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Doubly excited circular Ba(6p, 21c) states : e-e interaction effects in weak external fields

L. Chen, M. Chéret, M. Poirier, F. Roussel, T. Bolzinger and G. Spiess

Service des Photons, Atomes et Molécules, C.E. Saclay, F91191 Gif-sur-Yvette Cedex, France

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Résumé. — Nous étudions l'atome circulaire doublement excité en présence de champs électrique et magnétique faibles et parallèles. Nous diagonalisons, dans une base tronquée, l'hamiltonien incluant l'interaction entre les deux électrons excités, l'effet Stark et l'effet Zeeman. L'électron de Rydberg, initialement dans un état circulaire, subit un mélange d'états, portant sur les nombres quantiques orbital et magnétique et résultant de la présence des champs externes ainsi que de l'excitation de l'électron interne. Le mélange dépend de la symétrie spatiale du cœur excité et de l'amplitude du champ électrique. On peut le détecter grâce à la méthode d'ionisation par champ qui constitue une nouvelle voie d'approche pour l'étude des états di-excités non autoionisants.

Abstract. — The behaviour of doubly excited circular atoms in weak parallel electric and magnetic fields has been studied. The Hamiltonian, including the e-e interaction between the two excited electrons, Stark and Zeeman effects, is diagonalized in a truncated basis. The Rydberg electron, initially in a circular state, experiences a mixing of its orbital and magnetic quantum numbers, due to the presence of the external fields and to the excitation of the inner electron. This mixing depends on the spatial symmetry of the excited core and on the amplitude of the electric field. It can be detected by the field-ionization method which provides a new way for studying non-autoionizing doubly excited states.

1. Introduction.

A two-electron atom is one of the simplest and most fundamental three-body Coulomb problem of quantum mechanics. It has been shown that a breakdown of the independent electron model and of the single configuration picture can occur in doubly excited states of atoms [1]. These so-called correlation effects are related to the Coulomb repulsion between the excited electrons [2]. Correlation effects have also been observed in alkaline-earth atoms. They are more pronounced when the two electron orbitals are highly excited with comparable radial extensions [3] or when one electron is in a ℓ -degenerate hydrogenic state [4]. Correlated electron states have been addressed using several theoretical approaches such as hyperspherical coordinates [5, 6], Lie group theory [7, 8] and molecular models [9, 10]. Besides, the behaviour of single-excited Rydberg states in external electric and magnetic fields has been the subject of numerous works [11]. However, for doubly excited states, only a limited number of studies take account of the effect of external fields [12-14]. Thus, from a

fundamental point of view, the physics of complex systems, such as doubly excited atoms in external fields, constitutes a new domain to be explored.

Experimentally, the preparation of a correlated state requires a multistep sequential excitation of each electron from the ground state of the atom (mostly an alkaline-earth atom). When this excitation takes place through intermediate doubly excited states with low angular momenta, the core penetration of the outer electron induces fast autoionization processes [15] which have proved to be a powerful means of investigation of these states [16]. In contrast, when the outer electron is in a high angular momentum state (quantum numbers $n_1, \ell_1 \gg 1$) while the inner electron is in a low-lying excited state ($n_2 \ll n_1$), the autoionization rate is strongly reduced [17, 18]. As shown in the Ba($6p_{1/2} n_1 \ell_1$) series [19], when $\ell_1 > 8$, the autoionization rate becomes slower than the radiative decay of the inner electron : 7.9 ns [20].

Our experiment has specialized in high- ℓ_1 doubly excited states since they are expected to have a practical interest in the preparation of correlated electron states. Several specific excitation schemes, overpassing the dipole selection rule, have been proposed [21-23] so as to raise one valence electron in high- ℓ_1 states. We have used in a barium atomic beam the recent Adiabatic Crossed-Field method (ACF) [24]. It offers the advantage of a selective electron excitation to a Rydberg circular [25] state $n_1 = 21$ (denoted 21c) whose angular momentum is both maximum ($\ell_1 = n_1 - 1$) and oriented ($\mu_1 = \ell_1$, μ_1 being the orbital magnetic quantum number). In an *oriented circular* state, the excited electron orbital has the shape of a torus (Fig. 1) around the classical Bohr orbit of radius $n_1^2 a_0$. For $n_1 \gg 1$, the outer electron does not penetrate the core and its wavefunction is *quasi-hydrogenic*. The ACF method is very efficient for any atomic species and has been already described in detail in previous publications [26-28]. A small external magnetic field ($B \sim 60$ gauss) removes the μ_1 degeneracy of the Rydberg electron and determines the orientation of its angular momentum along B .

Fig. 1. — Illustrative views of the two active-electron orbitals in an oriented circular Ba atom. The external circular orbital (drawn at scale for $n_1 = 21$ and denoted 21c) has the shape of a torus. Its angular momentum is maximum ($\ell_1 = n_1 - 1 = 20$) and oriented ($\mu_1 = \ell_1 = 20$) along the external electric field F (the magnetic field $B \parallel F$ is not represented). a) Single-excited circular atom Ba($6s_{1/2} 21c$). The inner orbital $6s_{1/2}$ is spherically symmetric (not at scale for visibility). b) Doubly excited circular atom Ba($6p_{3/2} 21c$). Note the marked anisotropic distribution of the inner orbital $6p_{3/2}(m_2 = 1/2)$ inducing a quadrupolar e-e interaction.

