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Autoionization of Rydberg states with large angular momentum: Application to alkaline-earth atoms

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This paper is devoted to the autoionization process of large-angular-momentum Rydberg states. After a brief account of autoionization formalism in nonrelativistic theory and single-configuration approximation, we apply it to atomic states with one electron of large angular momentum. The dominant contribution is the direct one and the exchange contribution is ignored. In this framework, the autoionization width varies with the principal quantum number as n^{-3} and exponentially with the angular momentum. When two excited electrons interact with a spherically symmetric core, it is demonstrated that the interaction between the Rydberg electron and the core polarized by the valence electron is proportional to the interaction between the two active electrons. Using newly derived radial matrix elements, we obtain a generally good agreement between our results and experiments on barium and strontium. Large-l Rydberg states are shown to be stable versus autoionization as soon as l is about 7. Possible refinements of our method are reviewed.

I. INTRODUCTION

Since the early work of Garton *et al.*,[1] special attention has been paid to autoionization of Rydberg states in alkaline-earth atoms.[2] The autoionization process gives a number of pieces of informations about the intraatomic interactions. Moreover, autoionization processes play an important role in plasma physics because they are the exact reverse of dielectronic recombination.[3] New experimental techniques, such as isolated-core excitation and Stark mixing of Rydberg states[4] have provided a way to reach autoionizing states with relatively large angular momentum. Such autoionizing states have equally stimulated theoreticians' work, mainly within the multichannel quantum-defect theory (MQDT) formalism.[5] For example, interference between different channels result in strong structures in the autoionizing profile of $(5d_{3/2}nd_{3/2})$ states of barium.[6] In strontium the autoionization properties of the $(5p_{3/2}nd_j)$ and $(5p_{1/2}nd_{5/2})$ series are interpreted by taking into account the excitation process from the $(5snd)\,{}^1D_2$, ${}^3D_2$ bound states.[7] Even the $(6p_{1/2}ng)(6p_{3/2}ng)$ series of barium interact, resulting in a Fano profile with q reversal in some cases.[8]

Furthermore, this latter work enlightens the interest of large-angular-momentum studies, first emphasized by Cooke.[4] The reason for that is multiple. On the one hand, when the angular momentum l_1 of Rydberg electron increases, the overlap with inner-electron wave function vanishes, canceling complex exchange effects: a reliable *ab initio* treatment becomes possible. On the other hand, large-angular-momentum autoionizing states appear to be especially stable. We thus know two classes of quasistable states in the continuum: the interference-stabilized states[6,9] and the ones considered here.

Autoionization of Rydberg states in the Coulomb formalism has been analytically investigated by Nikitin and Ostrovsky.[10] Here we propose an extension of their results. Coulomb bound-free matrix elements are computed numerically, avoiding the complex problem of uniform asymptotic expansions. Interaction between the outer electron and the core polarized by the inner electron is considered as well as the various coupling schemes of the dielectronic atom.

The present paper is organized as follows. In Sec. II we develop the Coulomb formalism for autoionization. Neglecting the exchange contribution is justified by physical considerations. In Sec. III we emphasize the main properties of Coulomb matrix elements between circular Rydberg states and continuum. Section IV is devoted to a study of static polarization of the atomic core by the two excited electrons. Bound-bound matrix elements for the valence electron are obtained in Sec. V. In Sec. VI we briefly show how to modify the calculated widths when going from LS coupling to the more realistic jl coupling. Section VII presents numerical results compared to experiments in strontium[4] and barium.[8] A discussion of the validity range of this method is presented in Sec. VIII. New asymptotic expansions for matrix elements of negative powers of r between a Rydberg state and a continuum state are discussed in Appendix A and the transformation formulas from LS to jj coupling are detailed in Appendix B.

II. AUTOIONIZATION FORMALISM IN THE SINGLE-CONFIGURATION APPROACH

Consider a diexcited atom, with the outer electron, hereafter called the "Rydberg electron" and labeled 1, much more excited than the inner electron referred to as the "valence electron" and labeled 2. The other electrons are named core electrons, and their influence will be studied in Sec. IV. At this step of the formalism, we ignore the spin-dependent part of the Hamiltonian. Following the Heisenberg approximation for helium, we write the atomic Hamiltonian, in Hartree units ($e=\hbar=m=1$):

$$H=H_0+V\ , \tag{2.1a}$$

with

$$H_0=\frac{p_1^2}{2}-\frac{Y}{r_1}+\frac{p_2^2}{2}-\frac{Z}{r_2}\ , \tag{2.1b}$$

$$V=\frac{1}{r_{12}}-\frac{1}{r_1}\ , \tag{2.1c}$$

and

$$Y=Z-1\ , \tag{2.1d}$$

Z being the net charge of the core, and Y being the remaining charge after autoionization. One should notice that Hamiltonian (2.1b) is unsymmetrical in the exchange of electrons 1 and 2. However, the Pauli principle holds even in such a case and perturbation theory can be adapted to it as discussed in the literature.[11] Assuming LS coupling, the zeroth-order solution for the eigenvalue equation is, in r representation

$$\Phi_L(r_1,r_2)=\sum_{m_1,m_2}\langle LM_L\,|\,l_1l_2m_1m_2\rangle Y_{l_1m_1}(\Omega_1)\times R_{n_1l_1}(r_1)Y_{l_2m_2}(\Omega_2)R_{n_2l_2}(r_2)\ , \tag{2.2a}$$

with the corresponding eigenvalue

$$E=-\frac{Z^2}{2n_2^2}-\frac{Y^2}{2n_1^2}\ . \tag{2.2b}$$

The properly symmetrized solution, including spin, is

$$\Psi_{LS}(r_1,r_2)=2^{-1/2}[\Phi_L(r_1,r_2)+(-1)^S\Phi_L(r_2,r_1)]\,|\,SM_S\rangle\ . \tag{2.2c}$$

In practical cases, one has $l_1\neq l_2$ and thus the two wave functions involved in (2.2c) are orthogonal.

If l_1 is sufficiently large, we can use *single-configuration wave functions.* Configuration mixing arises from perturbation by interaction (2.1c): it is a small effect as long as the two wave functions are spatially separated. There is experimental evidence for that: Kachru *et al.*[12] have shown that ($6png$) states of Ba do not mix with ($6pnd$) states, while a mixing is observed between $(6p_{3/2}nd_j)_{J=1}$ and $(6p_{3/2}ns_{1/2})_{J=1}$.

The autoionization probability is obtained from Fermi golden rule. Assuming that continuum wave functions are normalized as

$$\int_0^\infty dr\, r^2R_{\epsilon l}(r)R_{\epsilon' l}(r)=\delta(\epsilon-\epsilon')\ , \tag{2.3}$$

the autoionization rate from (n_2l_2,n_1l_1) configuration to $(n_0l_0,\epsilon l)$ configuration is written

$$\Gamma=2\pi\,|\,A_d+(-1)^SA_e\,|^2\ , \tag{2.4a}$$

where the direct and exchange amplitudes are defined as

$$A_d=\langle (n_0l_0,\epsilon l)_L\,|\,V\,|\,(n_2l_2,n_1l_1)_L\rangle\ , \tag{2.4b}$$

$$A_e=\langle (\epsilon l,n_0l_0)_L\,|\,V\,|\,(n_2l_2,n_1l_1)_L\rangle\ . \tag{2.4c}$$

After multipolar expansion of the electrostatic interaction, one gets the direct amplitude

$$A_d=(-1)^L[l,l_0,l_1,l_2]^{1/2}\times\sum_k(-1)^k\begin{bmatrix} l_1 & l & k\\ 0 & 0 & 0\end{bmatrix}\begin{bmatrix} l_2 & l_0 & k\\ 0 & 0 & 0\end{bmatrix}\begin{Bmatrix} l_1 & l_2 & L\\ l_0 & l & k\end{Bmatrix}A_d^k\ , \tag{2.5a}$$

with, for positive k,

$$A_d^k=\int_0^\infty dr_1r_1^2\int_0^\infty dr_2r_2^2\frac{r_<^k}{r_>^{k+1}}R_{\epsilon l}(r_1)R_{n_0l_0}(r_2)\times R_{n_1l_1}(r_1)R_{n_2l_2}(r_2)\ . \tag{2.5b}$$

We have adopted the notation

$$[j,k,l,\ldots]=(2j+1)(2k+1)(2l+1)\cdots \tag{2.6}$$

and $r_>$ ($r_<$) is the greater (smaller) of the radii (r_1,r_2). The 2^s-polar contribution to the exchange amplitude has for radial part

$$A_e^s=\int_0^\infty dr_1r_1^2\int_0^\infty dr_2r_2^2\frac{r_<^s}{r_>^{s+1}}R_{n_0l_0}(r_1)R_{\epsilon l}(r_2)\times R_{n_1l_1}(r_1)R_{n_2l_2}(r_2)\ . \tag{2.7}$$

Since wave functions of Rydberg electron and valence electron have a very small overlap, the integral (2.7) is negligible as long as n_1 is much larger than n_0 and n_2. Using a crude approximation for $R_{n_0l_0}$ and $R_{n_2l_2}$ (Slater wave functions) Nikitin and Ostrovsky[10] have shown that exchange effects are generally negligible for $l_1>2$. An equivalent simplification occurs for the direct amplitude itself: assuming that the valence electron is always closer to the core than the Rydberg electron (nonpenetration hypothesis), the direct amplitude reduces to the product

$$A_d^k\simeq\int_0^\infty dr_1r_1^2R_{\epsilon l}(r_1)r_1^{-k-1}R_{n_1l_1}(r_1)\times\int_0^\infty dr_2r_2^2R_{n_0l_0}(r_2)r_2^kR_{n_2l_2}(r_2)\ . \tag{2.8}$$

The polarization contribution to the quantum defect has been derived from this factorization.[13] The direct-product amplitude (2.8) involves two monoelectronic matrix elements. The Rydberg wave functions $R_{n_1l_1}$ and $R_{\epsilon l}$ will be considered as Coulombic (Sec. III): this is reasonable since measured quantum defects[8] are not greater than a few hundredths for $l>3$. On the other hand, the wave functions $R_{n_0 l_0}$ and $R_{n_2 l_2}$ will be drawn in Sec. IV from spectroscopic data, the Coulomb approximation being too crude for the valence states.

