (E1) matrix elements.

To evaluate $M = \sum_{q_1q_2}\left|M_{q_1q_2}\right|^2$, we perform the sums over q_1, q_2 and magnetic substates of v and w, and divide the result by $(2j_w + 1)$. The angular reduction yields

$$M = \frac{1}{2j_w+1}\sum_{m_vm_w}\sum_{q_1q_2}\left|M_{q_1q_2}\right|^2 = \frac{1}{2j_w+1} \times \sum_{nn'j}\frac{1}{2j+1}(D^{nj}(\omega_2)D^{n'j}(\omega_2) + D^{nj}(\omega_1)D^{n'j}(\omega_1)) + \frac{2}{2j_w+1}\sum_{nj}\sum_{n'j'}\begin{Bmatrix} j' & 1 & j_w \\ j & 1 & j_v\end{Bmatrix}(-1)^{j+j'}D^{nj}(\omega_2)D^{n'j'}(\omega_1). \tag{6}$$

For the $d_{5/2}$–$np_{3/2}$–$s_{1/2}$ 2E1 transition, we obtain

$$M = \frac{1}{2j_w+1}\sum_{m_v m_w}\sum_{q_1 q_2}\left|M_{q_1 q_2}\right|^2 = \frac{1}{24}\left[\sum_n D^{n3/2}(\omega_2) + \sum_n D^{n3/2}(\omega_1)\right]^2. \quad (7)$$

The result for the $d_{3/2}$–$np_{3/2}$–$s_{1/2}$ and $d_{3/2}$–$np_{1/2}$–$s_{1/2}$ 2E1 transitions is more complicated:

$$\begin{aligned} M = {} & \frac{1}{2j_w+1}\sum_{m_v m_w}\sum_{q_1 q_2}\left|M_{q_1 q_2}\right|^2 \\ = {} & \sum_{nn'}\left[\frac{1}{16}(D^{n3/2}(\omega_2)D^{n'3/2}(\omega_2) + D^{n3/2}(\omega_1)D^{n'3/2}(\omega_1)) \right. \\ & + \frac{1}{8}(D^{n1/2}(\omega_2)D^{n'1/2}(\omega_2) + D^{n1/2}(\omega_1)D^{n'1/2}(\omega_1)) \\ & + \left(-\frac{1}{12}D^{n3/2}(\omega_2)D^{n'3/2}(\omega_1) + \frac{1}{6}D^{n1/2}(\omega_2)D^{n'1/2}(\omega_1)\right) \\ & \left. + \frac{1}{12}\sqrt{\frac{5}{2}}(D^{n3/2}(\omega_2)D^{n'1/2}(\omega_1) + D^{n1/2}(\omega_2)D^{n'3/2}(\omega_1))\right]. \end{aligned} \quad (8)$$

Numerical evaluations of expressions in equations (7) and (8) are similar to the evaluation of frequency-dependent polarizabilities in monovalent atomic systems (see, for example [60]). The sums over n and n' in equations (7) and (8) converge rapidly. Therefore, only a few terms need to be calculated accurately. The details of numerical evaluation of the two-photon transition rates are discussed in detail in the following section.

3. Results and discussions

In table 3, we list reduced electric-dipole transition matrix elements in Ca^+, Sr^+ and Ba^+ calculated using a relativistic SD all-order method (columns 'SD'). Details of those calculations for the singly ionized Ca, Sr and Ba atomic systems were given in recent papers [35, 37, 61]. The $6s$–np_j ($n = 6$–9) electric-dipole matrix elements and $6s$–nd_j ($n = 5$–7) electric-quadrupole matrix elements in Ba^+ were calculated using the relativistic all-order method by Iskrenova-Tchoukova and Safronova [35]. Black-body radiation (BBR) shifts of the $5s$–$4d_{5/2}$ and $4s$–$3d_{5/2}$ clock transitions in $^{88}Sr^+$ and $^{43}Ca^+$ were calculated using the relativistic all-order method in [37, 61], respectively. Calculations of the BBR shifts involved the calculations of electric-dipole matrix elements needed for the present work.