Furthermore a fast-rising electric field F of adjustable amplitude (parallel to B) is needed to stabilize the circular atoms before their detection, using a *field-ionization* technique [29].

Once single-excited circular Ba($6s_{1/2} 21c$) atoms are produced, their long radiative lifetime (0.4 ms for $n_1 = 21$) facilitates the laser excitation of the inner $6s_{1/2}$ electron, according to the Isolated Core Excitation method [23]. This technique has recently been used in our laboratory [30, 31] to prepare doubly excited circular Ba($6p_{1/2} 21c$) and Ba($6p_{3/2} 21c$) atoms, in the presence of F and B fields. Note that the experimental conditions for studying doubly excited states in weak external fields are achieved with the ACF method.

When the core of the circular atom is in the ground state (Fig. 1a), the closed shells and the $6s_{1/2}$ valence orbital exhibit spatial spherical symmetry. Under these conditions, it is well known that the oriented circular state $|n_1, \ell_1 = n_1 - 1, \mu_1 = \ell_1\rangle$ is a *field eigenstate* [31]. But under the same external field conditions, does the outer electron remain in a pure circular state when the core is excited? (Fig. 1b). In other words, to what extent is an uncoupled electron model adapted for the description of a doubly excited circular atom? This question is of importance for future experiments. The preparation of correlated doubly excited states will involve a sequential excitation of the inner electron to non-penetrating orbitals. During this excitation process, it would be desirable to fully characterize the outer electron state. Furthermore, if any (μ_1 and/or ℓ_1)-mixing were induced during the inner electron excitation, it would be useful to find the experimental conditions under which the outer electron is not significantly perturbed from its circular orbit. Finally, as the autoionization rate of a state like Ba($6p_j 21c$) is much slower than the radiative decay of the inner electron, some new measurable parameters are needed for the study of these weakly- or non-autoionizing states.

This paper aims at clarifying the above problems by presenting a quantum analysis of doubly excited circular states in the presence of parallel electric and magnetic fields, including the e-e Coulomb interaction. We have calculated the perturbation experienced by a Rydberg circular $21c$ state in the presence of weak static fields when the inner valence electron is excited to a low-lying state. The dynamics of these doubly excited states may be analyzed while neglecting any coupling with the continuum. In the calculations, the magnetic field value is left constant ($B = 60$ gauss). The F electric field effects are studied between 0 and 60 V/cm. In section 2, we define the Hamiltonian of the atom interacting with the fields and we select an appropriate two-electron basis. Numerical results are given for the Ba ($6p, 21c$) states in section 3. After diagonalization of the Hamiltonian matrix, we show that the circular state may be mixed with some other neighbouring states of different ℓ_1 and μ_1 values. The calculated mixing coefficients are found to depend critically on the external electric field and on the spatial symmetry of the core determined by the total angular momentum j_2 of the inner electron. In section 4 we discuss the possibility of identifying the e-e interaction using the field-ionization technique. Brief comments on recent observations are also given.

2. General formalism in a truncated basis.

Let us consider a barium atom in an electric F field and a magnetic B field parallel to F (quantization axis). The outer Rydberg electron, labeled 1, is in a high- ℓ_1 state which is *quasi-hydrogenic* (its quantum defect is neglected). It is much more excited than the inner valence electron labeled 2. The atomic Hamiltonian can be written as follows (in atomic units)

$$H = H_0 + H' \quad (1a)$$

with

$$H_0 = \frac{p_1^2}{2} - \frac{1}{r_1} + \frac{p_2^2}{2} + V(r_2) + \xi(r_2) \mathbf{l}_2 \cdot \mathbf{s}_2 \quad (1b)$$

and

$$H' = \frac{1}{r_{12}} - \frac{1}{r_1} + (\mathbf{l}_1 + \mathbf{l}_2 + 2 \mathbf{s}_2) \cdot \frac{\mathbf{B}}{2} + \mathbf{r}_1 \cdot \mathbf{F}. \quad (1c)$$

The atomic units for the fields are $F = 5.14 \times 10^9$ V/cm and $B = 2.35 \times 10^5$ T. H_0 includes kinetic energy operators and potential energies for the two electrons as well as the spin-orbit coupling for the valence electron. The fine-structure splitting of the circular state $21c$ is $1.5 \times 10^{-6} \text{ cm}^{-1}$. The Rydberg electron spin s_1 is thus decoupled and produces only an energy shift. It will not be considered in the analysis. H_0 is the sum of contributions of two independent electrons. The Rydberg electron (e_1) is in the Coulomb potential of the Ba^+ ion. The valence electron (e_2) is in the central potential $V(r_2)$ of the Ba^{++} core introducing a quantum defect δ_2 . We write the wavefunctions of the two independent electrons in the usual way :