III. RYDBERG MATRIX ELEMENTS

Let us first consider the continuum wave functions $R_{\epsilon l}$. The linear momentum p is defined by

$$\epsilon=\frac{p^2}{2} \ . \tag{3.1}$$

As was shown by Nikitin and Ostrovsky,[10] the continuum wave function may be considered as a plane wave $J_{l+1/2}(2pr)$ only for fast ejected electrons. Using true Coulombic wave functions induces a corrective factor of order $\exp(\pi Y/2p)$, generally not negligible. We thus use the wave function

$$R_{\epsilon l}(r)=\frac{c_{pl}}{(2l+1)!}(2pr)^l \times e^{-ipr}\,{}_1F_1(l+1+iY/p;2l+2;2ipr) \ , \tag{3.2a}$$

where

$$c_{pl}=\left[\frac{2p}{\pi}\right]^{1/2}|\Gamma(l+1+iY/P)|\,e^{\pi Y/2p} =2\left[\frac{Y}{p}\right]^l\left[\frac{Y\prod\limits_{0\le q\le l}(1+q^2p^2/Y^2)}{1-e^{-2\pi Y/p}}\right]^{1/2} \ . \tag{3.2b}$$

In the same way, the only reliable description for the bound Rydberg wave function $R_{n_1 l_1}$ is the Coulomb one:

$$R_{n_1 l_1}=\frac{2}{n_1^2}\left[\frac{Y^3(n_1+l_1)!}{(n_1-l_1-1)!}\right]^{1/2}(2p_1r)^{l_1}e^{-p_1r}\sum_{q=0}^{n_1-l_1-1}\left[\begin{matrix}n_1-l_1-1\\ q\end{matrix}\right]\frac{(-2p_1r)^q}{(2l_1+1+q)!} \ , \tag{3.3a}$$

$$p_1=\frac{Y}{n_1} \tag{3.3b}$$

being the linear momentum of electron 1 on its Bohr orbit. This wave function is a linear combination of the so-called Slater wave functions:

$$R^{sl}_{p_1 l_1}(r)=\frac{(2p_1)^{l_1+3/2}}{[(2l_1+2)!]^{1/2}}r^{l_1}e^{-p_1r} \ . \tag{3.3c}$$

This latter wave function is the correct one for circular Rydberg states $(n_1=l_1+1)$. In this section we give analytic results relative to Slater wave functions (3.3c), while in Sec. VII we present numerical results involving exact wave functions (3.3a).

The bound-free matrix element involved in (2.8) is

$$\langle \epsilon l\,|\,r^{-k-1}\,|\,p_1 l_1\rangle=\frac{(2p_1)^{l_1+3/2}}{[(2l_1+2)!]^{1/2}}\frac{c_{pl}(2p)^l}{(2l+1)!}(l+l_1-k+1)!\frac{{}_2F_1(l+1+iY/p,l+l_1-k+2;2l+2;2ip/(p_1+ip))}{(p_1+ip)^{l+l_1-k+2}} \ . \tag{3.4}$$

Notation $|p_1 l_1\rangle$ stands for the Slater wave function (3.3c), while notation $|n_1 l_1\rangle$ is reserved for the Coulomb wave function (3.3a).

The main effort to get the bound-free matrix elements lies in the computation of the hypergeometric function, not expressible versus simpler transcendental functions when $l-l_1+k$ is positive. Asymptotic expansions for large l have been given by Nikitin and Ostrovsky[10] but unfortunately their validity range is quite restricted. Here we simply use a more conventional numerical method to evaluate the Gauss functions, and in Appendix A we outline a method to get asymptotic expansions of (3.4) for large l.

The Euler integral representation for ${}_2F_1$ is[14]

$${}_2F_1(a,b;c;z)=\frac{\Gamma(c)}{\Gamma(a)\Gamma(c-a)}\int_0^1 du\; u^{a-1}(1-u)^{c-a-1}(1-zu)^{-b} \ . \tag{3.5}$$

With the above-mentioned parameters, this representation is not convenient since the integrand rapidly oscillates. After deformation of the integration path in the complex u plane we get

$$\frac{{}_2F_1(l+1+iY/p,l+l_1-k+2;2l+2;2ip/(p_1+ip))}{(p_1+ip)^{l+l_1-k+2}}$$

$$=\rho_{lp}\left[\frac{2i\pi\sum \mathrm{Res}(f)}{(p_1+ip)^{l+l_1-k+2}}+\frac{e^{-\psi Y/p}2^{-2l-1}}{(p_1^2+p^2)^{(l+l_1-k+2)/2}}\right.$$

$$\left.\times\int_{-1}^{1}\frac{du(1+u)^{l+iY/p}(1-u)^{l-iY/p}}{\left[\cos\left[\frac{\psi}{2}-\theta\right]+iu\sin\left[\frac{\psi}{2}-\theta\right]\right]^{l+l_1-k+2}\left[\cos\left[\frac{\psi}{2}\right]+iu\sin\left[\frac{\psi}{2}\right]\right]^{l-l_1+k}}\right], \tag{3.6a}$$

with

$$\theta=\tan^{-1}(p_1/p)\ , \tag{3.6b}$$

$$\rho_{lp}=\frac{(2l+1)!}{|\Gamma(l+1+iY/p)|^2}\ . \tag{3.6c}$$

The symbol $\sum \mathrm{Res}(f)$ means the sum of residues of the function

$$f(s)=\frac{s^{l+iY/p}}{(1+e^{-2i\theta}s)^{l+l_1-k+2}(1+s)^{l-l_1+k}} \tag{3.6d}$$

in the sector of the complex plane such that $0<\arg(s)<\psi$, ψ being any angle in the range $(0,2\pi)$. The function f has a pole for $s=-1$ if $l-l_1+k$ is positive, and a pole for $s=-e^{2i\theta}$. A convenient choice for the integration angle ψ has proven to be $\pi+\theta$. With such a choice for ψ, and assuming

$$m\equiv l-l_1+k-1\geq 0\ , \tag{3.6e}$$

expression (3.6a) involves the residue of f at the pole $s=-1$. One has

$$\left.\frac{2i\pi\,\mathrm{Res}(f)}{(p_1+ip)^{l+l_1-k+2}}\right|_{s=-1}=\frac{(-i)^m2\pi e^{-\pi Y/p}}{m!(2p)^{l+l_1-k+2}}\frac{\Gamma(l+1+iY/p)}{\Gamma(l_1-k+2+iY/p)}$$

$$\times\,{}_2F_1(-m,l+l_1-k+2;l_1-k+2+iY/p;(p_1-ip)/(-2ip))\quad\text{for } m\geq 0\ . \tag{3.6f}$$

The Gauss function involved in (3.6f) is easy to evaluate since it is a low-degree polynomial.

General properties of matrix element $\langle \epsilon l\,|\,r^{-k-1}\,|\,p_1l_1\rangle$ and thus of autoionization amplitudes can be derived from their large-l asymptotic expansions. According to Nikitin and Ostrovski, the characteristic parameter is $l_1p_1^2/p^2$. In most physical cases, since n_1p^2/Y^2 is a large number, we have

$$l_1p_1^2/p^2\ll 1\ . \tag{3.7}$$

If the free wave function is Coulombic and the bound wave function is a Slater one, we get, assuming (3.7),[10]

$$\langle \epsilon l\,|\,r^{-k-1}\,|\,p_1l_1\rangle=\frac{\pi^{1/4}e^{-\pi Y/2p}2^{l_1+1}}{l_1^{3/4}}\ \frac{(p_1/p)^{l_1+3/2}(p/2)^k}{l_1^{(l_1-l+k)/2}\Gamma((l-l_1+k+1)/2)}\ . \tag{3.8}$$

This matrix element depends on the order k of multipolar expansion as $(p/2l_1^{1/2})^k/\Gamma((l-l_1+k+1)/2)$. The larger the angular momentum l_1 and the smaller the electron velocity p are, the faster it decreases. It is maximum for the smallest allowed value of k. This reflects the rapid convergence of multipolar expansion when r_1 is much greater than r_2. Assuming $k=1$ and $l=l_1+1$, this matrix element varies with l_1 as $(2Y/pn_1)^{l_1+3/2}/l_1^{3/4}$: it decreases exponentially with angular orbital momentum. In Sec. VII we show that this exponential behavior is still observed with more general Coulombic bound wave functions. Assuming p is not too small to preserve condition (3.7) and to neglect the variation of $\exp(-\pi Y/2p)$, we check that (3.8) depends on the ejected electron velocity as $p^{-l_1+k-3/2}$, which obviously favors the production of slow electrons. This behavior is quite generally observed.[15] Finally, one easily verifies that

$$\frac{\langle \epsilon l+2\,|\,r^{-k-1}\,|\,p_1l_1\rangle}{\langle \epsilon l\,|\,r^{-k-1}\,|\,p_1l_1\rangle}=\frac{2l_1}{l-l_1+k+1}\gg 1\ . \tag{3.9}$$

The maximum allowed value for l is the most probable. Such a result equally holds for bound-bound matrix elements but it is less obvious in the present case: since r^{-k-1} favors regions close to the core, one could expect the larger matrix element for the smaller l since the wave function comes then closer to the core.