In the present paper, we extend those calculations to obtain all E1 matrix elements involved in the evaluations of two-photon transitions given by equations (7) and (8). Additionally, we list the lowest order (DF) reduced E1 matrix elements in table 3 to illustrate the size of correlation corrections of individual matrix elements. Inclusion of correlation corrections significantly modifies the lowest order two-photon transition rates.

In table 4, we illustrate the evaluation of the two terms $D^{n3/2}(\omega_1)$ and $D^{n3/2}(\omega_2)$ in equation (7) needed for the evaluation of 2E1 two-photon $5d_{5/2}$–$6s$ decay rate in Ba^+. As discussed in the previous sections, only $5d_{5/2}$–$np_{3/2}$–$6s$ decay channels are allowed in this case. All matrix elements listed in table 4 are calculated using the SD all-order method, and

Table 3. Reduced electric-dipole transitions matrix elements (a.u.) in Ca^+, Sr^+ and Ba^+ calculated using relativistic SD all-order method (columns 'SD'). The lowest order DF data are given in columns 'DF' to illustrate the size of correlation corrections.

	$d_{j'}$–np_j		np_j–$s_{1/2}$	
np_j	DF	SD	DF	SD
Ca^+		$3d_{5/2}$–np_j–$4s_{1/2}$ transitions		
$4p_{3/2}$	−4.134 79	−3.245 23	−4.526 94	−4.098 86
$5p_{3/2}$	0.001 09	0.175 33	0.008 05	−0.088 94
$6p_{3/2}$	−0.040 97	−0.095 18	0.050 16	0.111 69
$7p_{3/2}$	0.038 00	0.064 66	−0.045 83	−0.089 81
$8p_{3/2}$	0.032 05	0.048 15	−0.038 12	−0.071 78
$9p_{3/2}$	−0.026 89	−0.037 85	0.031 70	0.058 59
Ca^+		$3d_{3/2}$–np_j–$4s_{1/2}$ transitions		
$4p_{1/2}$	−3.082 48	−2.417 31	3.201 19	2.897 84
$5p_{1/2}$	−0.006 26	0.125 36	0.006 13	0.075 07
$6p_{1/2}$	0.027 64	0.068 27	0.041 52	0.085 16
$7p_{1/2}$	0.026 57	0.046 44	0.036 31	0.067 47
$8p_{1/2}$	0.022 65	0.034 61	0.029 79	0.053 61
$9p_{1/2}$	0.019 11	0.027 21	0.024 60	0.043 63
$4p_{3/2}$	−1.376 35	−1.078 84	−4.526 94	−4.098 86
$5p_{3/2}$	0.000 80	0.058 99	0.008 05	−0.088 94
$6p_{3/2}$	−0.013 83	−0.031 93	0.050 16	0.111 69
$7p_{3/2}$	0.012 77	0.021 66	−0.045 83	−0.089 81
$8p_{3/2}$	0.010 75	0.016 12	−0.038 12	−0.071 78
$9p_{3/2}$	−0.009 02	−0.012 67	0.031 70	0.058 59
Sr^+		$4d_{5/2}$–np_j–$5s_{1/2}$ transitions		
$5p_{3/2}$	5.002 53	4.149 69	−4.921 10	−4.350 75
$6p_{3/2}$	−0.075 76	−0.141 95	0.160 58	0.034 06
$7p_{3/2}$	−0.080 08	−0.078 16	0.027 82	−0.052 61
$8p_{3/2}$	−0.064 58	−0.053 27	0.004 77	−0.053 46
$9p_{3/2}$	0.051 95	0.039 71	0.001 45	0.046 35
Sr^+		$4d_{3/2}$–np_j–$5s_{1/2}$ transitions		
$5p_{1/2}$	−3.729 22	−3.083 00	3.484 79	3.078 37
$6p_{1/2}$	−0.026 28	−0.078 47	0.066 42	−0.024 76
$7p_{1/2}$	−0.046 92	−0.044 87	−0.005 03	−0.062 59
$8p_{1/2}$	0.040 31	0.030 99	0.012 78	0.054 28
$9p_{1/2}$	0.033 16	0.023 22	0.012 76	0.044 68
$5p_{3/2}$	−1.657 17	−1.369 41	−4.921 10	−4.350 75
$6p_{3/2}$	0.028 43	0.051 05	0.160 58	0.034 06
$7p_{3/2}$	0.028 00	0.027 58	0.027 82	−0.052 61
$8p_{3/2}$	0.022 31	0.018 64	0.004 77	−0.053 46
$9p_{3/2}$	−0.017 86	−0.013 83	0.001 45	0.046 35
Ba^+		$5d_{5/2}$–np_j–$6s_{1/2}$ transitions		
$6p_{3/2}$	5.001 15	4.110 81	5.477 57	4.709 71
$7p_{3/2}$	0.542 54	0.448 91	0.260 98	0.086 82
$8p_{3/2}$	0.297 60	0.221 94	0.078 61	−0.033 10
$9p_{3/2}$	0.203 48	0.143 54	0.037 95	−0.043 79
Ba^+		$5d_{3/2}$–np_j–$6s_{1/2}$ transitions		
$6p_{1/2}$	3.745 45	3.054 55	3.890 92	3.338 01
$7p_{1/2}$	0.351 29	0.276 97	0.065 36	−0.062 03
$8p_{1/2}$	0.195 64	0.133 45	0.007 07	0.087 53
$9p_{1/2}$	0.134 57	0.085 08	0.014 41	0.072 72
$6p_{3/2}$	1.635 37	1.334 02	5.477 57	4.709 71
$7p_{3/2}$	0.186 36	0.154 95	0.260 98	0.086 82
$8p_{3/2}$	0.101 89	0.076 53	0.078 61	−0.033 10
$9p_{3/2}$	0.069 55	0.049 40	0.037 95	−0.043 79