$$\Psi_1(r_1) = R_{n_1 \ell_1}(r_1) Y_{\ell_1 \mu_1}(\theta_1, \phi_1) \quad (2a)$$

$$\Psi_2(r_2) = R_{\nu_2 j_2}(r_2) \Theta_{j_2 m_2 \ell_2}(\theta_2, \phi_2) \quad (2b)$$

where ν_2 is the effective quantum number for the n_2, ℓ_2, j_2 state of Ba^+ . $R_{n\ell}$, $Y_{\ell\mu}$ and $\Theta_{j m \ell}$ are normalized radial functions, spherical harmonics and angular spin-orbital functions respectively. m_2 is the valence-electron magnetic quantum number associated to j_2 . As $n_2 \ll n_1$ and $\ell_1 \gg 1$, the overlap between $\Psi_1(r_1)$ and $\Psi_2(r_2)$ is very small and the exchange effect is negligible. So the uncoupled eigenfunctions $\Psi_0(r_1, r_2)$ of H_0 and the corresponding eigenenergies E_0 are :

$$\Psi_0(r_1, r_2) = \Psi_1(r_1) \Psi_2(r_2) \quad (3)$$

$$E_0 = E_1 + E_2 = -\frac{1}{2} \left(\frac{1}{n_1^2} + \frac{4}{\nu_2^2} \right), \quad (4)$$

E_1 being the energy of the n_1, ℓ_1 hydrogenic state and E_2 that of the n_2, ℓ_2, j_2 state of Ba^+ . The high symmetry of the Hamiltonian H_0 induces degeneracy of the eigenstates. In the uncoupled basis $|n_2 \ell_2 j_2 m_2; n_1 \ell_1 \mu_1\rangle$, the energies E_0 define series of sub-spaces $\varepsilon_{E_0}(n_2 \ell_2 j_2; n_1)$ containing degenerate states. Within each sub-space the states can be further characterized by the set of quantum numbers m_2, μ_1 and ℓ_1 (for $\ell_1 \gg 1$).

H' contains the screened e-e electrostatic interaction (denoted by $\Gamma = \frac{1}{r_{12}} - \frac{1}{r_1}$), the

Zeeman effect on each electron and the Stark effect on the Rydberg electron (Stark effect on the valence electron is neglected, since it is much less polarizable). Under our very weak B field conditions, the diamagnetic terms are negligible.

As Γ commutes with the intermediate angular momentum $\mathbf{K} = \mathbf{j}_2 + \mathbf{l}_1$ [32], the $j_2 \ell_1$ coupled basis $|n_2 \ell_2 j_2; n_1 \ell_1; KM\rangle$ is well adapted to describe the electron interaction in a doubly excited state without external fields [33]. Owing to the electric field, K fails to be a good quantum number. Nevertheless, a theoretical model for the calculation of Stark spectra of autoionizing states has been presented in such a basis [14]. In the present work, for studying the evolution of $\ell_1 \mu_1$ characters of the doubly excited states, the uncoupled spherical basis is used and represents the most simple and convenient choice. The eigenstates of the atom are then obtained by diagonalizing H' . The diagonalization procedure is greatly simplified by the fact that the projection of $\mathbf{K}$ commutes with H and defines the total magnetic quantum number $M = \mu_1 + m_2$, leading to the block-diagonalization of H' matrix for M (see appendix A).

An appropriate dimension of the basis must be determined on physical grounds by comparing the order of magnitude of the H' matrix elements with the energy differences between neighbouring sub-spaces ε_{E_0} . The Zeeman shift of a circular state $21c$ is about $5 \times 10^{-2} \text{ cm}^{-1}$ and the separation between adjacent Zeeman sublevels is $2 \times 10^{-3} \text{ cm}^{-1}$ in a B field of 60 Gauss. The Stark separation between adjacent levels in a F field of 50 V/cm is about $7 \times 10^{-2} \text{ cm}^{-1}$. Typical energy shifts due to the Γ interaction are $2 \times 10^{-2} \text{ cm}^{-1}$ for a $\text{Ba}(6p_{3/2} 21c)$ atom. For high- ℓ_1 Rydberg states the energy separation $E_1(n_1 + 1) - E_1(n_1)$ is 22 cm^{-1} for $n_1 = 21$. For the valence electron the fine structure splitting $E_2(6p_{3/2}) - E_2(6p_{1/2})$ is 1691 cm^{-1} [34]. These data show that the truncated spherical basis generating a single sub-space $\varepsilon_{E_0}(n_2 \ell_2 j_2; n_1)$ contains most of the physical aspects of the problem and is sufficient in first approximation for our calculations. Disregarding the other sub-spaces in the basis can be compared to neglecting second-order effects in a perturbation treatment of the e-e interaction. From now on, the basis vectors of the sub-space ε_{E_0} are specified in the abbreviated form: $|m_2; \ell_1 \mu_1; M\rangle$, being understood that n_2, ℓ_2, j_2 and n_1 are given. For convenience, we call « m_2 -circular » the basis vectors $|m_2; 20, 20; M\rangle$, where $M = 20 + m_2$, describing the Rydberg electron in the oriented circular states ($\mu_1 = \ell_1 = 20$) and the valence electron in one of the sublevels m_2 ($-j_2 \leq m_2 \leq j_2$) of the state n_2, ℓ_2, j_2 . For studying the perturbation of a Rydberg circular electron by the excited valence electron, the relevant M sub-matrices are only those which deal with one of the « m_2 -circular » states. Such sub-matrices satisfy the condition: $(20 - j_2) \leq M \leq (20 + j_2)$. Thus only $2j_2 + 1$ sub-matrix blocks need to be diagonalized in H' .

