Multichannel quantum-defect theory of lifetimes for highly excited states of atoms: Calculation of Yb lifetimes in the perturbed $6snd\ ^{1,3}D_2$ sequences

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By combining the quantum theory of radiative transition with multichannel quantum-defect theory, we have derived a general formula to calculate the lifetimes of highly excited states for atoms. As an example, we have evaluated the lifetimes for the perturbed $6snd\ ^1D_2$ ($n=8$–40) and $6snd\ ^3D_2$ ($n=10$–26) Rydberg levels, and the perturbers of the ytterbium atom. We have not only obtained results that are in perfect agreement with the recent measurements, but also predicted the lifetimes of 18 other highly excited states. The results indicate that the dramatic variation for lifetimes of Rydberg states in the vicinity of perturbing states is due to the strong channel interaction.

I. INTRODUCTION

A considerable number of experiments to study the highly-excited-state structures of atoms has been performed in recent years. Meanwhile, multichannel quantum-defect theory (MQDT) has evolved into a powerful tool for the interpretation of these atomic data.[1–3] However, up to now most of these applications of MQDT have focused on the analyses of energy spectra of highly excited states (including bound and autoionization states). There have been only a few reports on research of the lifetimes for highly excited states of atoms using MQDT. Aymar *et al.* proposed a semiempirical formula and used it to calculate the lifetimes for Ba in the perturbed $6snd\ ^{1,3}D_2$ series[4] and $6sns\ ^1S_0$ series.[5] The purpose of the present paper is to develop a general MQDT formalism about the lifetimes for highly excited states of atoms, and to give an example of its applications—calculation of lifetimes of Yb in the perturbed $6snd\ ^{1,3}D_2$ Rydberg levels.

The ytterbium atom has a closed $4f$ subshell and two $6s$ electrons in its ground configuration, $[\mathrm{Xe}]4f^{14}6s^2$, and resembles an alkaline-earth element. In fact, its $4f$ electron can be easily excited and complex configurations $4f^{13}nln'l'n''l''$ with four valence electrons can be expected to strongly perturb the $4f^{14}6snl$ Rydberg series. Therefore the Yb spectrum presents much more complicated characters than those of alkaline-earth elements. Wyart and Camus,[6] Camus *et al.*,[7] and Aymar *et al.*[8] performed experimental investigations and theoretical analysis of the perturbed $6snl$ Rydberg series. Recently Baumann and co-workers,[9,10] Bai and Mossberg,[11] Wang *et al.*,[12] and Jiang *et al.*[13] measured the lifetimes for excited levels of the Yb atom. In this paper we report the computed results for Yb in the perturbed $6snd\ ^{1,3}D_2$ Rydberg levels. In Sec. II we derive the general formula to calculate the lifetimes for highly excited states of atoms by combining the quantum theory of radiative transition with MQDT. In Sec. III we apply this general formula to evaluate the lifetimes for the perturbed $6snd\ ^{1,3}D_2$ Rydberg levels of the Yb atom, and present the detailed calculated results and a discussion. Finally, we give several conclusions in Sec. IV.

II. MQDT FOR LIFETIMES OF HIGHLY EXCITED STATES OF ATOMS

In light of the quantum theory of radiative transition[14] the total probability per unit time of an atom in a specific level (γJ) making a spontaneous transition to the level $(\gamma' J')$ can be inclusively expressed as

$$\Gamma(\gamma'J';\gamma J)=\sum_k\left[\Gamma_k^E(\gamma'J';\gamma J)+\Gamma_k^M(\gamma'J';\gamma J)\right], \quad (1)$$

where Γ_k^E is the electric 2^k-pole transition probability and

$$\Gamma_k^E(\gamma'J';\gamma J)=\sum_M\sum_{M'}\sum_q|\langle\gamma'J'M'|\hat{Q}_{kq}|\gamma JM\rangle|^2, \quad (2)$$