Table 4. Example of evaluation of the two terms $D^{n3/2}(\omega_1)$ and $D^{n3/2}(\omega_2)$ in equation (7) needed for the evaluation of 2E1 two-photon $5d_{5/2}$–$6s_{1/2}$ transition rate in Ba^+. All matrix elements are calculated using SD all-order method, $E_n = E_{np_{3/2}} - E_{5d_{5/2}}$, $\epsilon = \omega_1 + \omega_2 = E_{5d_{5/2}} - E_{6s_{1/2}} = 5674.807\ \text{cm}^{-1} = 0.025\,856$ a.u. [62]. In this example, $\omega_1 = [1/100]\epsilon = 0.000\,258\,56$ a.u. and $\omega_2 = [99/100]\epsilon = 0.023\,27$ a.u. $D^{n3/2}(w) = \langle 5d_{5/2}\|D\|np_{3/2}\rangle\langle np_{3/2}\|D\|6s_{1/2}\rangle/(E_n + w)$.

$np_{3/2}$	E_n [62]	$E_n + w_1$	$E_n + w_2$	$\langle 5d_{5/2}\|D\|np_{3/2}\rangle$	$\langle np_{3/2}\|D\|6s_{1/2}\rangle$	$D^{n3/2}(w_1)$	$D^{n3/2}(w_2)$
$6p_{3/2}$	0.0742	0.0744	0.0998	4.111	4.710	260.2	194.1
$7p_{3/2}$	0.2020	0.2023	0.2276	0.449	0.087	0.193	0.171
$8p_{3/2}$	0.2550	0.2552	0.2806	0.222	−0.033	−0.029	−0.026
$9p_{3/2}$	0.2825	0.2828	0.3081	0.144	−0.044	−0.022	−0.020