The Zeeman matrix is diagonal in the spherical basis. It is worth remarking that the break of the μ_1 degeneracy caused by the B field is essential for the preparation of an oriented ($\mu_1 = \ell_1$) circular state in the ACF method. As the Rydberg electron is hydrogenic, the Stark matrix elements may be calculated analytically. They are off-diagonal and connect the basis states according to the coupling rules: $\Delta\mu_1 = 0$ and $\Delta\ell_1 = \pm 1$. The electrostatic interaction Γ is developed into multipolar expansion:

$$\Gamma = \frac{1}{r_{12}} - \frac{1}{r_1} = \sum_{q=1}^{\infty} \sum_{\lambda=-q}^{+q} \frac{4\pi}{2q+1} \frac{r_2^q}{r_1^{q+1}} Y_{q\lambda}^*(\theta_1, \phi_1) Y_{q\lambda}(\theta_2, \phi_2), \quad (5)$$

where the non-penetration condition ($r_2 < r_1$) has been accounted for. Within the truncated basis, one can readily show that, due to selection rules, all the odd-order terms of the electron interaction Γ , as well as the even-order terms with $q > 2j_2$, have zero matrix elements [see appendix A].

3. Numerical analysis.

When the valence electron is in a $j_2 = 1/2$ state, from the previous discussion on the Γ matrix elements, we arrive at the conclusion that the electrostatic interaction between the two electrons gives no contribution to the H' matrix. It follows that, at our level of approximation, a doubly excited circular atom like $\text{Ba}(6p_{1/2} 21c)$ is fully described by an uncoupled electron model. It remains an eigenstate of the total Hamiltonian H in the presence of parallel B and F fields. This is also true when the valence electron is in one of the $n_2s_{1/2}$ or $n_2p_{1/2}$ states ($n_2 \ll n_1$). Note that when $j_2 = 1/2$ the spatial distribution of the inner-electron spin-orbital wavefunction is spherically symmetric [35], which gives some vision into the decoupling of the electrons.

In the remaining of the paper, we analyze in detail the specific case of $\text{Ba}(6p_{3/2} 21c)$. Note that this notation implies an uncoupled electron description. Generally, for $j_2 = 3/2$ and

$-3/2 \leq m_2 \leq 3/2$ the inner electron orbital is anisotropic (Fig. 1b). It follows that a coupling, due to the e-e interaction, arises from the *quadrupolar* term ($q = 2$) according to the selection rules: $\Delta \ell_1 = 0$ and $\Delta \mu_1 = -\Delta m_2 = 0, \pm 1, \pm 2$ (see appendix A). As discussed earlier, only the sub-matrix blocks with $M = 21.5, 20.5, 19.5$ and 18.5 have to be considered. All these sub-matrices contain coupling elements acting on the « m_2 -circular » (as defined in Sect. 2) states $|m_2; 20, 20; M\rangle$. The dimensions of the four blocks are 1, 3, 6 and 10 respectively.

The sub-matrix with the *maximum* M value ($M = 21.5$), contains a single element and deals with the particular « m_2 -circular » state $|3/2; 20, 20; M\rangle$ verifying $m_2 = j_2 = 3/2$. It is the only eigenstate of $\text{Ba}(6p_{3/2} 21c)$ described by a single vector of the uncoupled basis. For this state, the uncoupled electron model applies. Using a σ^+ -circularly polarized light from a single-mode CW laser, it should be possible to selectively populate this state from the sublevel $m_2 = 1/2$ of $\text{Ba}(6s_{1/2} 21c)$ since the transitions ($6s_{1/2}, m_2 = 1/2 \rightarrow 6p_{3/2} m_2' = 3/2$) and ($6s_{1/2}, m_2 = -1/2 \rightarrow 6p_{3/2} m_2' = 1/2$) differ by 56 MHz in a B field of 60 Gauss. More generally, during a sequence of selective σ^+ -excitations, sublevels $m_2 = j_2$ for the inner electron could be successively populated without perturbation of the outer circular electron as long as $n_2 \leq n_1$. Hence, doubly excited circular atoms, such as $\text{Ba}(n_2 d_{5/2} 21c)$, $\text{Ba}(n_2 f_{7/2}, 21c)$ etc. could be prepared.