in which the electric moment operator

$$\hat{Q}_{kq}=\frac{2(2k+1)(k+1)}{[(2k+1)!!]^2k}\frac{(2\pi\sigma)^{2k+1}}{\hbar}\frac{1}{2J+1}\times\left[-e\sum_i r_i^kC_{kq}(\theta_i;\phi_i)\right], \quad (3)$$

and Γ_k^M is the magnetic 2^k-pole transition probability and

$$\Gamma_k^M(\gamma'J';\gamma J)=\sum_M\sum_{M'}\sum_q|\langle\gamma'J'M'|\hat{\mathcal{M}}_{kq}|\gamma JM\rangle|^2, \quad (4)$$

in which magnetic moment operator

$$\hat{\mathcal{M}}_{kq}=\frac{2(2k+1)(k+1)}{[(2k+1)!!]^2k}\frac{(2\pi\sigma)^{2k+1}}{\hbar}\frac{1}{2J+1}\times\left[-\frac{e\hbar}{mc}\sum_i\nabla\gamma_i^kC_{kq}(\theta_i;\phi_i)\left[\frac{l_i}{2k+1}+\mathbf{s}_i\right]\right]. \tag{5}$$

On the other hand, for a highly excited state $|\gamma JM\rangle$, according to MQDT,[1,2] the normalized wave function is represented for $r>r_0$ as a superposition of the dissociation channels (the i channels) in the form

$$|\gamma JM\rangle=\sum_i\phi_iP_i^{(n)}Z_i^{(n)}, \tag{6}$$

where $P_i^{(n)}$ is the electron wave function and can be expressed in terms of the analytically known Whittaker function,[3] and ϕ_i denotes the wave functions of the residual ion core, the spin and the angular momentum coupling in the i channel. The coefficients $Z_i^{(n)}$ measure the mixing between the dissociation channels for the nth state, and depend on the MQDT basic parameters μ_α and $U_{i\alpha}$,

$$Z_i^{(n)}=(-1)^{l_i+1}(\nu_i^{(n)})^{3/2}\times\sum_\alpha U_{i\alpha}\cos[\pi(\nu_i^{(n)}+\mu_\alpha)]A_\alpha^{(n)}/N_n, \tag{7}$$

where N_n is the normalization factor,[2] $A_\alpha^{(n)}$ are the coefficients which measure the mixing between the compound channels (the α channels),[2] and $\nu_i^{(n)}$ is a MQDT effective quantum number. Therefore the total radiative decay rate of the nth level can be written as

$$\Gamma_n=\sum_i\sum_j Z_i^{(n)}Z_j^{(n)}\Gamma_{ij}^{(n)}, \tag{8}$$

where

$$\Gamma_{ij}^{(n)}=\sum_{\gamma'}\sum_{J'}\sum_{K}\sum_{M}\sum_{M'}\sum_{q}(\langle\gamma'J'M'|\hat{Q}_{kq}|\phi_i^{(n)}P_i^{(n)}\rangle\langle\phi_j^{(n)}P_j^{(n)}|\hat{Q}_{kq}|\gamma'J'M'\rangle+\langle\gamma'J'M'|\hat{\mathcal{M}}_{kq}|\phi_i^{(n)}P_i^{(n)}\rangle\langle\phi_j^{(n)}P_j^{(n)}|\hat{\mathcal{M}}_{kq}|\gamma'J'M'\rangle). \tag{9}$$

Equation (8) can be also rewritten as

$$\Gamma_n=\sum_i(Z_i^{(n)})^2\Gamma_{ii}^{(n)}+\sum_i\sum_{\substack{j\\(j\neq i)}}Z_i^{(n)}Z_j^{(n)}\Gamma_{ij}^{(n)}. \tag{8$'$}$$

Here $(Z_i^{(n)})^2\Gamma_{ii}^{(n)}$ on the right side of Eq. (8′) means the decay rate of the atom in the nth level making spontaneous transitions to all possible lower levels through the i channel, and the cross term $Z_i^{(n)}Z_j^{(n)}\Gamma_{ij}^{(n)}$ $(i\neq j)$ represents the mixing decay rate due to the interaction between the i channels. It is worthwhile to point out that neglecting all cross terms in Eq. (8′), and taking $\Gamma_{ii}^{(n)}=\gamma_i/(n^*)^3$ for the Rydberg series and $\Gamma_{ii}^{(n)}=\gamma_i$ for the perturbing channels, Eq. (8) can be reduced to the semiempirical formula proposed by Aymar and co-workers.[4,5] We expect that Eq. (8) should provide a satisfactory description for the effects of the channel interaction and the cancellation interference on the decay rates of atoms.