As a summary, the dipolar contribution to multipolar expansion is preponderant if the valence-electron transition allows it; electrons are preferentially produced with the lowest velocity and the higher angular momentum (l_1+1 for a dipolar transition of the valence electron). The bound Rydberg electron must be described by a Coulomb wave function and not simply by a Slater one. Unfortunately, no simple analytical result can be obtained in practical cases: the first few terms of the Coulomb wave function, varying as $r_1^{l_1+q}e^{-p_1r_1}$ with $q=0,1,2,\ldots$ give contributions of the same order of magnitude. In Sec. VII matrix elements $\langle \epsilon l \mid r^{-k-1} \mid n_1 l_1 \rangle$ come from a numerical computation, based on the above-mentioned integral representation. Nevertheless, conclusions derived in this section for Slater wave functions remain qualitatively correct for Coulomb wave functions.

IV. CORE-POLARIZATION EFFECTS

It has been shown for long now[13,16] that spectroscopic properties of alkali atoms cannot be understood without taking into account the electrostatic interaction between valence electron and the closed-shell core. When the valence electron does not penetrate the core this interaction is named a polarization process. Besides, the action of this electron on the core is not instantaneous. A theory of nonadiabatic (or dynamic) polarization has been given by several authors.[17] This effect is now taken into account in model potential calculations[18] and investigated by a careful measurement of quantum defects.[19,20]

Core polarization has also to be considered in autoionization. Nonadiabatic effects are not explicitly taken into account in this work. However, we prove that interaction between the core and a single valence electron depends on the multipolar polarizabilities in the same way as the interaction between the core and the two active electrons in autoionization. Thus, introducing in the present formalism an effective polarizability accounting for nonadiabaticity seems quite reasonable. Finally, nonadiabatic polarization effects should be moderate for closed-shell cores at least for dipolar polarizability.

Interaction between the core and the two excited electrons can be reliably taken into account assuming the nonpenetration hypothesis:

$$r_j < r_2 < r_1 \ , \tag{4.1}$$

r_j being the radius vector of any of the core electrons. The Hamiltonian for two electrons and a core is split as follows:

$$H=H_0+V_{2c}+V_{1c}+V \ , \tag{4.2a}$$

$$H_0=H_c+\frac{p_2^2}{2}-\frac{Z}{r_2}+\frac{p_1^2}{2}-\frac{Y}{r_1} \ . \tag{4.2b}$$

H_0 is the free Hamiltonian for the noninteracting core (H_c), the valence electron, and the Rydberg electron. The interaction between core and valence electron is

$$V_{2c}=\sum_j\left[\frac{1}{r_{2j}}-\frac{1}{r_2}\right] . \tag{4.2c}$$

Core-polarization effects mainly originate in this interaction. V is the interaction between the two excited electrons (2.1c), responsible for autoionization. Finally, V_{1c} is the interaction between Rydberg electron and core:

$$V_{1c}=\sum_j\left[\frac{1}{r_{1j}}-\frac{1}{r_1}\right] . \tag{4.2d}$$

Condition (4.1) infers the following hierarchy of the averaged interactions:

$$|\langle H_0\rangle| > |\langle V_{2c}\rangle| > |\langle V\rangle| , \quad |\langle V_{1c}\rangle| \ . \tag{4.3}$$

We first consider core polarization by the valence electron only. The core energy and wave function at second and first order in V_{2c}, respectively, are derived from perturbation theory. The multipolar expansion of $1/r_{2j}$ is, according to (4.1),

$$V_{2c}=\sum_{k\geq 0}\sum_j\left[P_k(\cos\theta_{2j})\frac{r_<^k}{r_>^{k+1}}-\frac{\delta_{k0}}{r_2}\right] \tag{4.4a}$$

$$\simeq \sum_{k\geq 1}\frac{1}{r_2^{k+1}}\sum_j P_k(\cos\theta_{2j})r_j^k \ . \tag{4.4b}$$

Using the sum rule for spherical harmonics,

$$\sum_m Y_{lm}(\Omega_1)Y_{lm}^*(\Omega_2)=\frac{2l+1}{4\pi}P_l(\cos\theta_{12}) \ , \tag{4.5}$$

where Ω_q represents the angular coordinates of R_Q, we obtain

$$V_{2c}=\sum_{\substack{k\geq 1\\ \kappa}}\frac{4\pi}{2k+1}\frac{Y_{k\kappa}^*(\Omega_2)}{r_2^{k+1}}T_\kappa^{(k)} \ . \tag{4.6}$$

$T_\kappa^{(k)}$ is the irreducible tensorial operator defined in r-representation as

$$T_\kappa^{(k)}=\sum_j Y_{k\kappa}(\Omega_j)r_j^k \ . \tag{4.7}$$

Matrix elements of $T_\kappa^{(k)}$ between the ground state (cJ_cM_c) and an excited state ($c'J_c'M_c'$) of the core are obtained using Wigner-Eckart theorem:

$$\langle c'J_c'M_c' \mid T_\kappa^{(k)} \mid cJ_cM_c\rangle=(-1)^{J_c'-M_c'}\begin{pmatrix} J_c' & k & J_c \\ -M_c' & \kappa & M_c\end{pmatrix}\langle c'J_c'\|T^{(k)}\|cJ_c\rangle \ . \tag{4.8}$$

If $E_{cc'}$ is the energy difference $E_c - E_c'$, the second-order energy of the polarized core is

$$\tilde{E}_c = \sum_{c'\,(\neq c)} \langle c' \mid V_{2c} \mid c \rangle \frac{1}{E_{cc'}} \langle c \mid V_{2c} \mid c' \rangle$$

$$= \sum_{\substack{k,l\\ \kappa,\lambda}} \frac{4\pi}{2k+1} \frac{Y_{k\kappa}(\Omega_2)}{r_2^{k+1}} \frac{4\pi}{2l+1} \frac{Y_{l\lambda}^*(\Omega_2)}{r_2^{l+1}} \sum_{\substack{c'\,(\neq c)\\ J_c',M_c'}} \frac{1}{E_{cc'}} \begin{bmatrix} J_c' & k & J_c \\ -M_c' & \kappa & M_c \end{bmatrix} \begin{bmatrix} J_c' & l & J_c \\ -M_c' & \lambda & M_c \end{bmatrix}$$

$$\times \langle c'J_c' \| T^{(k)} \| cJ_c \rangle^* \langle c'J_c' \| T^{(l)} \| cJ_c \rangle \; . \tag{4.9}$$

If the core is *spherically symmetric,* J_c and M_c are zero and thus k and l equal J_c', and κ and λ equal M_c'. Using the value of $\left(\begin{smallmatrix} l & l' & 0 \\ -\lambda & \lambda & 0 \end{smallmatrix}\right)$ (Ref. 21) and the sum rule (4.5), one gets

$$\tilde{E}_c = -\tfrac{1}{2} \sum_{l \geq 1} \frac{\alpha_l}{r_2^{2l+2}} \; , \tag{4.10a}$$

with the static polarizability of order 2^l:

$$\alpha_l = -\frac{8\pi}{(2l+1)^2} \times \sum_{c'\,(\neq c)} \frac{1}{E_{cc'}} \mid \langle c'J_c' = l \| T^{(l)} \| cJ_c = 0 \rangle \mid^2 \; . \tag{4.10b}$$

The perturbed core wave function is, up to first order,

$$\mid c\tilde{J}_c M_c \rangle = \mid cJ_c M_c \rangle + \sum_{\substack{c'\,(\neq c),\\ J_c',M_c'}} \mid c'J_c'M_c' \rangle \frac{\langle c'J_c'M_c' \mid V_{2c} \mid cJ_cM_c \rangle}{E_{cc'}} \; . \tag{4.11}$$

We now express the mean value of the interaction between Rydberg electron and core, assuming nonpenetration (4.1),

$$\langle V_{1c} \rangle = \langle c\tilde{J}_cM_c \mid V_{1c} \mid c\tilde{J}_cM_c \rangle$$

$$= \sum_{\substack{l,\lambda,\\ k,\kappa}} \frac{4\pi}{2l+1} \frac{Y_{l\lambda}(\Omega_1)}{r_1^{l+1}} \frac{4\pi}{2k+1} \frac{Y_{k\kappa}^*(\Omega_2)}{r_2^{k+1}} S + \text{c.c.} \; , \tag{4.12a}$$

with

$$S = \sum_{\substack{c'\,(\neq c),\\ J_c',M_c'}} \frac{1}{E_{cc'}} \langle c'J_c' \| T^{(l)} \| cJ_c \rangle^* \langle c'J_c' \| T^{(k)} \| cJ_c \rangle \times \begin{bmatrix} J_c' & l & J_c \\ -M_c' & \lambda & M_c \end{bmatrix} \begin{bmatrix} J_c' & k & J_c \\ -M_c' & \kappa & M_c \end{bmatrix} . \tag{4.12b}$$

