



HAL
open science

Calculation of radial matrix elements and radiative lifetimes for highly excited states of alkali atoms using the Coulomb approximation

F. Gounand

► **To cite this version:**

F. Gounand. Calculation of radial matrix elements and radiative lifetimes for highly excited states of alkali atoms using the Coulomb approximation. *Journal de Physique*, 1979, 40 (5), pp.457-460. 10.1051/jphys:01979004005045700 . jpa-00209126

HAL Id: jpa-00209126

<https://hal.science/jpa-00209126>

Submitted on 4 Feb 2008

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Classification
Physics Abstracts
32.70

Calculation of radial matrix elements and radiative lifetimes for highly excited states of alkali atoms using the Coulomb approximation

F. Gounand

Centre d'Etudes Nucléaires de Saclay, Service de Physique Atomique, B.P. n° 2, 91190 Gif sur Yvette, France

(Reçu le 25 octobre 1978, révisé le 3 janvier 1979, accepté le 22 janvier 1979)

Résumé. — Les éléments de matrice radiaux mettant en jeu des états fortement excités des atomes alcalins sont calculés à l'aide de l'approximation Coulombienne. Le choix du critère de coupure a fait l'objet d'une étude détaillée. Ces éléments de matrice (disponibles sur demande adressée à l'auteur) peuvent être utilisés pour le calcul des forces d'oscillateur, durées de vie, rapports de branchement, polarisabilités des états de Rydberg des alcalins. Nous présentons le calcul des durées de vie radiative des états S, P, D et F très excités ($10 \leq n \leq 28$) des atomes alcalins. Les durées de vie calculées sont en bon accord avec les résultats expérimentaux disponibles.

Abstract. — Radial matrix elements have been computed involving highly excited states of alkali atoms. An entirely analytical Coulomb method has been used. Particular attention has been paid in the choice of the cut criterion. The extensive data are available from the author upon request and can be used to compute, for example, oscillator strengths, radiative lifetimes, branching ratios and polarizabilities of alkali Rydberg states. In order to test the results, radiative lifetimes have been derived for highly excited ($10 \leq n \leq 28$), S, P, D and F states of alkali atoms. The computed lifetimes are reported and are observed to be in good agreement with the available experimental data.

1. **Introduction.** — The interest in studying the properties of Rydberg atoms has been clearly pointed out by recent experimental and theoretical work [1-5]. A knowledge of oscillator strengths, radiative lifetimes and polarizabilities for highly excited states is often needed in these studies. All these quantities require the calculation of radial matrix elements involving highly excited levels. There exists in the literature some theoretical results, mainly concerning the oscillator strengths, but they are, in general, limited to the lowest states [6, 7] ($n \sim 10$) or to some particular spectroscopic series [8-10]. Only Anderson and Zilitis [11, 12] have reported extensive oscillator strength calculations (up to $n \sim 18$) made by using a parametric potential. But it seems difficult to extrapolate their results to more highly excited states for which experimental results begin to appear [13-15]. Thus extensive tables of radial matrix elements involving alkali Rydberg states would clearly be of some interest for the physicists working in this area of research. To our knowledge such results are not presently available for highly excited states.

The use of an elaborate theoretical model taking into account accurate radial wave functions (i.e. including core polarization as well as spin-orbit effects) would require prolonged computation time.

Thus, only approximate methods can be considered for extensive calculations of radial matrix elements. The well known Coulomb approximation [16] (here after referred as C.A.) seems to provide the best compromise between computation time and accuracy. We will see that a proper choice of the cut-off criterion for the asymptotic expansion (see § 2) and the use of high precision subroutines allow the obtainment of the radial matrix elements even for high principal quantum number n values. We have computed all the radial matrix elements involving S, P, D and F levels of alkali atoms up to $n = 28$. For obvious reasons all these elements are not listed here but are available upon request from the author [17]. We report here, as an example of application, the results of calculations concerning the radiative lifetimes of highly excited ($10 \leq n \leq 28$) S, P, D and F levels of alkali atoms. Only states with $n \geq 10$ have been considered (somewhat arbitrarily) as Rydberg states and are therefore concerned in the present work. However, the calculations have also been performed for low-lying states.

2. **Method.** — We use the very well known method first proposed by Bates and Damgaard [16]. The basic idea was that asymptotic forms of bound state Cou-

lomb wave functions can be used because the contribution to the dipole integral from the region of space near the origin (i.e. for $r \rightarrow 0$), where this form is invalid, is small. We only summarize now the main features of the method [18].