Similarly, if $|\gamma JM\rangle$ is represented as a superposition of the α-channel wave functions

$$|\gamma JM\rangle=\sum_\alpha A_\alpha^{(n)}\psi_\alpha^{(n)}, \tag{10}$$

the total decay rate Γ_n can be expressed in the form

$$\Gamma_n=\sum_\alpha\sum_\beta A_\alpha^{(n)}A_\beta^{(n)}\Gamma_{\alpha\beta}^{(n)}, \tag{11}$$

where

$$\Gamma_{\alpha\beta}^{(n)}=\sum_{\gamma'}\sum_{J'}\sum_{K}\sum_{M}\sum_{M'}\sum_{q}(\langle\gamma'J'M'|\hat{Q}_{kq}|\psi_\alpha^{(n)}\rangle\langle\psi_\beta^{(n)}|\hat{Q}_{kq}|\gamma'J'M'\rangle+\langle\gamma'J'M'|\hat{\mathcal{M}}_{kq}|\psi_\alpha^{(n)}\rangle\langle\psi_\beta^{(n)}|\hat{\mathcal{M}}_{kq}|\gamma'J'M'\rangle). \tag{12}$$

Finally, we obtain the natural lifetime of the atom in the nth excited state

$$\tau_n=1/\Gamma_n, \tag{13}$$

where Γ_n is given by Eq. (8) or (11).

III. LIFETIME OF Yb IN PERTURBED $6snd$ $^{1,3}D_2$ RYDBERG SERIES

As stated above, the lifetimes of atoms in highly excited states can be calculated in terms of Eqs. (8), or (11), and (13). However, from Eq. (9) we see that $\Gamma_{ij}^{(n)}$ is a complicated integral whose value varies with energy level and depends on the value of the pair of (i,j). Its direct integration calculation, generally, should concern the wave functions for the states with different parities and different values of J, L, and S. In the case of Yb $6snd$ $^{1,3}D_2$ Rydberg series, we need to know at least the wave functions with odd parity and $L,J=1,2,3$ for the dipole transition. Therefore this kind of integrating is very difficult. On the other hand, we can make appropriate adaptations to determine $\Gamma_{ij}^{(n)}$. Taking account of the dependences of $\Gamma_{ij}^{(n)}$ on energy level (n value) and channel

TABLE I. Values of Γ ($\Gamma_{ij}=\Gamma_{ji}$); units are $10^9\ \mathrm{s}^{-1}$.

$i \backslash j$	1	2	3	4	5
1	0.156 611				
2	−0.456 763	0.274 980			
3	−0.188 263	0.329 265	−0.029 869		
4	0.844 282	−0.167 901	−0.070 387	0.401 210	
5	−0.365 318	−0.337 527	0.515 642	−0.195 643	0.028 235

(i,j), we assume that the dependence of $\Gamma_{ij}^{(n)}$ on energy can be separated from its channel dependence. For example, let

$$\Gamma_{ij}^{(n)}=(\nu_i^{(n)}\nu_j^{(n)})^p\Gamma_{ij} , \tag{14}$$

where Γ_{ij} is no longer energy dependent, $\nu_i^{(n)}$ and $\nu_j^{(n)}$ are effective quantum numbers defined in MQDT, and p is an adjustable parameter. Γ_{ij} can be determined by fitting experimental data of lifetimes. Additionally, $\Gamma_{ij}^{(n)}$ can be expressed as a polynomial with respect to $1/n^*$, where n^* is the effective principal quantum number corresponding to the first ionization limit, namely,

$$\Gamma_{ij}^{(n)}=\sum_k C_{ij}^{(k)}(1/n^*)^k , \tag{15}$$

where the coefficients $C_{ij}^{(k)}$ are obtained by fitting experimental values of lifetimes.