Assuming again a spherically symmetric core, we get from orthogonality property of $3j$ symbols

$$S = \frac{\delta_{kl}\delta_{\kappa\lambda}}{2l+1} \sum_{c'\,(\neq c)} \frac{1}{E_{cc'}} \mid \langle c', J_c' = l \| T^{(l)} \| c, J_c = 0 \rangle \mid^2$$

$$= -\frac{2l+1}{8\pi} \alpha_l \delta_{kl} \delta_{\kappa\lambda} \; . \tag{4.12c}$$

Finally the mean value of the interaction between the Rydberg electron and the polarized core is

$$\langle V_{1c} \rangle = -\sum_{l \geq 1} \frac{\alpha_l}{r_1^{l+1} r_2^{l+1}} \frac{2\pi}{2l+1} \times \sum_{\lambda} Y_{l\lambda}(\Omega_1) Y_{l\lambda}^*(\Omega_2) + \text{c.c.} \tag{4.13}$$

This is, using (4.5) again,

$$\langle V_{1c} \rangle = -\sum_{l \geq 1} \alpha_l \frac{P_l(\cos\theta_{12})}{r_1^{l+1} r_2^{l+1}} \; . \tag{4.14}$$

On the other hand, with the hypothesis (4.1), one has

$$V = \sum_{l \geq 1} P_l(\cos\theta_{12}) \frac{r_2^l}{r_1^{l+1}} \; . \tag{4.15}$$

The interaction between the Rydberg electron and the valence electron is thus screened by the interaction between the Rydberg electron and the core polarized by the valence electron. From (4.14) and (4.15),

$$V + \langle V_{1c} \rangle = \sum_{l \geq 1} P_l(\cos\theta_{12}) \frac{r_2^l}{r_1^{l+1}} \left[1 - \frac{\alpha_l}{r_2^{2l+1}} \right] . \tag{4.16}$$

If the core is not spherically symmetric, the result is not so simple since V_{2c} induce a first-order energy shift $\tilde{E}_c$, due to the quadrupolar interaction. Nevertheless, relations (4.10) and (4.14) hold after averaging over the core magnetic quantum number M_c.

Expression (4.16) is unpractical for small radius r_2; to account for penetration of the valence electron inside the core, one usually introduces a phenomenological cutoff function on the screened multipole and the polarization energy. Following Norcross,[18] the radial matrix elements are derived by changing (4.10a) into

$$\tilde{E}_c = -\tfrac{1}{2} \sum_{l} \frac{\alpha_l}{r_2^{2l+2}} \left[1 - \exp - \left[\frac{r_2}{r_c} \right]^{4l+2} \right] \tag{4.17}$$

for the polarization potential and by changing (4.16) into

TABLE I. Matrix elements $\langle n_0 l_0 \,|\, r^k \,|\, n_2 l_2 \rangle$ in barium II. All wave functions are taken positive for large r. All quantities are in a.u. Computations are made with the polarizabilities (Ref. 23) $\alpha_1 = 10.61$, $\alpha_2 = 45.96$, $\alpha_l = 0$ for $l \geq 3$ and the core radius (Ref. 24) $r_c = 1.85$. Columns a,b,c: this work, with, respectively, $\alpha_1 \neq 0$ and $\alpha_2 \neq 0$, $\alpha_1 \neq 0$ and $\alpha_2 = 0$, $\alpha_1 = 0$ and $\alpha_2 = 0$. Column d: Lindgård and Nielsen (Ref. 30). Columns e and f: Gallagher (Ref. 32), for the fine-structure component $j_2 = l_2 + \frac{1}{2}$ and $j_2 = l_2 - \frac{1}{2}$, respectively.

$n_2 l_2$	$n_0 l_0$	k	a	b	c	d	e	f
$5d$	$6s$	2	13.14	13.95	17.63			
$6p$	$6s$	1	3.781	3.727	4.24	4.19	4.06±0.11	4.10±0.15
$6p$	$5d$	1	2.522	2.499	3.842	2.455	2.66±0.17	2.60±0.17
		3	81.43	81.52	109.4			

$$V + \langle V_{1c} \rangle = \sum_{l \geq 1} P_l(\cos\theta_{12}) \frac{r_2^l}{r_1^{l+1}} \times \left[1 - \frac{\alpha_l}{r_2^{2l+1}} \left\{ 1 - \exp\left[- \left[\frac{r_2}{r_c} \right]^{2l+1} \right] \right\} \right] \tag{4.18}$$

for the screened multipolar expansion of the dielectronic interaction. There is no adjustable parameter in expressions (4.17) and (4.18) since values are available for the multipolar polarizabilities[22,23] and for the radius r_c.[24,25]

V. BOUND-BOUND MATRIX ELEMENTS

As shown in Sec. IV, core-polarization effects can be included in the two-electron formalism of autoionization by introducing in the direct amplitude

$$\langle n_0 l_0 \,|\, r^k \,|\, n_2 l_2 \rangle \langle \epsilon l \,|\, r^{-k-1} \,|\, n_1 l_1 \rangle$$

a properly screened operator r^k. A number of oscillator strengths in alkaline-earth ions like Ba II or Sr II are available.[26] But as shown in Sec. II, matrix elements of r^k with k greater than unity may be involved in the autoionization amplitude. Thus we have computed new multipolar elements of Sr II and Ba II. The spin of the valence electron is neglected. This restriction is easy to withdraw; furthermore, spin-orbit interaction will not stronly affect radial matrix elements between low-lying states.

Matrix elements of the valence electron are computed by direct integration of the Schrödinger equation using the Numerov method, in the spirit of the work of Zimmerman *et al.*[27] The polarization potential includes multipolar up to quadrupolar interaction, with appropriate cutoff functions:

$$V_{\text{pol}} \equiv \langle V_{1c} \rangle = -\frac{\alpha_1}{2r^4} \left\{ 1 - \exp\left[- \left[\frac{r}{r_c} \right]^6 \right] \right\} - \frac{\alpha_2}{2r^6} \left\{ 1 - \exp\left[- \left[\frac{r}{r_c} \right]^{10} \right] \right\} \tag{5.1}$$

and matrix elements of r^k are screened according to Sec. IV results. Static polarizabilities for Sr II and Ba II are reasonably well known.[22,23] Multipolar polarizabilities higher than quadrupolar are poorly known, although Sen[28] has derived numerical fits for α_1 to α_4. Furthermore, nonadiabatic corrections mentioned in Sec. IV are much more difficult to estimate. Gallagher *et al.*[20] have studied nonadiabatic effects on core polarization in Ba but nothing equivalent has been done for Ba II. We decided not to include these effects in the computation, keeping in mind that dipolar polarizability α_1 is slightly modified while the correction to the quadrupolar constant α_2 may be more significant. The overall effect on matrix elements of polarization corrections beyond the dipolar one should remain moderate (less than 10%) as shown by a direct computation including successively the various polarizabilities in the series (4.17). Finally, we do not specify the intracore potential: radial integration is only performed inward, using energies from spectroscopic tables, with an average over fine-structure doublets. The inner bound of integration is determined by the short-range behavior of the solution: closer to the nucleus than the classical inner turning point, the integration terminates as soon as the solution begins to diverge.

The new values for radial matrix elements are listed in Tables I and II. Results on Ba II (Table I) show that inclusion of quadrupolar polarizability bears a small influence upon matrix elements, even on $\langle 5d \,|\, r^2 \,|\, 6s \rangle$

TABLE II. Matrix elements $\langle n_0 l_0 \,|\, r^k \,|\, n_2 l_2 \rangle$ in strontium II (a.u.). Computations are made with the polarizabilities (Ref. 23) $\alpha_1 = 5.813$, $\alpha_2 = 17.15$, $\alpha_l = 0$ for $l \geq 3$ and the core radius (Ref. 24) $r_c = 1.57$. For other details see Table I.

$n_2 l_2$	$n_0 l_0$	k	a	b	c	d	e	f
$4d$	$5s$	2	11.89	13.02	16.21			
$5p$	$5s$	1	3.551	3.529	3.892	3.847	3.79±0.08	3.75±0.08
$5p$	$4d$	1	2.620	2.749	3.988	2.821	2.77±0.24	3.03±0.30
		3	72.26	75.82	105.9			

which is screened by the core quadrupole. We have tried to vary the core radius r_c to test its influence on matrix elements. Such a procedure has been previously used[29] to *determine* r_c by minimization. We have observed that matrix elements vary very slowly with r_c in its range of relevance (1–3 a.u., for instance).