The typical structure of the other M sub-matrices will be exemplified here for $M = 20.5$ corresponding to the excitation of the valence electron to the sublevel $m_2 = 1/2$. Figure 2 gives a qualitative view of this 3×3 matrix showing the different coupling

			m_2		
			$\frac{1}{2}$	$\frac{3}{2}$	$\frac{3}{2}$
M=20.5			ℓ_1	20	19
			μ_1	20	19
m_2'	ℓ_1'	μ_1'			
$\frac{1}{2}$	20	20	$\begin{pmatrix} Q+Z & Q & 0 \\ Q & Q+Z & S \\ 0 & S & Q+Z \end{pmatrix}$		
$\frac{3}{2}$	20	19			
$\frac{3}{2}$	19	19			

Fig. 2. — Coupling matrix for $\text{Ba}(6p_{3/2} 21c)$ when the projection of the intermediate angular momentum $M = m_2 + \mu_1$ is 20.5. The uncoupled basis states are labeled using the magnetic quantum numbers m_2, μ_1 and the outer electron angular momentum ℓ_1 . (Thick symbols: circular basis state.) Q : quadrupolar e-e interaction (block-diagonal for ℓ_1); S : Stark effect (off diagonal with $\Delta \ell_1 = \pm 1, \Delta \mu_1 = 0$); Z : Zeeman effect (diagonal).

terms between the three basis states: $|1\rangle = |1/2; 20, 20; M\rangle$, $|2\rangle = |3/2; 20, 19; M\rangle$ and $|3\rangle = |3/2; 19, 19; M\rangle$. $|1\rangle$ is the « m_2 -circular » state with $\mu_1 = 20$, $|2\rangle$ and $|3\rangle$ are named in this work, for convenience, « *quasi-circular* » states with $\mu_1 = 19$. The quadrupolar matrix elements, referred to as Q , may be arranged into diagonal blocks with respect to ℓ_1 . The Stark matrix elements (S), connect the nearest Q blocks, according to the coupling rules: $\Delta \ell_1 = \pm 1$ and $\Delta \mu_1 = \Delta m_2 = 0$. The Zeeman elements (Z) are diagonal. Without electron interaction ($Q = 0$) the « m_2 -circular » state $|1\rangle$ would remain an eigenstate of the total Hamiltonian in the F, B parallel fields. Besides, without Stark effect ($S = 0$), the « m_2 -circular » state is coupled only with the $|3/2; 20, 19; M\rangle$ state by a quadrupolar term Q . Then the angular momentum of the Rydberg circular electron keeps its maximum value ($\ell_1 = 20$) whereas only its orientation may be perturbed: there is no ℓ_1 -mixing of the Rydberg circular state. Finally, when the three interactions in H' are included, the « m_2 -

circular » state may be coupled with the two quasi-circular states of the $M = 20.5$ sub-matrix. It follows that both the orientation and the magnitude of the ℓ_1 angular momentum are likely to be perturbed, giving rise to a ℓ_1 -mixing of the state. Note that, in this case, only the values $\ell_1 = 20$ and $\ell_1 = 19$ may be mixed. Clearly the numerical diagonalization of the H' matrix will determine the energies and the mixing coefficients for the atomic eigenstates which then are *linear superpositions* of the three basis states.

For the three eigenstates related to the $M = 20.5$ sub-matrix, we have adopted the notations $|I\rangle$, $|II\rangle$ and $|III\rangle$. Their calculated eigenenergies are presented in figure 3 in function of the F electric field, for $B = 60$ Gauss. In zero F -field conditions, the separations

Fig. 3. — Calculated eigengenergies of $Ba(6p_{3/2} 21c)$. The $M = 20.5$ matrix of figure 2 has been diagonalized in function of F and for $B = 60$ gauss. The energy of the uncoupled-electron state without fields is the zero reference. Near the avoided crossing ($F_0 = 13$ V/cm), the F field perturbation on state $|II\rangle$ is comparable to the e-e interaction. In large fields $F > 50$ V/cm, the uncoupled electron model applies for $|I\rangle$, $|II\rangle$ and $|III\rangle$ states, where the outer electron is found in parabolic eigenstates.

between the energy levels are mainly due to the e-e interaction, whereas the overall energy shift is due to the Zeeman effect. An avoided-crossing between states $|I\rangle$ and $|II\rangle$ occurs at the field value :

$$F_0 = 13 \text{ V/cm} . \quad (6)$$

For this field, the Stark perturbation and the e-e interaction produce comparable energy shifts. Figures 4a to 4c show the mixing coefficients $C_{i,j}$ given by the square of the projections of the three eigenstates on the three basis states (in $C_{i,j}$, index i marks the eigenstates I, II, III ; and j the basis states 1, 2, 3). When $F \approx 0$, it is the state $|I\rangle$ which carries the dominant circular character ($C_{I,1} = 0.93$), slightly mixed with a $\ell_1 = 20$, $\mu_1 = 19$ quasi-circular character ($C_{I,2} = 0.07$). On the contrary, in the vicinity of the avoided crossing, both states $|I\rangle$ and $|II\rangle$ share the circular character $C_{i,1} \approx 0.5$, which is strongly mixed with those of the two other basis states. As F increases, the circular character is gradually transferred from state $|I\rangle$ to state $|II\rangle$ which presents a nearly-pure circular character $C_{II,1} > 0.99$, when