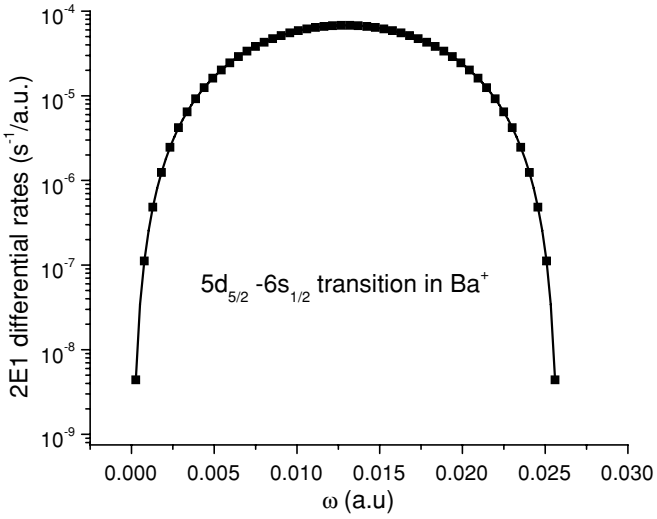

Figure 1. Differential rate $\frac{dW}{d\omega}$ for two-photon decay of the $5d_{5/2}$ level in Ba II.

experimental energies are used to evaluate $D^{n3/2}(\omega)$ terms. The value of $\epsilon = \omega_1 + \omega_2$ is equal to the energy difference between final and initial states. Here, we use the value $\epsilon = 5674.807\ \text{cm}^{-1} = 0.025\,856\,32$ a.u. from NIST Website [62]. To perform numerical integration over ω_1 needed for the evaluation of total decay rate W in equation (1), we divide this energy difference ϵ into 100 intervals with the step $[1/100]\epsilon$ and calculate $D^{n3/2}(\omega_1)$ and $D^{n3/2}(\omega_2)$ at each point ($\omega_2 = \epsilon - \omega_1$). The values in table 4 are calculated for $\omega_1 = [1/100]\epsilon = 0.000\,258\,56$ a.u. and $\omega_2 = [99/100]\epsilon = 0.023\,27$ a.u. The sum over intermediate states converges extremely rapidly and is nearly completely saturated by the first term $n = 6$. The quantity $\sum_n D^{n3/2}(w)$ only weakly depend on ω as the difference between $\sum_n D^{n3/2}(w)$ at the first ω grid point and last grid point is only 25%. The reason for such weak dependence is comparatively small interval $w_1 + w_2 = 0.0259$ a.u. in comparison with the $E_{6p_{3/2}} - E_{5d_{5/2}} = 0.0742$ a.u. energy difference.

The final results for quantity M defined by equation (7) for the 2E1 $5d_{5/2}$–$6s$ transition vary only weakly with ω (from 8607 to 8247 a.u.). Multiplying these values by a factor of $\frac{8}{9\pi}\alpha^6\omega_1^3\omega_2^3$ (see equation (1)) and integrating over ω, we find the two-photon decay rate for the $5d_{5/2}$–$6s$ 2E1 transition. In figure 1, we illustrate the differential rate $dW/d\omega$ for the 2E1 two-photon $5d_{5/2}$–$6s$ transition in Ba II. The total 2E1 decay rate is equal to $8.079 \times 10^{-7}\ \text{s}^{-1}$.