It appears that our spin-independent wave functions are as good as those of Lindgård and Nielsen[30] or those computed with Bates and Damgaard tables.[31] For example, the radiative width of $6P$ states in Ba II is now accurately known (1%); our value (1.3, in units of $10^8\ \mathrm{s}^{-1}$) lies between the determinations for $6P_{1/2}$ and $6P_{3/2}$ by Gallagher[32] (1.28 and 1.60, respectively) or Kuske[33] (1.26 and 1.58, respectively), while Lindgård and Nielsen obtain 1.602. Discrepancies with experimental results could be explained by some peculiarity of the core potential of Ba II, as suggested by recent results of Lahiri and Manson.[34] Anyway, these discrepancies are moderate and we thus believe that our higher transition moments are reliable estimates.

VI. TRANSFORMATION TO OTHER COUPLING SCHEMES

Formalism of Sec. II was developed in LS coupling, with spin included only to satisfy the Pauli principle. The discussion in Sec. V suggests that the wave function of the valence electron is not drastically modified when spin is included. Spin-orbit effects are expected to be even smaller for the slower high-l_1 Rydberg electron. In this work we account for spin only to identify correctly the autoionizing state. If a Rydberg electron with l_1 not too small is interacting with a low-lying valence electron, electrostatic interaction $1/r_{12}-1/r_1$ is smaller than spin-orbit coupling for the valence electron, but greater than spin-orbit coupling for Rydberg electron. The appropriate coupling is the jl (or intermediate) coupling. If the angular momentum of Rydberg electron increases, spin-orbit interaction decreases (like $\alpha n_1^{-3}/[(l_1+\frac{1}{2})(j_1+\frac{1}{2})]$) while the electrostatic interaction decreases much more rapidly, as well as polarization effects. Then for l_1 sufficiently large (usually about 10), both electrons appear as almost noninteracting and a better coupling turns to be the jj coupling as for fragmented systems. Here we give the transformation formulas from LS to jl coupling; the corresponding transformation from LS to jj coupling is studied in Appendix B.

In jl coupling, angular momenta are coupled in the following order:

$$\mathbf{j}_2=\mathbf{l}_2+\mathbf{s}_2\ , \tag{6.1a}$$

$$\mathbf{k}=\mathbf{j}_2+\mathbf{l}_1\ , \tag{6.1b}$$

$$\mathbf{J}=\mathbf{k}+\mathbf{s}_1\ . \tag{6.1c}$$

From now on, we omit the principal quantum numbers (n_1,n_2) for the sake of conciseness. The transformation matrix is[21]

$$\begin{aligned}|((l_2s_2)j_2l_1)ks_1JM\rangle=&\sum_{L,S}(-1)^{J+s_1-j_2-l_1}[(2L+1)(2S+1)(2k+1)(2j_2+1)]^{1/2}\\&\times\begin{Bmatrix}L & S & J\\ s_1 & k & s_2\end{Bmatrix}\begin{Bmatrix}l_1 & l_2 & L\\ s_1 & k & j_2\end{Bmatrix}\times|(l_2l_1)L(s_2s_1)SJM\rangle\ .\end{aligned} \tag{6.2}$$

The principal interest of this scheme is that the valence-electron Hamiltonian as well as the electrostatic interaction between electrons are diagonal with respect to k. To get the autoionization probability $\Gamma^{kJ}_{l_2j_2l_1\to l_0j_0l}$ we must compute the square matrix element of V between (6.2) and an autoionized state within the same coupling. The derived expression is lengthy and involves interference between the amplitudes relative to each LS value. But is simplifies if we do not measure the angular momentum j_0 of the ion produced. We have from (6.2) and from orthogonality property of $6j$ symbols:[21]

$$\sum_{j_0}\Gamma^{kJ}_{l_2j_2l_1\to l_0j_0l}=(2k+1)(2j_2+1)\sum_{L,S}(2L+1)(2S+1)\begin{Bmatrix}L & S & J\\ \frac{1}{2} & k & \frac{1}{2}\end{Bmatrix}^2\begin{Bmatrix}l_1 & l_2 & L\\ \frac{1}{2} & k & j_2\end{Bmatrix}^2\Gamma^{LS}_{l_2l_1\to l_0l}\ . \tag{6.3}$$

Furthermore, if we neglect exchange, Γ^{LS} is independent of S. Using the normalization relation for the $6j$ coefficient, we finally obtain

$$\sum_{j_0}\Gamma^{kJ}_{l_2j_2l_1\to l_0j_0l}=(2j_2+1)\sum_{L}(2L+1)\begin{Bmatrix}l_1 & l_2 & L\\ \frac{1}{2} & k & j_2\end{Bmatrix}^2\Gamma^{L}_{l_2l_1\to l_0l}\ . \tag{6.4}$$

Transformation coefficients can be derived from tabulated expressions.[21] One finds

$$(2j_2+1)(2L+1)\begin{Bmatrix}l_1 & l_2 & L\\ \frac{1}{2} & k & j_2\end{Bmatrix}^2=\frac{(l_1+l_2-k+\frac{1}{2})(l_1+k-l_2+\frac{1}{2})}{(2k+1)(2l_2+1)} \tag{6.5a}$$

if $(j_2,L)=(l_2-\frac{1}{2},k-\frac{1}{2})$ or if $(j_2,L)=(l_2+\frac{1}{2},k+\frac{1}{2})$, and

$$(2j_2+1)(2L+1)\begin{Bmatrix}l_1 & l_2 & L\\ \frac{1}{2} & k & j_2\end{Bmatrix}^2=\frac{(l_1+l_2+k+\frac{3}{2})(l_2+k-l_1+\frac{1}{2})}{(2k+1)(2l_2+1)} \tag{6.5b}$$

TABLE III. Transformation from *LS* coupling to *jl* coupling. Widths Γ^k in *jl* coupling are expressed versus Γ_-, Γ_0, and Γ_+ which are the *LS*-coupling widths for *L* respectively equal to l_1-1, l_1, and l_1+1. The orbital angular momentum of the inner electron is $l_2=1$.

j_2	k	J	$\Gamma^k_{l_2 j_2 l_1 \rightarrow l_0 j_0 l}$
$\frac{3}{2}$	$l_1-\frac{3}{2}$	l_1-2, l_1-1	Γ_-
$\frac{1}{2}$	$l_1-\frac{1}{2}$	l_1-1, l_1	$\frac{2l_1-1}{3l_1}\Gamma_- + \frac{l_1+1}{3l_1}\Gamma_0$
$\frac{3}{2}$	$l_1-\frac{1}{2}$	l_1-1, l_1	$\frac{l_1+1}{3l_1}\Gamma_- + \frac{2l_1-1}{3l_1}\Gamma_0$
$\frac{1}{2}$	$l_1+\frac{1}{2}$	l_1, l_1+1	$\frac{l_1}{3(l_1+1)}\Gamma_0 + \frac{2l_1+3}{3(l_1+1)}\Gamma_+$
$\frac{3}{2}$	$l_1+\frac{1}{2}$	l_1, l_1+1	$\frac{2l_1+3}{3(l_1+1)}\Gamma_0 + \frac{l_1}{3(l_1+1)}\Gamma_+$
$\frac{3}{2}$	$l_1+\frac{3}{2}$	l_1+1, l_1+2	Γ_+

if $(j_2,L)=(l_2-\frac{1}{2},k+\frac{1}{2})$ or if $(j_2,L)=(l_2+\frac{1}{2},k-\frac{1}{2})$. In the special case $l_1=1$, we have listed in Table III the allowed values of j_2, k, and Γ^{kJ} expressed versus Γ^L. In intermediate coupling, the autoionization width depends on k but not on J, since the whole Hamiltonian is independent of the Rydberg-electron spin.

VII. APPLICATION TO BARIUM AND STRONTIUM

Using the monoelectronic bound-bound matrix elements or r^k derived in Sec. V and bound-free matrix elements of r^{-k-1} evaluated as explained in Sec. III, we have obtained the autoionization width of $(6p,n_1l_1)$,$(5d,n_1l_1)$ states of Ba and the $(5p,n_1l_1)$ state of Sr. As emphasized previously, present results are reliable for l_1 not too small ($\gtrsim 3$). The classical n_1^{-3} dependence of the widths is very well reproduced in the present calculation. The l_1 dependence is presented in Table IV for the $(6p,n_1l_1)$ states of Ba, with a detail of each autoionization channel probability. The dominant channel is $(5d;\epsilon,l=l_1+1)$. Channels $l=l_1\pm 3$ are unfavored because they involve only octopolar bound-bound matrix elements. In *LS* coupling all states of a given configuration have an equivalent autoionization width, with a small predominance for $L=l_1+1$ if l_1 is smaller than 5 and for $L=l_1-1$ otherwise. Since the bound-bound matrix elements as well as angular factors are of the same order of magnitude for each of these probabilities, these considerations reflect properties of bound-free matrix element $\langle \epsilon l \,|\, r^{-k-1} \,|\, n_1 l_1 \rangle$. In Table V we have written the autoionization width of the $(6pj_2,24l_1)k$ state in *jl* coupling. Setting aside the results relative to $l_1=2$, for which the large-angular-momentum expressions may fail, we find a greater width for $k=l_1+\frac{1}{2}$ or for $k=l_1-\frac{3}{2}$ according to whether l_1 is smaller than 5 or not.