Fig. 4. — Calculated mixing coefficients of the Ba($6p_{3/2} 21c$) eigenstates for $M = 20.5$ in function of F and for $B = 60$ gauss. a) $C_{I,1} = |\langle 1|i \rangle|^2$ circular character ($\ell_1 = \mu_1 = 20$). When $F \approx 0$ the eigenstate $|I\rangle$ has a dominant circular character (93 %). When $F > 50$ V/cm the eigenstate $|II\rangle$ has a quasi-pure circular character (> 99 %). b) $C_{I,2} = |\langle 2|i \rangle|^2$ « quasi-circular » character ($\ell_1 = 20, \mu_1 = 19$). c) $C_{I,3} = |\langle 3|i \rangle|^2$ « quasi-circular » character ($\ell_1 = 19, \mu_1 = 19$) leading to ℓ_1 -mixing between $\ell_1 = 20$ and $\ell_1 = 19$.

F is larger than $F_1 = 50$ V/cm. In increasing electric fields, when the Stark effect on the Rydberg electron becomes dominant, a *decoupling* of the two electrons occurs progressively. Then each state $|I\rangle$, $|II\rangle$ and $|III\rangle$ tends to factorize into standard parabolic eigenstate for the outer electron. State $|III\rangle$ has a very weak circular character for all the field values.

Similar results are derived from the two other sub-matrices $M = 19.5$ ($m_2 = -1/2$) and $M = 18.5$ ($m_2 = -3/2$) which are not detailed here. Under weak electric field conditions

$F \sim F_0$, their related eigenstates may be described by a superposition of basis states in the range $18 \leq \ell_1$, $\mu_1 < 20$ for $M = 19.5$, and in the range $17 \leq \ell_1$, $\mu_1 < 20$ for $M = 18.5$. But in the field regime of $F > F_1$ (50 V/cm), for each sub-matrix M , there is one eigenstate which presents a nearly-pure circular character. It is remarkable that the uncoupled electron model becomes a good approximation when the electric field effect dominates over the e-e interaction.

4. Discussion.

Let us now examine an ideal experimental situation. We consider an inner electron transition from the single-excited circular state Ba($6s_{1/2} 21c$) to the sublevel $m_2 = 1/2$ of the doubly excited state Ba($6p_{3/2} 21c$). Taking account of the e-e interaction and of the fields, the three atomic eigenstates $|I\rangle$, $|II\rangle$ and $|III\rangle$ discussed above for $M = 20.5$ can be excited. The excitation probability to one of these states is proportional to its circular character $C_{i,1}$ and to the oscillator strength for the inner electron transition $6s_{1/2} \rightarrow 6p_{3/2}$. This expresses the conditions for Isolated Core Excitation [23]. In a weak field $F \sim F_0$, mainly the eigenstates $|I\rangle$ and $|II\rangle$ are populated (see Fig. 4a). They are described by linear superpositions of the three basis states $|1\rangle$, $|2\rangle$ and $|3\rangle$. The Rydberg electron exhibits then mixed circular ($\ell_1 = \mu_1 = 20$) and quasi-circular ($\ell_1 = 20$, $\mu_1 = 19$ and $\ell_1 = 19$, $\mu_1 = 19$) characters. These doubly excited high- ℓ_1 states have their autoionization lifetimes much longer than the radiative lifetime of the $6p_{3/2}$ valence electron: 6.3 ns [20]. In a few ns the inner electron radiates to $6s_{1/2}$ with a branching ratio of about 70 % (the other 30 % radiates to the metastable states $5d_j$, which are not considered here). Once the inner electron has decayed back to $6s_{1/2}$, the atom is single-excited, the Ba core being spherically symmetric. The outer electron state keeps some traces of its mixed character; it is now described by a *statistical mixture* of $\mu_1 = 20$ circular and $\mu_1 = 19$ quasi-circular field eigenstates. In other words, *via* an excitation-deexcitation cycle $6s$ - $6p$ - $6s$ of the valence electron, the e-e quadrupolar interaction in the presence of fields induces partial *transfers* of the Rydberg electron from its initial circular state $21c$ to the nearest quasi-circular states $\mu_1 = 19$. If one is able to detect these transfers, the mixing of an oriented circular state with quasi-circular states will thus appear as a sensitive probe of the e-e interaction in the doubly excited state Ba($6p_{3/2} 21c$). The field-ionization technique is precisely adapted to discriminate quasi-circular field eigenstates which do not ionize at the same field threshold as the initial circular state. For $n_1 = 21$ the circular state ionizes in a field of 3 970 V/cm whereas one of the two quasi-circular states ionizes in a field of 4 000 V/cm and the other in a field of 3 790 V/cm [36]. The last one can be distinguished from the circular-state signal under an improvement of the previous experimental setup [30]. Preliminary measurements have shown that the field ionization peak corresponding to the $n_1 = 21$ circular state population exhibits a reproducible shoulder in the vicinity of 3 800 V/cm after the excitation of the inner electron to the $6p_{3/2}$ state. This feature is the first evidence of the transfers discussed above. In agreement with the calculations, no shoulder is observed during the excitation of the Ba($6p_{1/2} 21c$) state. Under large electric field conditions $F > 50$ V/cm, state $|II\rangle$ is preferentially excited ($C_{II,1} \rightarrow 1$, see Fig. 4a), and tends to factorize into a pure « m_2 -circular » state without $\ell_1 - \mu_1$ mixing. After the radiative decay of the inner electron, the atom returns to its initial state Ba($6s_{1/2} 21c$). In this case, the Rydberg circular electron has behaved as a perfect spectator. Since the mixing with lower- ℓ_1 states would significantly increase the autoionization probability [17], one then predicts an electric-field induced stabilization against autoionization. Experimentally, the absence of ℓ_1 -mixing has been pointed out by the fact that the transfers discussed above disappear under large electric field conditions; a complete analysis of these results as well as details about the excitation and detection conditions will be given in a forthcoming paper.