We want to compute

$$S = \langle n' l' | r | n l \rangle = \int_0^\infty P_{n'l'}(r) r P_{nl}(r) dr. \quad (2.1)$$

Using the asymptotic form of the bound state Coulomb wave functions $P_{n'l'}(r)$ and $P_{nl}(r)$ one finally obtains

$$\begin{aligned} S &= KK' \sum_{p=0} A_p \left(\frac{1}{n^{*'}} + \frac{1}{n^*} \right)^{-(n^{*'} + n^* + 2 - p)} \times \\ &\quad \times \Gamma(n^{*'} + n^* + 2 - p) \\ &= KK' \sum_{p=0} T(p) \end{aligned} \quad (2.2)$$

where K and K' are the normalization factors [19] corresponding respectively to the (n, l) and (n', l') levels and n^* and $n^{*'}$ their effective quantum numbers ($n^* = n - \delta$, δ being the quantum defect). A_p is given by

$$A_p = \sum_{\substack{t, t' \\ \text{for } t+t'=p}} a_t a_{t'} = \sum_{t=0}^p a_t a_{t-p} \quad (2.3)$$

where a_t (and $a_{t'}$) are coefficients that are calculated from the following equations :

$$\begin{aligned} a_0 &= 1 \\ a_t &= a_{t-1} \left(\frac{n^*}{2t} \right) [l(l+1) - (n^* - t)(n^* - t + 1)]. \end{aligned} \quad (2.4)$$

It is well known that the numerical results are sensitive to the number of terms included in the summation (2.2) and that it is very difficult to give any precise justification for the choice of a given cut criterion. In their original paper [16] Bates and Damgaard used the condition $(n^{*'} + n^* - p) \geq 1$. However, one can easily see that the first neglected term is not always small compared to the sum of the others. The behaviour of the asymptotic expansion (2.2) has been investigated for all the following series of Na, K, Rb and Cs : S \leftrightarrow P, P \leftrightarrow D, D \leftrightarrow F and F \leftrightarrow G. When considering the sign, the same behaviour was observed : first the sign of $T(p)$ alternates, then for some value of p the terms keep the same sign until p_0 , the value for which the sign changes. For Na, Rb and Cs we use the cut-off criterion proposed by Bebb [18], i.e. one terminates the series for $p = p_0 - 1$ and adds the average of the two following terms (of opposite sign). Thus :

$$S = KK' \left[\sum_0^{p_0-1} T(p) + \frac{1}{2} (T(p_0) + T(p_0 + 1)) \right]. \quad (2.5)$$

In the case of potassium it is observed that $T(p_0 + 1)$ is always much greater than $T(p_0)$, indicating that the expansion can be assumed to terminate exactly. In this later case we use :

$$S = KK' \sum_0^{p_0} T(p). \quad (2.6)$$

Our choice was confirmed by considering the very sensitive $(n_0 S - nP)$ oscillator strength series (see below for the calculation) for which elaborate calculations [9, 10] as well as precise determinations [8, 20] are available. The procedure chosen appears to be the most efficient when using an entirely analytical C.A. method.

For a given alkali atom the basic parameter of the C.A. method is the effective quantum number n^* , which is determined from the energy levels $E_{n,l}$ [19]. For the lower states accurate data are available [21-23] allowing the obtainment by a numerical fit, of an extended Ritz formula :

$$\begin{aligned} \delta_l &= n - n^* = a_0 + a_1(n^*)^{-2} + \\ &\quad + a_2(n^*)^{-4} + a_3(n^*)^{-6} \end{aligned} \quad (2.7)$$

where δ_l is the quantum defect depending only on l . We solved (2.7) for n^* and verified that the corresponding $E_{n,l}$ values were in good agreement with those quoted in the tables of Moore [24] or, when available, with recent experimental results [25, 26]. This method provides a consistent set of energy values and eliminates some suspicious values appearing in the available tables.

3. Results and accuracy. — The calculations were performed on a CDC 7600 computer. Double precision was used, corresponding to about 27 decimal digits. The Γ functions were computed using the results of refs. [27, 28]. Such a high precision is required for high n values. The use of single precision limited the calculations to $n < 17$. All the matrix elements were obtained in a time less than 100 s.

It is obvious that the accuracy of the results depends upon the $E_{n,l}$ values used. Obtaining these from an extended Ritz formula eliminates local accidents. The accuracy of the C.A. method has been widely discussed [7, 29]. The main cause of uncertainty is due to the choice of the cut criterion, for which no precise theoretical justification can be given. To try to avoid such a problem, numerical C.A. methods have been proposed [7, 29]. But they require computing times much greater than the present method, the accuracy of which is observed to be comparable even for the case of the very sensitive S \leftrightarrow P series.