Experimental data are available for $(6p,n_1l_1)$ of Ba.[35,36] For instance, the autoionization width of $(6p_{1/2},24d)k=\frac{5}{2}$ is found to be 1.2 cm^{-1} while we calculate 10 cm^{-1} in Table IV. Exchange contribution to autoionization amplitude is far from being negligible for the 6*pnd* state as indicated theoretically by Nikitin and Ostrovski's work and experimentally by the quantum defect of 2.74: penetration of Rydberg electron with $l_1=2$ inside the valence orbital is not negligible. Taking into account spin-orbit interaction would modify slightly the radial wave function R_{6p}, and there is no evidence for strong series interaction near the above-mentioned Ba state.

Results by Jaffe *et al.*[8] provide a better test of our calculation. The measured widths of $(6p_{3/2},24g)k,J=5$ are 0.87 cm^{-1} and 0.69 cm^{-1} for $k=\frac{9}{2}$ and $k=\frac{11}{2}$, respec-

TABLE IV. Autoionization probabilities for the processes $(6p,24l_1)L \rightarrow (5d,\epsilon l)L$ or $(6s,\epsilon l)L$ in barium. All widths are in a.u. (219 475 cm^{-1}). Left columns, ion state (5*d* or 6*s*); *L* value, ejected-electron angular momentum. Right columns, autoionization probabilities, each column for one l_1 value.

Ion state L	l	$l_1=2$	4	6	8
5*d*	l_1-3		1.62×10^{-10}	3.20×10^{-13}	3.66×10^{-16}
	l_1-1	3.59×10^{-4}	5.06×10^{-8}	1.55×10^{-10}	4.50×10^{-13}
$L=l_1-1$	l_1+1	4.97×10^{-5}	2.66×10^{-6}	5.96×10^{-8}	4.58×10^{-10}
5*d*	l_1-1	3.22×10^{-5}	2.12×10^{-11}	6.55×10^{-11}	4.60×10^{-13}
$L=l_1$	l_1+1	2.92×10^{-6}	1.04×10^{-6}	2.76×10^{-8}	2.21×10^{-10}
5*d*	l_1-1	4.19×10^{-6}	4.80×10^{-8}	4.44×10^{-10}	1.84×10^{-12}
	l_1+1	1.42×10^{-5}	7.15×10^{-7}	1.42×10^{-8}	1.01×10^{-10}
$L=l_1+1$	l_1+3	3.84×10^{-8}	1.88×10^{-8}	7.55×10^{-10}	7.57×10^{-12}
6*s* $L=l_1-1$	l_1-1	3.74×10^{-6}	5.23×10^{-8}	3.08×10^{-10}	7.57×10^{-13}
6*s* $L=l_1+1$	l_1+1	3.27×10^{-5}	2.21×10^{-6}	3.37×10^{-8}	1.59×10^{-10}

TABLE V. Autoionization width of $(6pj_2,24l_1)k$ state of Ba in jl coupling (a.u.). Left column, values of k and j_2. Right columns, autoionization width of each state, each column for one l_1 value.

j_2	k	$l_1=2$	4	6	8
$\frac{3}{2}$	$l_1-\frac{3}{2}$	4.12×10^{-4}	2.77×10^{-6}	6.01×10^{-8}	4.59×10^{-10}
$\frac{1}{2}$	$l_1-\frac{1}{2}$	2.24×10^{-4}	2.05×10^{-6}	4.75×10^{-8}	3.70×10^{-10}
$\frac{3}{2}$	$l_1-\frac{1}{2}$	2.24×10^{-4}	1.76×10^{-6}	4.03×10^{-8}	3.11×10^{-10}
$\frac{1}{2}$	$l_1+\frac{1}{2}$	4.75×10^{-5}	2.48×10^{-6}	4.30×10^{-8}	2.56×10^{-10}
$\frac{3}{2}$	$l_1+\frac{1}{2}$	3.86×10^{-5}	1.57×10^{-6}	3.38×10^{-8}	2.36×10^{-10}
$\frac{3}{2}$	$l_1+\frac{3}{2}$	5.11×10^{-5}	3.00×10^{-6}	4.91×10^{-8}	2.70×10^{-10}

tively. In Table V we get, respectively, 0.34 cm^{-1} and 0.66 cm^{-1}. The agreement has been improved as expected.

Computations have also been made for the autoionization of $(5d,n_1l_1)$ to $(6s,\epsilon l)$ state, less probable since it involves a quadrupolar transition of the inner electron. The $(5d_{3/2}16d_{3/2})J=0$ width is found to be of the order of 10^{-3} cm^{-1}, much greater than the value measured by Van Woerkom *et al.*:[9] in this case, the disagreement is explained by strong orbital penetration and by series interaction[6] which accidently destroys the autoionization probability near $n=16$ for the $(5d_{3/2}nd_{3/2})J=0$ series. For l_1 greater than 3, results are detailed in Table VI. Though the autoionization probability is a little smaller for $(5d,n_1l_1)$ states than for $(6p,n_1l_1)$ states, it should be easier to measure since the $5d$ state spontaneously decays by quadrupolar emission only.

On the other hand, by comparing our results in Sr (Table VII) to those of Cooke *et al.*[4] corrected for laser bandwidth, we find a better agreement with increasing l_1 (from 3 to 5). When Sr II is left in the $4d$ state, electrons are much slower ($p=0.288$ a.u.) than when it is left in the $5s$ state ($p=0.466$ a.u.). One can observe in Table VII that for l_1 greater than 3, slow electrons are preferentially produced: this behavior mentioned for autoionization of circular Rydberg states (Sec. III) is more general.

Analyzing the various experimental data, we note that the $(6p,n_1l_1)$ series in Ba are much narrower than the corresponding $(5p,n_1l_1)$ series of Sr. For example, in Sr the width of $(5p_{1/2}16f)$ is about 20 cm^{-1}; thus the width of $(5p_{1/2},24f)$ should be 5.9 cm^{-1} assuming n_1^{-3} scaling: this is much larger than the width of $(6p_{1/2},24f)$ in Ba. Atomic-structure effects increase the autoionization width in Sr and decrease it in Ba; the Coulomb theory ignoring series interaction gives a medium width.

TABLE VI. Autoionization width of $(5d,24l_1)L$ states of Ba (a.u.) in LS coupling. Since the final ionic state is $6s$, the ejected electron momentum is $l=L$. For other details see Table IV.

L	$l_1=4$	6	8
l_1-2	2.49×10^{-9}	5.57×10^{-11}	7.63×10^{-13}
l_1	2.69×10^{-7}	7.30×10^{-9}	1.46×10^{-10}
l_1+2	9.68×10^{-8}	2.26×10^{-8}	1.57×10^{-9}

VIII. DISCUSSION

To improve the validity range of the present model, one has to ask which approximation should be removed. First, penetration cannot be totally neglected for small l_1 values (less than 4), as suggested by the value of quantum defects which cannot be interpreted by pure core polarization. Exchange effects are expected to be still important for $l_1 \lesssim 3$ and then to decrease very rapidly. Spin-orbit effects are not expected to drastically modify most of the present results. They decrease rapidly with l_1, though less rapidly than Coulomb interaction between electrons; spins have been included only to identify the autoionizing state.

In most cases the interaction responsible for autoionization is the electrostatic repulsion between electrons $1/r_{12}$. Spin-dependent interaction must be invoked exceptionally[12] when two terms of a different series are accidentally very close.

The single-configuration approximation becomes more and more reliable as l increases. Configuration interaction involves matrix elements of $1/r_{12}$ between bound states, much like those studied here, which have been shown to decrease rapidly with l_1. Thus single-configuration approximation should hold for large l_1 since then different series do not interact.[12]

It appears from Tables IV and VII that for n_1 close to 24 and l_1 close to 7 the autoionization width of an atomic state becomes smaller than typical rates for dipolar electric emission. Such diexcited states decay by spontaneous emission and not by autoionization, the atom being left in a long-lived monoexcited Rydberg state. The present paper deals with the autoionization process alone, and it does not concern the excitation line shape, unless the autoionization process has the dominant probability.

IX. CONCLUSION

Autoionization is essentially a two-electron process; for large-angular-momentum states, it can be reduced to a single-electron description. In the large-l_1 limit, we have shown that core polarization due to both excited electrons can be reliably taken into account. Using numerical wave functions for the inner electron and a Coulombic description for the outer electron, we have computed a set of autoionization widths in reasonable agreement

TABLE VII. Autoionization probabilities for the process $(5p,16l_1)L \rightarrow (4d,\epsilon l)L$ or $(5s,\epsilon l)L$ in strontium (a.u.). The first lines detail each channel probability. The last lines are the total width for a given state in *LS* coupling, and the experimental results of Cooke *et al.* (Ref. 4).