5. Conclusion.

From previous experimental analysis [30], it has been possible to infer a high stability for barium states such as $(5d_{3/2} 21c)$, and an even greater stability for $(5d_{3/2} 21c)$. However, the measured lifetimes did not agree quantitatively with preliminary (unpublished) computations in zero electric field. Besides, it turned out that, increasing the small electric field defining the orientation of the circular Rydberg electron, the stability *versus* autoionization was even increased [30]. Finally, as mentioned in the previous section, the field-ionization signal provides experimental evidence of population transfers between the circular and quasi-circular states when the inner electron is excited. To give a tentative interpretation of such experimental results, the present work accounts for the influence of weak parallel electric and magnetic fields on doubly excited circular states.

Starting from a truncated uncoupled basis $|n_2 \ell_2 j_2 m_2; n_1 \ell_1 \mu_1\rangle$ for two independent electrons, we have diagonalized the matrix containing the e-e interaction as well as the two field effects. The projection M of the intermediate angular momentum $\mathbf{K} = \mathbf{j}_2 + \mathbf{l}_1$ is conserved, which leads to a block-diagonal matrix.

In the presence of fields, the oriented circular state is not perturbed by the excitation of the inner electron only if one of the two following conditions is fulfilled :

- i) $j_2 = 1/2$ (spherical symmetry of the excited core)
- ii) $m_2 = j_2$ (doubly excited state with maximum M value).

These conditions define some inner-electron excitation schemes free of perturbation of the circular state.

In general, the circular oriented orbital is perturbed and experiences μ_1 and/or ℓ_1 -mixing when the inner electron is excited to anisotropic core states $j_2 > 1/2$. The calculated mixing coefficients depend on the electric field value and on the relative populations of the m_2 magnetic sublevels. Once the inner electron has decayed radiatively to the $6s_{1/2}$ state, the Rydberg electron is found in a statistical mixture including the initial circular state and some quasi-circular states $\mu_1, \ell_1 < n_1 - 1$. Transfers of the Rydberg electron state are thus induced during an excitation-deexcitation cycle of the inner electron. In the specific case $j_2 = 3/2$, the circular state can be mixed with other states $17 \leq \ell_1, \mu_1 < 20$ via a combined quadrupolar e-e interaction and electric field effects. More precisely when the inner electron of the $\text{Ba}(6s_{1/2} 21c)$ atom is excited to $6p_{3/2}$, the mixing is important in the vicinity of $F = 13$ V/cm (for a magnetic field of 60 Gauss) and becomes negligible when $F > 50$ V/cm, so that the Rydberg circular electron is stabilized in large fields. Such an electric field-stabilization effect is also expected in the other doubly excited circular states.

The field-ionization technique appears as a new means to investigate non-autoionizing doubly excited circular states thanks to the selective detection of the outer-electron transfers.

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Appendix A

Explicit form for the matrix elements of Γ .

The matrix elements of the screened e-e interaction term $\Gamma = \frac{1}{r_{12}} - \frac{1}{r_1}$ are calculated in the

uncoupled spherical basis. The multipolar expansion allows us to separate radial and angular parts of the matrix elements for each electron,

$$\begin{aligned} \langle n_2' \ell_2' j_2' m_2'; n_1' \ell_1' \mu_1' | \frac{1}{r_{12}} - \frac{1}{r_1} | n_2 \ell_2 j_2 m_2; n_1 \ell_1 \mu_1 \rangle = \\ = \sum_{q=1}^{\infty} \frac{4\pi}{2q+1} \langle \nu_2' j_2' | r_2^q | \nu_2 j_2 \rangle \langle n_1' \ell_1' | \frac{1}{r_1^{q+1}} | n_1 \ell_1 \rangle \langle T_q \rangle \quad (A1) \end{aligned}$$

where ν_2 is the effective quantum number for the valence electron. After some algebraic transformations, the angular matrix element $\langle T_q \rangle$ becomes :