4. Application to the determination of radiative lifetimes. — The oscillator strengths and Einstein coefficients are given by the following equations [30] (one considers two levels a and b, with $E_b > E_a$) :

$$f_{a \rightarrow b} = \frac{303.75 |S|^2 \max(l_a, l_b)}{g_a} \quad (4.1)$$

and
$$A_{b \rightarrow a} = \frac{6.6702 \times 10^{15} g_a f_{a \rightarrow b}}{\lambda^2 g_b} \quad (4.2)$$

where λ (in Å) is the wavelength of the (b → a) transition, S (in a.u.) the dipole integral given by (2.2) and g the statistical weight of the level (i.e. $2l + 1$). The lifetime of a given level is calculated by :

$$\tau_b = \frac{1}{\sum_f A_{b \rightarrow f}} \quad (4.3)$$

Table I. — Lifetimes τ (in 10^{-6} s) for rubidium excited states.

n	S	P	D	F
10	0.427	1.19	1.07	0.686
11	0.628	1.71	1.41	0.904
12	0.887	2.40	1.83	1.17
13	1.21	3.23	2.33	1.47
14	1.60	4.23	2.91	1.83
15	2.07	5.41	3.61	2.24
16	2.62	6.80	4.40	2.71
17	3.26	8.41	5.30	3.25
18	4.00	10.2	6.32	3.85
19	4.85	12.3	7.47	4.52
20	5.81	14.7	8.75	5.26
21	6.88	18.0	10.2	6.08
22	8.08	21.1	11.7	6.98
23	9.41	24.5	13.5	7.97
24	10.9	28.3	15.4	9.04
25	12.5	32.5	17.4	10.2
26	14.2	37.0	19.7	11.5
27	16.2	41.9	22.1	12.8
28	18.3	47.2	24.8	14.3

where the summation holds for all levels f ($E_f < E_b$) radiatively connected to the level b . Table I gives the computed lifetimes in the case of rubidium and table II reports the τ_0 and α parameters obtained from a numerical fit of the τ values ($10 \leq n \leq 28$) to the formula (which is currently used to fit the experimental data [31])

$$\tau = \tau_0 n^{*\alpha} \quad (4.4)$$

All the α values are close to 3 which is the value expected in the limit of n large from the consideration of the oscillator strength sum rules [8] ⁽¹⁾. Comparison between some recent experimental results and our data are reported in table III for sodium and rubidium.

Table II. — α and τ_0 (in 10^{-9} s) parameters of the equation $\tau = \tau_0 n^{*\alpha}$ (see text) for the alkali atoms.

		S	P	D	F
Na	α	3.00	3.11	2.99	2.96
	τ_0	1.38	8.35	0.96	1.13
K	α	3.00	2.78	2.82	2.95
	τ_0	1.32	6.78	5.94	0.83
Rb	α	2.94	3.02	2.85	2.95
	τ_0	1.43	2.76	2.09	0.76
Cs	α	2.96	2.94	2.93	2.94
	τ_0	1.43	4.42	0.96	0.69

⁽¹⁾ The consideration of the partial sum rule (eq. (3) of ref. [8]) for the (n_0 S-nP) series easily explains (the first term being close to unity, and the sum being unity) the extreme sensitivity of these series to cancellation effects in any method of calculation.

Table III. — Comparison between experimental and theoretical lifetimes for various highly excited alkali levels. All lifetimes are given in 10^{-6} s.

Alkali	Level	This work	Exp. [32, 14, 13, 15]	Th. [11, 12]	Th. [7]
Na	10S	0.90	1.02 ± 0.05	1.06	0.91
Na	11S	1.25	1.28 ± 0.13	1.43	1.26
Na	13S	2.18	2.27 ± 0.17	2.52	
Na	10D	0.92	0.97 ± 0.035	0.95	0.92
Na	12D	1.59	1.65 ± 0.15	1.58	1.57
Na	13D	2.02	2.12 ± 0.40	2.09	
Na	13F	2.26	2.27 ± 0.40		
Na	14F	2.81	2.64 ± 0.45		
Na	15F	3.45	3.54 ± 0.50		
Rb	12P	2.40	1.55 ± 0.20	2.22	
Rb	14P	4.23	2.60 ± 0.40	3.95	
Rb	17P	8.41	6.40 ± 1.30	7.93	
Rb	22P	21.1	14.0 ± 5.0		
Rb	11F	0.90	0.90 ± 0.14		
Rb	13F	1.47	1.62 ± 0.24		
Rb	15F	2.24	1.96 ± 0.29		
Rb	17F	3.25	2.96 ± 0.44		
Rb	19F	4.52	4.00 ± 0.80		
Rb	21F	6.08	6.70 ± 1.70		

All the computed values agree well with the experimental ones, except for the P levels of rubidium, for which better agreement is obtained by the parametric potential method. But more results are needed to draw any firm conclusion. The results concerning the F levels agree quite well with the measured values. This is due to the fact that these levels are almost hydrogenic, even for the heaviest alkalis.