Ion state L	l	$l_1=3$	4	5
$4d$	l_1-3	2.24×10^{-9}	2.44×10^{-10}	1.89×10^{-11}
	l_1-1	5.68×10^{-6}	2.30×10^{-7}	1.82×10^{-8}
$L=l_1-1$	l_1+1	5.40×10^{-5}	1.81×10^{-5}	4.65×10^{-6}
$4d$	l_1-1	2.22×10^{-7}	1.37×10^{-8}	8.34×10^{-9}
$L=l_1$	l_1+1	2.05×10^{-5}	8.46×10^{-6}	2.31×10^{-6}
$4d$	l_1-1	2.01×10^{-6}	3.52×10^{-7}	5.43×10^{-8}
	l_1+1	1.51×10^{-5}	4.64×10^{-6}	1.11×10^{-6}
$L=l_1+1$	l_1+3	2.37×10^{-8}	2.04×10^{-8}	8.63×10^{-9}
$5s$ $L=l_1-1$	l_1-1	1.22×10^{-6}	1.14×10^{-7}	8.36×10^{-9}
$5s$ $L=l_1+1$	l_1+1	2.72×10^{-5}	4.99×10^{-6}	6.17×10^{-7}
$L=l_1-1$ (total)		6.09×10^{-5}	1.85×10^{-5}	4.67×10^{-6}
$L=l_1$ (total)		2.07×10^{-5}	8.47×10^{-6}	2.32×10^{-6}
$L=l_1+1$ (total)		4.43×10^{-5}	1.00×10^{-5}	1.79×10^{-6}
Experiment[a]		1.0×10^{-4}	3.9×10^{-5}	4.1×10^{-6}[b]

[a] Reference 4.

[b] Laser bandwidth subtracted.

with present experiments where l_1 ranges from 3 to 5. Possible refinements of the theory have been reviewed. We have proven that for l_1 large, which practically means $l_1 > 7$, diexcited states are stable versus autoionization. Then, the line broadening reflects the width of the bound-bound ionic transition only. New experiments involving greater l_1 are clearly needed to test the validity of the present predictions. In this sense, there is a serious hope in new methods for production of circular Rydberg states.[27]

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APPENDIX A: ASYMPTOTIC EXPANSION FOR THE BOUND-FREE COULOMB MATRIX ELEMENTS

Here we outline the elements of a large-l asymptotic expansion of

$$ {}_2F_1(l+1+iY/p,\, l+l_1-k+2;\, 2l+2;\, 2ip/(p_1+ip)) \;. $$

It is assumed that l,l_1 are large with respect to $|l-l_1|,k$. The present approximation is uniform versus parameters p,p_1. Basically it utilizes a complex-plane integration and an expansion of the rapidly varying part of the integrand near the saddle point.

We start from the integral representation of the Gauss function [cf. Sec. III, formulas (3.5) and (3.6)]:

$$ {}_2F_1(l+1+iY/p,\, l+l_1-k+2;\, 2l+2;\, 2ip/(p_1+ip)) = \rho_{lp}\int_0^{\infty} ds\, f(s) \;, \qquad \text{(A1a)} $$

with

$$ f(s)=\exp[A(s)]/(1+s)^{l-l_1+k} \;, \qquad \text{(A1b)} $$

$$ A(s)=(l+iY/p)\ln s-(l+l_1-k+2)\ln(1+e^{-2i\hat{\theta}}s) \;. \qquad \text{(A1c)} $$

The direction of integration in the s plane can be rotated of any angle ψ such that

$$ 0 \leq \psi < \pi + 2\tan^{-1}(p_1/p) \;. \qquad \text{(A2)} $$

If ψ is greater than π and if $l-l_1+k$ is positive, the contribution of pole -1 is exactly taken into account using expression (3.6f). The complex amplitude $A(s)$ admits a saddle point when $A'(s)$ cancels, i.e., when s equals s_0 defined by

$$ s_0=\frac{l+iY/p}{l_1-k+2-iY/p}\,\frac{p_1+ip}{p_1-ip} \;. \qquad \text{(A3)} $$

The variation of $A(s)$ near its maximum is characterized by the number

$$ Q^2=-\tfrac{1}{2}s_0^2A''(s_0)=\frac{(l+iY/p)(l_1-k+2-iY/p)}{2(l+l_1-k+2)} \;, \qquad \text{(A4a)} $$

the phase of Q being defined by

$$|\arg(Q)| \leq \pi/4 \ . \tag{A4b}$$

Since $|Q|$ is large when l is large, whatever p or p_1 are, we can transform the integral in the s_0 direction from $\int_0^{s_0\infty}$ to $\int_{-s_0\infty}^{s_0\infty}$, and neglect in the expansion of $A(s)$ near s_0 terms of order higher than 2. This gives

$$\int_0^{s_0\infty} ds\, f(s) \simeq s_0 f(s_0) \left[\frac{1+s_0}{s_0}\right]^{l-l_1+k} \times I_{l-l_1+k-1}\left[Q, \frac{1+s_0}{s_0}\right] , \tag{A5}$$

with

$$I_m(Q,Z) = \int_{-\infty}^{+\infty} dt \frac{\exp(-Q^2t^2)}{(t+Z)^{m+1}} \ . \tag{A6}$$

This integral is defined for m integer, $\arg(Q)$ are not greater than $\pi/4$ and Z not real. The factor $(1+s)^{-l+l_1-k}$ in (A1b) is rapidly varying around s_0 when the maximum s_0 is close to the pole -1, so it is taken into account exactly in (A5). The integral (A6) can be expressed versus simpler transcendental functions, namely, versus parabolic cylinder functions with integer index.[38] More explicitly, if m is negative,

$$I_m(Q,Z) = 2i\pi^{1/2}(2iQ)^m H_{-m-1}(iQZ) , \tag{A7}$$

H_n being the Hermite polynomial of order n, and if m is non-negative,

$$I_m(Q,Z) = \mp \frac{i\pi}{m!} \left[-\frac{d}{dZ}\right]^m [e^{-Q^2Z^2} \operatorname{erfc}(\mp iQZ)] \ . \tag{A8}$$

The upper (lower) sign in (A8) corresponds to $\operatorname{Im}(Z)$ positive (negative). The complementary error function is defined as

$$\operatorname{erfc}(z) = 1 - \frac{2}{\pi^{1/2}} \int_0^z dt\, e^{-t^2} \ . \tag{A9}$$

For numerical computations, the function (A8) can be expressed either as an entire series or as an asymptotic expansion:

$$I_m(Q,Z) = \frac{\mp i\pi^{1/2}}{m!}(\mp 2iQ)^m \times \sum_{r=0}^{\infty} \frac{\Gamma((r+m+1)/2)}{r!}(\pm 2iQZ)^r \ . \tag{A10}$$

This series converges everywhere in the complex plane. If the product QZ is large, one can prefer the asymptotic expansion

$$I_m(Q,Z) \sim \frac{\pi^{1/2}}{QZ^{m+1}}\, {}_2F_0(m/2+1,(m+1)/2;\,;1/Q^2Z^2) \ . \tag{A11}$$

Expressions (A5)–(A10) have been compared to the "exact" one derived from numerical integration. When l is large we obtain a reasonable agreement (better than 30% for l equal to 10) but the computed expressions have a non-negligible imaginary part. Simple (and real) analytic equivalents can be obtained beyond the case considered in Sec. III ($l_1p_1^2/p^2$ small), when

$$\frac{l+1}{1+p^2/p_1^2}\left[1-\frac{n_1}{l+1}\right]^2 \gg 1, \quad |l-l_1+k|^{1/2} \ . \tag{A12}$$

This condition mainly holds for low-ejected electron energy (p of the order of p_1), but its practical range of applicability is restricted; in particular, it obviously cannot hold for circular Rydberg states (n_1 equal to l_1+1). Incidentally, condition (A12) reflects the following analogy for the autoionization of diexcited Rydberg atoms: a quasicircular state ($l_1 \simeq n_1$) behaves like a Rydberg state ejecting a fast electron (p much greater than p_1), both having a very small autoionization probability.

APPENDIX B: TRANSFORMATION FROM *LS* COUPLING TO *jj* COUPLING

For a large-l_1 Rydberg electron, the angular momenta are obtained in the jj scheme rather than in the jl scheme. Besides, jj coupling treats both electrons on the same footing: it is more convenient if one wishes to estimate the exchange autoionization amplitude. The transformation relation from LS coupling to jj coupling is[21]

$$|(n_2l_2j_2,n_1l_1j_1)JM\rangle = \sum_{L,S}[(2j_2+1)(2j_1+1)(2L+1)(2S+1)]^{1/2} \begin{Bmatrix} l_2 & l_1 & L \\ \frac{1}{2} & \frac{1}{2} & S \\ j_2 & j_1 & J \end{Bmatrix} |(n_2l_2n_1l_1)LSJM\rangle \ . \tag{B1}$$

As in Sec. VI, we take the matrix element of the interaction V and raise to square. After summation over the angular momentum of the ion (j_0) and of the ejected electron (j), we get

$$\sum_{j_0,j} \Gamma^J_{l_2j_2l_1j_1\to l_0j_0lj} = \sum_{L,S}(2j_1+1)(2j_2+1)(2L+1)(2S+1) \begin{Bmatrix} l_1 & l_2 & L \\ \frac{1}{2} & \frac{1}{2} & S \\ j_1 & j_2 & J \end{Bmatrix}^2 \Gamma^{LS}_{l_2l_1\to l_0l} \ . \tag{B2}$$

Neglecting exchange, Γ^{LS} does not depend on S. We thus have to sum expression (B2) over S. To do so, one can remark that coefficients involved in (B2) and (6.4) are related by