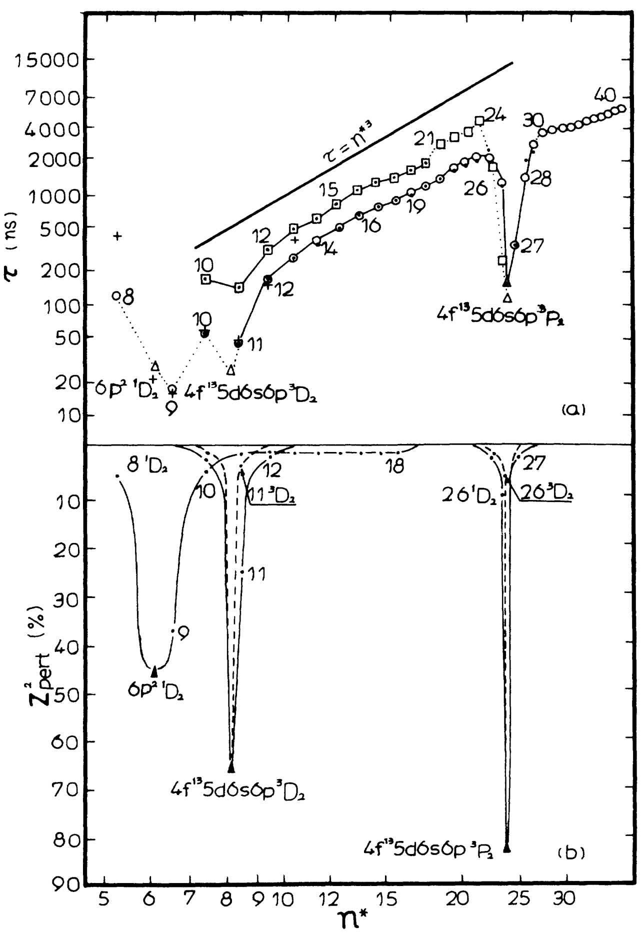

FIG. 1. (a) Lifetime values τ of Yb even-parity $J=2$ levels plotted against the effective principal quantum number n^* of a ln-ln scale. The symbols are + for experimental values from Ref. 10, ● for experimental values from Ref. 13, □ for theoretical values of $6snd\ ^3D_2$, ○ for theoretical values of $6snd\ ^1D_2$, and Δ for theoretical values of perturbers. (b) Fractional admixture of the perturbing levels (▲) in the $6snd\ ^{1,3}D_2$ levels (●).

Using the MQDT model with three ionization limits and five channels (which was proposed by Aymar *et al.*[8]) and the MQDT basic parameters obtained by revising the parameters of Aymar *et al.*,[8] we have calculated the mixing coefficients $Z_i^{(n)}$ for $6snd\ ^{1,3}D_2$ Rdyberg series. The results are shown in Fig. 1(b). Based on this, we have evaluated the lifetimes of Yb in the perturbed $6snd\ ^1D_2$ ($n=8$–40) series from Eq. (14) and $6snd\ ^3D_2$ ($n=10$–26) series from Eq. (15). Tables I and II give values of Γ_{ij} (for $p=-0.75$) and $C_{ij}^{(k)}$, respectively, obtained through the least-squares-fitting procedure. The calculated values for natural lifetimes of Yb in the $6snd\ ^{1,3}D_2$ series (including perturbers) in this work together with the recent measurement values[10,13] are listed in Table III. Figure 1(a) shows the ln-ln plot of the theoretical and experimental lifetimes versus the effective principal quantum number n^* ($\equiv\nu_1$). The admixture of the perturbers in the Rydberg series is shown in Fig. 1(b).