5. **Conclusion.** — Radial matrix elements have been computed for highly excited alkali atoms over a wide range of principal n and orbital l quantum number values. Such data should be of interest for any one working in the field of Rydberg states. The method uses an entirely analytical C.A. method. Particular

attention has been paid to the choice of the cut criterion. We have also derived the radiative lifetimes of highly excited alkali atoms. The computed values are observed to be, in general, in agreement with the experimental results. For higher n values ($n > 30$) the use of the C.A. method is possible but requires computation procedures different from the brute force one used in the present article [33-35]. We should finally like to emphasize that the usefulness of the present work lies mainly in the completeness and the self consistency of the results.

Acknowledgments. — The author would like to thank Dr. J. Berlande for helpful discussions.

References

- [1] GALLAGHER, T. F., EDELSTEIN, S. A. and HILL, R. M., *Phys. Rev. Lett.* **35** (1975) 644.
- [2] GALLAGHER, T. F., EDELSTEIN, S. A. and HILL, R. M., *Phys. Rev. A* **15** (1977) 1945.
- [3] FABRE, C., HAROCHE, S. and GOY, P., *Phys. Rev. A* **18** (1978) 229.
- [4] OMONT, A., *J. Physique* **38** (1977) 1343.
- [5] GOUNAND, F., HUGON, M., FOURNIER, P. R. and BERLANDE, J., *J. Phys. B.* (to be published).
- [6] WARNER, B., *Mon. Not. R. Astron. Soc.* **139**(1968) 115.
- [7] LINDGARD, A. and NIELSEN, S. E., *Atom. Data Nucl. Data Tables* **19** (1977) 534.
- [8] MARR, G. V. and CREEK, D. M., *Proc. R. Soc. A* **304** (1968) 245.
- [9] WEISHEIT, J. C., *Phys. Rev. A* **5** (1972) 1621.
- [10] NORCROSS, D., *Phys. Rev. A* **7** (1973) 606.
- [11] ANDERSON, E. M. and ZILITIS, V. A., *Opt. Spektrosk.* **16** (1964) 177; *Opt. Spectrosc.* **16** (1964) 99.
- [12] ANDERSON, E. M. and ZILITIS, V. A., *Opt. Spektrosk.* **16** (1964) 382; *Opt. Spectrosc.* **16** (1964) 211.
- [13] GOUNAND, F., FOURNIER, P. R., CUVELLIER, J. and BERLANDE, J., *Phys. Lett.* **59A** (1976) 23.
- [14] GALLAGHER, T. F., COOKE, W. E. and EDELSTEIN, S. A., *Phys. Rev. A* **17** (1978) 904.
- [15] HUGON, M., GOUNAND, F. and FOURNIER, P. R., *J. Phys. B* **11** (1978) L-605.
- [16] BATES, D. R. and DAMGAARD, A., *Phil. Trans. R. Soc. A* **242** (1949) 101.
- [17] GOUNAND, F., unpublished C.E.A. report.
- [18] BEBB, H. B., *Phys. Rev.* **149** (1966) 25.
- [19] BURGESS, A. and SEATON, M. J., *Mon. Not. R. Astron. Soc.* **120** (1960) 121.
- [20] PICHLER, G., *J. Quant. Spectrosc. Radiat. Transfer* **16** (1976) 147.
- [21] RISBERG, P., *Ark. Fys.* **10** (1956) 583.
- [22] JOHANSSON, I., *Ark. Fys.* **20** (1961) 135.
- [23] KLEIMAN, H., *J. Opt. Soc. Am.* **52** (1962) 441.
- [24] MOORE, C. E., Atomic Energy Levels (NBS Washington) 1971.
- [25] FERGUSON, A. I. and DUNN, M. H., *Opt. Commun.* **23** (1977) 227.
- [26] MIRZA, M. Y. and DULEY, W. W., *J. Phys. B.* **11** (1978) 1917.
- [27] WRENCH, J. W., *Math. Comp.* **22** (1968) 620.
- [28] SPIRA, R., *Math. Comp.* **25** (1971) 317.
- [29] FRIEDRICH, H., KATTERBACH, K. and TREFFTZ, E., *J. Quant. Spectrosc. Radiat. Transfer* **10** (1970) 11.
- [30] CORNEY, A., *Adv. Electron. Electron Phys.* **29** (1970) 119.
- [31] DEECH, J. S., LUYPAERT, R., PENDRILL, L. R. and SERIES, G. W., *J. Phys. B.* **10** (1977) L-137.
- [32] GALLAGHER, T. F., EDELSTEIN, S. A. and HILL, R. M., *Phys. Rev. A* **11** (1975) 1504.
- [33] EDMONDS, A. R. and KELLY, B. A. 1978 (to be published).
- [34] PICART, J., EDMONDS, A. R. and TRAN MINH, N., *J. Phys. B.* **11** (1978) L-651.
- [35] VAN REGEMORTER, H., HOANG BINH, D. and PRUD'HOMME, M., (1978) to be published.