$$\begin{aligned} \langle T_q \rangle = \sum_{\lambda=-q}^q \langle \ell_2' j_2' m_2'; \ell_1' \mu_1' | Y_{q\lambda}^*(\theta_1, \phi_1) Y_{q\lambda}(\theta_2, \phi_2) | \ell_2 j_2 m_2; \ell_1 \mu_1 \rangle = \\ = (-1)^{\mu_1 + m_2' - 1/2} \delta_{M', M} \frac{2q+1}{4\pi} [\ell_1, \ell_1', \ell_2, \ell_2', j_2, j_2']^{1/2} \begin{pmatrix} \ell_1 & q & \ell_1' \\ 0 & 0 & 0 \end{pmatrix} \\ \begin{pmatrix} \ell_2 & q & \ell_2' \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} j_2 & q & j_2' \\ \ell_2' & 1/2 & \ell_2 \end{Bmatrix} \begin{pmatrix} \ell_1' & q & \ell_1 \\ -\mu_1' & \mu_1' - \mu_1 & \mu_1 \end{pmatrix} \begin{pmatrix} j_2' & q & j_2 \\ -m_2' & m_2' - m_2 & m_2 \end{pmatrix} \quad (A2) \end{aligned}$$

where the notation $[\ell_1, \ell_1', \dots]^{1/2}$ means $[(2\ell_1 + 1)(2\ell_1' + 1) \dots]^{1/2}$. One has $M' = m_2' + \mu_1'$ and $M = m_2 + \mu_1$. Note that there is no coupling between states of different M values. The matrix of Γ is block-diagonal in M .

Within the truncated basis of the sub-space $\varepsilon_{E_0}(n_2 j_2 \ell_2; n_1)$, the radial matrix element of the Rydberg electron, considered as hydrogenic, verifies the Pasternack-Sternheimer identity [37],

$$\langle n_1 \ell_1' | \frac{1}{r_1^{q+1}} | n_1 \ell_1 \rangle = 0, \quad \text{except if} \quad |\ell_1' - \ell_1| < q. \quad (A3)$$

For the dipolar matrix elements ($q=1$), the condition (A3) requires the equality $\ell_1' = \ell_1$ which makes the first 3- j symbol of $\langle T_1 \rangle$ vanish. Hence the e-e dipolar interaction gives no contribution to the Γ matrix elements as long as the Rydberg electron is in a hydrogenic state ($\ell_1 \geq 1$) and is much more excited than the valence electron ($n_1 \gg n_2$).

For the higher multipolar terms $q \geq 2$, one has $j_2' = j_2$ and $\ell_2' = \ell_2$ in the expression (A2). In this situation, the second and fourth 3- j symbols of $\langle T_q \rangle$ will be zero unless the two following conditions are simultaneously satisfied :

$$q \text{ even and } q \leq \min(2\ell_2, 2j_2). \quad (A4)$$

Thus, as a general rule, all the odd order terms and the even order terms with $q > 2j_2$ do not contribute to the Γ matrix elements.

When $j_2 = 1/2$ (valence electron in $s_{1/2}$ or $p_{1/2}$ state), it is not possible to fulfil the conditions (A4). It follows that all the Γ matrix elements vanish.

When $j_2 = 3/2$ (valence electron in $p_{3/2}$ or $d_{3/2}$ state), one finds from (A4) that only the quadrupolar term $q=2$ contributes to the e-e interaction. In the angular matrix element $\langle T_2 \rangle$, the first 3- j symbol is zero unless $|\Delta\ell_1| = |\ell_1' - \ell_1| = 0$ or 2. Considering condition (A3) only the coupling rule $|\Delta\ell_1| = 0$ has to be retained. From the projection conditions in the third and fourth 3- j symbols of $\langle T_2 \rangle$, we have the additional coupling rules : $|\Delta\mu_1| = |\mu_1' - \mu_1| \leq 2$ and $|\Delta m_2| = |m_2' - m_2| \leq 2$. Finally, the conservation of the quantum number M requires $\Delta\mu_1 = -\Delta m_2$.

The radial matrix element of the valence electron in the state $6p_{3/2}$ has been calculated. Its value ($33 a_0^2$) is in good agreement with previous determinations [33, 38].

To illustrate this discussion, here are given the matrix elements of the e-e interaction for a $6p_j$ valence electron. Formulae (A1) and (A2) are now written as

$$\begin{aligned} \langle 6p_{j_2} m_2'; n_1 \ell_1' \mu_1' | \frac{1}{r_{12}} - \frac{1}{r_1} | 6p_{j_2} m_2; n_1 \ell_1 \mu_1 \rangle = \\ = \delta_{\ell_1, \ell_1'} \delta_{j_2, 3/2} \delta_{m_2 + \mu_1, m_2' + \mu_1'} (-1)^{\ell_1 + \mu_1 + m_2' - 1/2} \\ \frac{4 \langle 6p_{3/2} | r^2 | 6p_{3/2} \rangle n_1^{-3}}{[5 \ell_1 (\ell_1 + 1) (2 \ell_1 - 1) (2 \ell_1 + 1) (2 \ell_1 + 3)]^{1/2}} \times \\ \times \begin{pmatrix} \ell_1 & 2 & \ell_1 \\ -\mu_1' & \mu_1' - \mu_1 & \mu_1 \end{pmatrix} \begin{pmatrix} \frac{3}{2} & 2 & \frac{3}{2} \\ -m_2' & m_2' - m_2 & m_2 \end{pmatrix}. \quad (\text{A5}) \end{aligned}$$

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