From Fig. 1 we find that in the vicinity of the perturbers, $6p^2\ ^1D_2$, $4f^{13}5d6s6p\ ^3D_2$, and $4f^{13}5d6s6p\ ^3P_2$,

TABLE II. Values of $C^{(k)}$ ($C_{ij}^{(k)}=C_{ji}^{(k)}$); units are $10^9\ \mathrm{s}^{-1}$.

i	$j \backslash k$	1	2	3
1	1	−0.030 865	0.416 073	0.130 130
1	2	0.015 645	−0.990 219	8.452 151
1	3	0.104 765	2.764 967	−44.235 480
1	4	−0.047 649	0.560 673	−18.623 360
1	5	−0.199 329	−1.187 768	26.767 830
2	2	0.020 634	−0.239 706	−0.669 654
2	3	−0.064 156	0.255 056	−6.253 032
2	4	−0.081 106	−1.464 362	8.655 601
2	5	−0.046 219	1.147 486	−5.079 033
3	3	0.106 145	0.682 683	−0.801 074
3	4	−0.510 911	−2.350 052	3.255 799
3	5	−0.126 730	0.863 408	−5.140 790
4	4	0.086 573	−0.027 086	−22.653 180
4	5	−0.160 662	−0.294 530	49.314 530
5	5	0.361 610	−1.089 784	−8.867 341

the lifetimes of levels in the Rydberg series are dramatically influenced and considerably departed from the expected rule of $\tau \propto (n^*)^3$ because of channel interaction. Though the values of parameters listed in Table I are obtained in terms of experimental data of Jiang *et al.*[13] ($n \geq 10$), the computed lifetimes of $6s9d\ ^1D_2$, $6p^2\ ^1D_2$, and $6s8d\ ^1D_2$ are fairly well compatible with the measurement results of Baumann *et al.*[10] which were re-

TABLE III. Lifetimes of perturbed $6snd\ ^{1,3}D_2$ and perturbing levels.

