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Configuration-interaction Hartree-Fock calculations for two-electron atoms using a pseudopotential

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We have developed an approach to study doubly excited Rydberg states of atoms or ions with two optically active electrons outside an ionic closed-shell core. The interaction between the core and one valence electron is modeled by an accurate semiempirical pseudopotential. For any given parity and total angular momentum, single configuration Hartree-Fock calculations are performed to build a basis set of numerical two-electron wave functions. Configuration-interaction calculations then provide the energy positions of the correlated states and their compositions in terms of the single configuration basis set. Atomic properties, such as autoionization linewidths, can be derived. Results concerning neutral barium are reported to illustrate the approach. They are compared with available experimental and theoretical data, and discussed. Energy positions of the bound and autoionizing $J=0$ even-parity and $J=1$ odd-parity states of barium below the $5d\ ^2D_{5/2}$ threshold are predicted as well as associated autoionization linewidths. The symmetrical ns^2 $(n=7-11)$, $7p^2$, and $6d^2$ configurations are also studied. The overall agreement is satisfactory and especially good for high-lying doubly excited Rydberg states. [S1050-2947(98)04911-7]

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I. INTRODUCTION

To treat the many-electron problem, many *ab initio* approaches have been based on the Hartree-Fock approximation [1]. For heavy systems, these approaches are numerically complex and time consuming, even with the help of modern supercomputers. As many electrons lie in closed shells and play a minor role in comparison with the valence electrons, several methods have been developed in which the effects of these shells are replaced by an effective interaction [2]. These methods have been proven to be competitive and to provide even better results than *ab initio* approaches in many areas of physics. In this paper we present an approach using such an effective interaction combined with the configuration-interaction (CI) framework to study atoms or ions with two optically active electrons outside an ionic closed-shell core. A number of calculations of this type have been proposed before [2–6], which mainly dealt with low-lying energy levels of two-electron atoms. Our approach uses numerical Hartree-Fock two-electron wave functions to perform CI calculations in the spirit of Ref. [3]. Usually one carries out CI calculations using either numerical one-electron wave functions or trial analytical basis sets. In our approach, we expect that high-lying energy levels will be predicted and identified without encountering linear dependence problems in the CI matrix and with a tractable number of functions. Our main purpose is to show that this approach, which combines generality, simplicity, and accuracy at the same time, can provide reliable spectroscopic information on a large energy scale, including highly excited states.

Alkaline-earth atoms are examples of two-electron systems that have attracted a lot of attention during the past two decades. This was connected with the development of new experimental laser techniques and successful applications of the multichannel quantum-defect theory (MQDT) [7] as well as the eigenchannel *R*-matrix theory combined with the MQDT [8]. One interesting property of doubly excited states, when coupled to the continuum, is their ability to autoionize. As autoionization is mainly induced by the dielectronic Coulomb repulsion, it is essential to account for the electronic correlations to describe this process properly. In this respect, simple independent-particle models are irrelevant. Another interesting problem is the perturbation of Rydberg series by bound doubly excited states, which has been extensively analyzed by means of MQDT.

The computational method is outlined in Sec. II. We first reduce the complex atom with two active electrons to a three-body problem where the core-valence interaction is described by a semiempirical pseudopotential depending on a few parameters, and which cannot support any core electron bound state (Sec. II A). For any given parity and total angular momentum, a basis set of two-electron wave functions is built by successive numerical integrations of the single configuration Hartree-Fock equations (Sec. II B). Each basis set is then used to perform a CI calculation that accounts for the full valence-valence correlations. Obviously, as the core states are not explicitly involved, the number of needed configurations is efficiently reduced. The CI calculation provides the positions of the energy levels and their compositions in terms of the single configuration Hartree-Fock wave functions (Sec. II C). We conclude Sec. II by showing how some atomic properties can be derived in this framework (Sec. II D). Section III is devoted to the presentation of some results for bound and autoionizing states in neutral barium in order to demonstrate the effectiveness of our approach. Comparisons and discussions are made concerning the energy positions and the autoionization linewidths. We draw conclusions in Sec. IV.