TABLE VIII. Transformation from *LS* coupling to *jj* coupling. Widths Γ^J in *jj* coupling are expressed vs Γ_-, Γ_0, and Γ_+ which are the *LS*-coupling widths for L respectively equal to l_1-1, l_1, and l_1+1. The orbital angular momentum of the inner electron is $l_2=1$. Notations: $P=2l_1^2+3l_1+4$, $Q=(2l_1+1)(2l_1^2-l_1+1)$, $R=(2l_1+1)(2l_1^2+5l_1+4)$, $S=2l_1^2+l_1+3$.

j_1	j_2	J	Γ^J
$l_1-\frac{1}{2}$	$\frac{3}{2}$	l_1-2	Γ_-
$l_1-\frac{1}{2}$	$\frac{1}{2}$	l_1-1	$[(2l_1-1)\Gamma_-+(l_1+1)\Gamma_0]/3l_1$
$l_1-\frac{1}{2}$	$\frac{3}{2}$	l_1-1	$[P\Gamma_-+4(l_1^2-1)\Gamma_0]/[3l_1(2l_1+1)]$
$l_1+\frac{1}{2}$	$\frac{3}{2}$	l_1-1	$[(l_1+1)(2l_1-1)\Gamma_-+\Gamma_0]/[l_1(2l_1+1)]$
$l_1-\frac{1}{2}$	$\frac{1}{2}$	l_1	$[2l_1-1)\Gamma_-+Q\Gamma_0+4l_1^2(2l_1+3)\Gamma_+]/[3l_1(2l_1+1)^2]$
$l_1+\frac{1}{2}$	$\frac{1}{2}$	l_1	$[4(l_1+1)^2(2l_1-1)\Gamma_-+R\Gamma_0+(2l_1+3)\Gamma_+]/[3(l_1+1)(2l_1+1)^2]$
$l_1-\frac{1}{2}$	$\frac{3}{2}$	l_1	$[4(l_1+1)^2\Gamma_-+(2l_1-1)R\Gamma_0+l_1^2(2l_1-1)(2l_1+3)\Gamma_+]/[3l_1(l_1+1)(2l_1+1)^2]$
$l_1+\frac{1}{2}$	$\frac{3}{2}$	l_1	$[(l_1+1)^2(2l_1-1)(2l_1+3)\Gamma_-+(2l_1+3)Q\Gamma_0+4l_1^2\Gamma_+]/[3l_1(l_1+1)(2l_1+1)^2]$
$l_1+\frac{1}{2}$	$\frac{1}{2}$	l_1+1	$[l_1\Gamma_0+(2l_1+3)\Gamma_+]/[3(l_1+1)]$
$l_1-\frac{1}{2}$	$\frac{3}{2}$	l_1+1	$[\Gamma_0+l_1(2l_1+3)\Gamma_+]/[(l_1+1)(2l_1+1)]$
$l_1+\frac{1}{2}$	$\frac{3}{2}$	l_1+1	$[4l_1(l_1+2)\Gamma_0+S\Gamma_+]/[3(l_1+1)(2l_1+1)]$
$l_1+\frac{1}{2}$	$\frac{3}{2}$	l_1+2	Γ_+

$$\sum_S (2j_1+1)(2j_2+1)(2L+1)(2S+1)\begin{Bmatrix} l_1 & l_2 & L \\ s_1 & s_2 & S \\ j_1 & j_2 & J \end{Bmatrix}^2 = \sum_k (2j_1+1)(2j_2+1)(2k+1)(2L+1)\begin{Bmatrix} l_1 & l_2 & L \\ s_2 & k & j_2 \end{Bmatrix}^2 \begin{Bmatrix} j_1 & j_2 & J \\ k & s_1 & l_1 \end{Bmatrix}^2 , \tag{B3}$$

or, after summation over the angular momentum j_1 of the Rydberg electron,

$$\sum_{j_1,S} (2j_1+1)(2j_2+1)(2L+1)(2S+1)\begin{Bmatrix} l_1 & l_2 & L \\ s_1 & s_2 & S \\ j_1 & j_2 & J \end{Bmatrix}^2 = \sum_k (2j_2+1)(2L+1)\begin{Bmatrix} l_1 & l_2 & L \\ s_2 & k & j_2 \end{Bmatrix}^2 . \tag{B4}$$

The transformation matrix of coefficients involved in (B2) and (B3) is written in Table VIII in the particular case of the p valence electron ($l_2=1$).

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[1] W. R. S. Garton, G. L. Grasdalen, W. H. Parkinson, and E. M. Reeves, J. Phys. B **1**, 114 (1968).

[2] W. Sandner, Comments At. Mol. Phys. **20**, 171 (1987).

[3] R. H. Bell and M. J. Seaton, J. Phys. B **18**, 1589 (1985).

[4] W. E. Cooke, T. F. Gallagher, S. A. Edelstein, and R. M. Hill, Phys. Rev. Lett. **40**, 178 (1978).

[5] M. J. Seaton, Rep. Prog. Phys. **46**, 167 (1983).

[6] M. Aymar, J. Phys. B **18**, L763 (1985).

[7] E. Y. Xu, Y. Zhu, O. C. Mullins, and T. F. Gallagher, Phys. Rev. A **35**, 1138 (1987).

[8] S. M. Jaffe, R. Kachru, H. B. van Linden Van den Heuvell, and T. F. Gallagher, Phys. Rev. A **32**, 1480 (1985).

[9] L. D. van Woerkom, J. G. Story, and W. E. Cooke, Phys. Rev. A **34**, 3457 (1986).

[10] S. I. Nikitin and V. N. Ostrovsky, J. Phys. B **13**, 1961 (1980).

[11] H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms* (Plenum, New York, 1977).

[12] R. Kachru, H. B. van Linden van den Heuvell, and T. F. Gallagher, Phys. Rev. A **31**, 700 (1985).

[13] J. H. van Vleck and N. G. Whitelaw, Phys. Rev. **44**, 551 (1933).

[14] H. Bateman, *Higher Transcendental Functions* (McGraw-Hill, New York, 1953), Vol. 1.

[15] F. Gounand, T. F. Gallagher, W. Sandner, K. A. Safinya, and R. Kachru, Phys. Rev. A **27**, 1925 (1983).

[16] J. E. Mayer and M. Goeppert-Mayer, Phys. Rev. **43**, 605 (1933).

[17] H. Eissa and U. Öpik, Proc. Phys. Soc. London **92**, 556 (1967); C. J. Kleinman, Y. Hahn, and L. Spruch, Phys. Rev. **165**, 53 (1968); R. H. Young and W. J. Deal, J. Quantum Chem. **9**, 835 (1975).

[18] D. W. Norcross, Phys. Rev. A **7**, 606 (1973).

[19] R. R. Freeman and D. Kleppner, Phys. Rev. A **14**, 1614 (1976).

[20] T. F. Gallagher, R. Kachru, and N. H. Tran, Phys. Rev. A **26**, 2611 (1982).

[21] A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton University Press, Princeton, NJ, 1968).

[22] H. Coker, J. Phys. Chem. **80**, 2078 (1976); P. C. Schmidt, A. Weiss, and T. P. Das, Phys. Rev. B **19**, 5525 (1979).

[23] W. R. Johnson, D. Kolb, and K. N. Huang, At. Data Nucl. Data Tables **28**, 333 (1983).

[24] C. C. Lu, T. A. Carlson, F. B. Malik, T. C. Tucker, and C. W. Nestor, Jr., At. Data Nucl. Data Tables **3**, 1 (1971).

[25] J. P. Desclaux, At. Data Nucl. Data Tables **12**, 311 (1973).

[26] Y. I. Ostrovskii and N. P. Penkin, Opt. Spectrosk. **10**, 8 (1961) [Opt. Spectrosc. (USSR) **10**, 3 (1961)]; **11**, 565 (1961) [**11**, 307 (1961)]; V. P. Shevelko, *ibid.* **36**, 14 (1974) [**36**, 7 (1974)]; P. Hafner and W. H. E. Schwarz, J. Phys. B **11**, 2975 (1978).

[27] M. L. Zimmerman, M. G. Littman, M. M. Kash, and D. Kleppner, Phys. Rev. A **20**, 2251 (1979).

[28] K. D. Sen, Int. J. Quantum Chem. **26**, 1051 (1984).

[29] G. Laplanche, M. Jaouen, and A. Rachman, J. Phys. B **16**, 415 (1983).

[30] A. Lindgård and S. E. Nielsen, At. Data Nucl. Data Tables **19**, 533 (1977).

[31] D. R. Bates and A. Damgaard, Philos. Trans. R. Soc. London, Ser. A **242**, 101 (1949).

[32] A. Gallagher, Phys. Rev. **157**, 24 (1967).

[33] P. Kuske, N. Kirchner, W. Wittmann, H. J. Andrä, and D. Kaiser, Phys. Lett. **64A**, 377 (1978).

[34] J. Lahiri and S. T. Manson, Phys. Rev. A **37**, 1047 (1988).

[35] S. A. Bhatti, C. L. Cromer, and W. E. Cooke, Phys. Rev. A **24**, 161 (1981).

[36] F. Roussel, P. Breger, F. Gounand, and G. Spiess, Europhys. Lett. **5**, 309 (1988).

[37] D. Delande and J. C. Gay, Europhys. Lett. **5**, 303 (1988).

[38] H. Bateman, *Higher Transcendental Functions* (McGraw-Hill, New York, 1953), Vol. 2.