Assignment	Level (cm^{-1})	Lifetimes (ns) Observed Ref. 16	Lifetimes (ns) Observed Ref. 14	Lifetimes (ns) Calculated
$6s8d\ ^1D_2$	46 405.6		466(70)	123.8
$6p^2\ ^1D_2$	47 421.0		21.8(9)	28.6
$6s9d\ ^1D_2$	47 821.8		16.1(7)	17.1
$6s10d\ ^3D_2$	48 357.6	174(10)		174.0
$6s10d\ ^1D_2$	484 403.5	57.4(41)	58.5(87)	57.4
$4f^{13}5d6s6p\ ^3D_2$	48 762.5			25.5
$6s11d\ ^3D_2$	48 838.1	152.5(52)		152.5
$6s11d\ ^1D_2$	48 883.1	47.3(25)	49.4(74)	47.3
$6s12d\ ^3D_2$	49 161.6	319(17)		319.0
$6s12d\ ^1D_2$	49 176.0	177.2(69)	153(23)	177.4
$6s13d\ ^3D_2$	49 399.1	494(16)		494.0
$6s13d\ ^1D_2$	49 408.6	260.6(90)	415(62)	255.9
$6s14d\ ^3D_2$	49 576.4	616(21)		616.0
$6s14d\ ^1D_2$	49 583.3	363(12)		385.1
$6s15d\ ^3D_2$	49 712.1	840(39)		840.0
$6s15d\ ^1D_2$	49 717.1	533(27)		514.3
$6s16d\ ^3D_2$	49 818.2	1101(64)		1101.0
$6s16d\ ^1D_2$	49 822.1	654(30)		632.6
$6s17d\ ^3D_2$	49 902.8	1269(64)		1269.0
$6s17d\ ^1D_2$	49 905.8	752(43)		752.6
$6s18d\ ^3D_2$	49 971.3	1420(60)		1420.0
$6s18d\ ^1D_2$	49 973.7	874(44)		895.1
$6s19d\ ^3D_2$	50 027.7	1715(87)		1715.0
$6s19d\ ^1D_2$	50 029.6	1024(54)		1077.6
$6s20d\ ^3D_2$	50 074.4	2070(120)		2070.0
$6s20s\ ^1D_2$	50 076.1	1199(73)		1185.7
$6s21d\ ^3D_2$	50 113.7			2878.7
$6s21d\ ^1D_2$	50 115.2	1402(76)		1363.6
$6s22d\ ^3D_2$	50 147.0			3224.5
$6s22d\ ^1D_2$	50 148.6	1641(71)		1761.3
$6s23d\ ^3D_2$	50 175.6			3519.9
$6s23d\ ^1D_2$	50 176.5	1839(63)		1913.6
$6s24d\ ^3D_2$	50 200.0			4627.4
$6s24d\ ^1D_2$	50 201.0	2050(100)		2002.8
$6s25d\ ^3D_2$	50 221.5			1749.9
$6s25d\ ^1D_2$	50 222.1	2380(120)		2133.9
$6s26d\ ^3D_2$	50 240.1			264.1
$6s26d\ ^1D_2$	50 240.2	1286(64)		1284.1
$4f^{13}5d6s6p\ ^3P_2$	50 244.4	163.8(75)		163.8
$6s27d\ ^1D_2$	50 257.3	361(26)		364.7
$6s28d\ ^1D_2$	50 271.6	2020(130)		1433.6
$6s29d\ ^1D_2$	50 284.4	2370(150)		3010.0
$6s30d\ ^1D_2$	50 295.8			3753.1
$6s31d\ ^1D_2$	50 306.0			3827.4
$6s32d\ ^1D_2$	50 315.2			3994.9
$6s33d\ ^1D_2$	50 323.6			4173.3
$6s34d\ ^1D_2$	50 331.1			4361.4
$6s35d\ ^1D_2$	50 337.9			4604.7
$6s36d\ ^1D_2$	50 344.1			4859.3
$6s37d\ ^1D_2$	50 349.8			5160.2
$6s38d\ ^1D_2$	50 355.0			5410.4
$6s39d\ ^1D_2$	50 359.8			5734.7
$6s40d\ ^1D_2$	50 364.2			6112.2

ceived recently. Here the long lifetime of $6s8d\ ^1D_2$ level can be interpreted in terms of the cancellation interference effect due to the cross terms on the right side of Eq. (8). Moreover, we have also predicted the lifetimes of the ytterbium atom in the $6snd\ ^1D_2$ ($n=30$–40) and $6snd\ ^3D_2$ ($n=21$–26) Rydberg levels. There exist no measurements suitable for comparison yet. The computed lifetime of the perturber $4f^{13}5d6s6p\ ^3P_2$ by using the parameters listed in Table II which are obtained in terms of the data of $6snd\ ^3D_2$ series is also in good agreement with the experimental value.[13]

IV. CONCLUSION

In general, the lifetimes of atoms in single-electron excited states are much longer than those of double-electron or many-electron excited states, and basically vary with n^* as $(n^*)^3$. However, in the vicinity of perturbers the lifetimes of the perturbed Rydberg states are dramatically changed due to the channel interaction. This sensitivity of lifetimes for Rydberg states of atoms to perturbation provides an important criterion to test the MQDT wave functions. In the present paper the wave function is expressed as a superposition of all dissociation channels [see Eq. (6)], including the contributions from either long-lived Rydberg series or short-lived perturbing channels. The general expression of the radiative decay rate, Eq. (8), which includes the cross terms, ensures that all effects of channel interaction and cancellation interference on the total decay rate of atoms are taken into consideration. All these enable us to reproduce the relative variation of the observed lifetimes of Yb in $6snd\ ^{1,3}D_2$ Rydberg levels exactly and to predict the lifetimes of other highly excited states reasonably. These predicted lifetimes remain to be examined by new measurement results. The direct integration of $\Gamma_{ij}^{(n)}$ in Eq. (8) is a subject to be further probed into.

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