II. THE MODEL

In this section, we sketch out the main features of our model. The formalism used here is suitable either for nonrelativistic calculations (carried out in LS coupling) or, by including the spin-orbit interaction implicitly, for semirelativistic calculations (carried out in LSJ or jj couplings).

A. Semiempirical pseudopotential

We consider an atom or an ion A consisting of a nucleus of charge Z surrounded by $N+2$ electrons, N of them forming a closed-shell polarizable core A^{2+} with the nucleus. We suppose that no excited core configuration is embedded in the spectrum of the system A^{+} composed of one valence electron and the ionic core A^{2+}. We begin with our nonrelativistic Hamiltonian for A^{+}. It simply reads (atomic units are used throughout Sec. II)

$$h=-\tfrac{1}{2}\Delta+U(r), \tag{1}$$

where $U(r)$ is a pseudopotential that represents the interaction between the valence electron and the core. We choose the following explicit form:

$$U(r)=-\frac{Z-N}{r}+V^{\mathrm{LR}}(r)+\sum_{l=0}^{\infty} V_l^{\mathrm{SR}}(r)\sum_{m=-l}^{l}|lm\rangle\langle lm|, \tag{2}$$

where

$$V^{\mathrm{LR}}(r)=-\frac{\alpha}{2r^4}(f(r))^2, \tag{3}$$

$$V_l^{\mathrm{SR}}(r)=(a_l+b_lr+c_lr^2)\frac{\exp(-\beta_lr^p)}{r^q}. \tag{4}$$

Besides the Coulomb term, the pseudopotential in Eq. (2) has been conveniently divided into a long-range (LR) local part and a short-range (SR) semilocal part. ''Semilocal'' means l dependent, l being the orbital quantum number of the valence electron. This feature increases the flexibility of the pseudopotential and hence its ability to describe accurately the short-range interactions, the character of which is essentially nonlocal.

The long-range part in Eq. (3) is a polarization term that arises because the core loses its spherical symmetry with respect to the frozen-core approximation: the electric field created by the valence electron polarizes the core and thus modifies the potential that the valence electron actually experiences. This term can be seen as a core-valence correlation potential for nonpenetrating orbits. Higher-order polarization terms exist [9] but the static dipole polarizability of the core α is responsible for the largest part of the correction. The cutoff function f in Eq. (3) prevents the polarization potential from diverging at small r by making it tend towards zero inside the core. We choose the quite arbitrary form $r^3/(r^3+r_c^3)$ inspired from Sienkiewicz and Baylis [10], where r_c is approximately the radius of the core. Many papers have been written about the derivation of this polarization term and its influence upon energies and oscillator strengths [11]. To be consistent, the multipole operators have to be corrected as well.

Let L be the largest value of the l orbitals corresponding to the occupied states of the core A^{2+} in its ground state $^1S_0$, and K_l their number. Then, in a pseudopotential approach, we impose that the number of nodes of the nl radial function of the valence electron is given by $n-l-1-K_l$. Consequently, the lowest valence state of a given l orbital has no node, ensuring that none of the solutions of the Hamiltonian in Eq. (1) with the pseudopotential $U(r)$ in Eq. (2) is a core electron wave function. Therefore, the short-range potential in Eq. (4) accounts mainly for the incomplete screening of the nucleus charge Z by the N core electrons for any l-orbital value of the valence electron and also for the antisymmetrical effects due to the Pauli principle for $l\leqslant L$. Consequently, for $l\leqslant L$, the short-range potential must be repulsive. In fact, in order to increase the accuracy of our approach, two analytical forms of $V_l^{\mathrm{SR}}(r)$ have been used, depending on the value of l. We choose $(p,q)=(2,0)$ if $l\leqslant L$ in Eq. (4) so that the leading Gaussian term is repulsive provided $a_l>0$. For $l>L$ we choose $(p,q)=(1,1)$ in Eq. (4) where the leading term of this potential accounts for the partial screening of the nucleus charge, and we set $a_l=-N$ to fulfill the asymptotic condition

$$U(r)\overset{r\to 0}{\sim}-\frac{Z}{r}. \tag{5}$$

This analytical form of the short-range potential for $l>L$ was found well suited to represent the double-valley potential experienced by the lowest f orbitals in Ba^{+}, as a result of a fine balance between the Coulomb attraction and the centrifugal barrier $l(l+1)/2r^2$ [12]. The parameters a_l, b_l, c_l, and β_l are determined for each value of l so that the Schrödinger equation solved for the valence electron gives the observed *spin-averaged* spectrum of A^{+}. Practically, two parameters are used to fit exactly the two lowest levels of a l series while the others are adjusted to predict the next levels the most accurately in the root-mean-square sense.