In table 5, we list the results for two-photon transition rates (s^{-1}) for the $4s$–$3d_j$ transitions in Ca^+, $5s$–$4d_j$ transitions in Sr^+ and $6s$–$5d_j$ transitions in Ba^+. We note that the Sr^+ result was previously quoted in [37]. We list both the lowest order DF results (in column labelled 'lowest order') and our final SD all-order results (in column labelled 'All order'). We find very large differences (factors of 10–50) between the lowest order and final all-order results. These differences are due in part to use of different $\epsilon = w_1 + w_2$ intervals in these calculations. These intervals are defined by the energy difference between the final and initial transition states, $E_{nd_j} - E_{(n+1)s}$. In the lowest order calculation, the lowest order values of the intervals ϵ are used, while in the final all-order calculation, the experimental values of these intervals are used. For the example given in table 4, the DF value of $\epsilon = 0.0350$ a.u. is 1.35 larger than the experimental value. The values of reduced electric-dipole transition matrix elements also decrease with inclusion of the correlation effects (compare results in columns with 'DF' and 'SD' labels in table 3). As a result, the values of $\sum D^{n3/2}(w_1)$ and $\sum D^{n3/2}(w_2)$ decrease by a factor of 2 and the coefficient of $\frac{8}{9\pi}\alpha^6\omega_1^3\omega_2^3$ in equation (1) decreases by a factor of 5.6 in the case of the $5d_{5/2}$–$6s$ transition in Ba^+.

Table 5. Two-photon decay rates (s^{-1}) for the nd_j–$(n+1)s$ transitions in Ba^+ ($n = 5$), Sr^+ ($n = 4$) and Ca^+ ($n = 3$) ions. The contributions of the 2E1 decay channel to the nd lifetimes are given in column labelled 'Contr.' in %.

Ion	Transition	Lowest order	All order	Contr.
Ca^+	$3d_{5/2}$–$4s$	6.809 [−3]	1.989 [−4]	0.02
Ca^+	$3d_{3/2}$–$4s$	6.925 [−3]	1.960 [−4]	0.02
Sr^+	$4d_{5/2}$–$5s$	5.436 [−3]	7.614 [−4]	0.03
Sr^+	$4d_{3/2}$–$5s$	5.554 [−3]	7.050 [−4]	0.03
Ba^+	$5d_{5/2}$–$6s$	2.026 [−5]	8.079 [−7]	0.006
Ba^+	$5d_{3/2}$–$6s$	1.478 [−5]	3.077 [−7]	0.001

It is interesting to compare the small 2E1 contributions found here with the small M1 contributions to the $nd_{5/2}$ decay rate given in [38] and elsewhere. For the $3d_{5/2}$ state of Ca^+ the M1 rate $2.41 \times 10^{-6}\ \text{s}^{-1}$ is much smaller than the 2E1 rate $1.99 \times 10^{-4}\ \text{s}^{-1}$. For the $4d_{5/2}$ state of Sr^+ the M1 rate $2.38 \times 10^{-4}\ \text{s}^{-1}$ is comparable to the 2E1 rate $7.61 \times 10^{-4}\ \text{s}^{-1}$. Finally, for the $5d_{5/2}$ state of Ba^+ the M1 rate $5.54 \times 10^{-3}\ \text{s}^{-1}$ is much larger than the 2E1 rate $8.08 \times 10^{-7}\ \text{s}^{-1}$. Among these small corrections, only the M1 rate for Ba^+ has any significance at the present level of experimental accuracy.

4. Conclusion

We have calculated two-photon decay rates for the $4s$–$3d_j$ transitions in Ca^+, $5s$–$4d_j$ transitions in Sr^+ and $6s$–$5d_j$

transitions in Ba^+. We find that the lowest order values of these rates are strongly modified by correlation corrections. The lowest-order calculation overestimates the values of these decay rates by factors of 10–50. Our final all-order results show that the contributions of the 2E1 decay channel to the lifetimes of metastable nd levels of Ca^+, Sr^+ and Ba^+ is negligible (0.001–0.03%) at the present level of theoretical and experimental precision. For even A isotopes, further improvement in theoretical nd_j lifetimes requires more refined understanding of many-body corrections to atomic wavefunctions and for odd A isotopes ($^{43}Ca^+$,$^{87}Sr^+$,$^{131,\,133}Ba^+$), hyperfine quenching is expected to modify the existing calculations significantly.

Acknowledgments

We would like to thank Charles W Clark for bringing this problem to our attention. This work was supported in part by US National Science Foundation grant No. PHY-07-58088.

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