This technique can easily be extended to account for the spin-orbit interaction (SO) and other minor splitting effects, which appear of importance in heavy atoms [4,13]. Since we use a pseudopotential, we cannot express the spin-orbit interaction by its usual explicit form. Its radial contribution indeed includes the first derivative of the potential, which is not correct in the pseudopotential approach. Therefore, we treat the splitting effects of the spin-orbit interaction implicitly. As this is essentially a short-range interaction, we change our semilocal potential, which then reads [4,13]

$$\sum_{l=0}^{\infty}\sum_{j=|l-1/2|}^{l+1/2}V_{lj}^{\mathrm{SR}}(r)\sum_{m=-j}^{j}|ljm\rangle\langle ljm|. \tag{6}$$

The (l,j)-dependent parameters of the $V_{lj}^{\mathrm{SR}}(r)$ potential [written similarly to Eq. (4)] are calculated to provide the observed *fine-structure* spectrum of A^{+}. We can recover the radial contribution of the spin-orbit interaction mentioned above, which reads [14]

$$V_l^{\mathrm{SO}}(r)=\frac{1}{l+1/2}[V_{l,l+1/2}^{\mathrm{SR}}(r)-V_{l,|l-1/2|}^{\mathrm{SR}}(r)]. \tag{7}$$

We verify that the j-dependent potential V_{lj}^{SR} on the one hand, and the nonrelativistic potential V_l^{SR} associated with

TABLE I. Ba^+ pseudopotential parameters: $k=0$ for spin-averaged levels, $k=1$ for $j=l+1/2$, and $k=-1$ for $j=l-1/2$.

l	k	a	b	c	β
0	0	8.58	0.00	−0.730	0.384
1	0	9.10	−3.07	0.323	0.270
	1	8.90	−3.08	0.314	0.250
	−1	9.00	−2.84	0.303	0.300
2	0	0.80	−1.48	0.076	0.380
	1	0.80	−1.42	0.049	0.380
	−1	0.80	−1.53	0.070	0.390
⩾3	0	−54.0	52.6	−49.9	2.492
	1	−54.0	52.7	−49.5	2.486
	−1	−54.0	52.4	−50.2	2.499

the spin-orbit potential V_l^{SO} on the other hand, both give very similar fine-structure levels, the latter, however, being slightly less accurate.

We have determined the parameters of the nonrelativistic potential and of the j-dependent potential for the singly ionized barium atom Ba^+ $(Z=56, N=54, \text{and } L=2)$. We have chosen the values $\alpha=10.61$ given by Johnson *et al.* [15] for the static dipole polarizability and $r_c=1.924$ given by Desclaux [16] for the core radius, which is somewhat arbitrary but this parameter has negligible effects on the results. Table I presents the parameters resulting from the fit for both potentials. The largest discrepancy between the predicted levels and experiment [17] never exceeds 2 cm^{-1} for any value of n and l. The accuracy of this pseudopotential has been further tested by calculating some oscillator strengths and lifetimes of Ba^+ with the j-dependent potential. Tables II and III present our results for the lowest excited levels of Ba^+ compared with experimental data [18–23] and with other theoretical calculations [24,25]. Our oscillator strengths lie within the experimental error bars. Our lifetimes appear somewhat underestimated. Nevertheless the relative error does not exceed 7% in the worse case and we are confident in the accuracy of our pseudopotential.

B. Single configuration Hartree-Fock basis sets

TABLE II. Some oscillator strengths in Ba^+.

Transition	This work	Experiment [a]	Other calc. [b]
6 $^2P_{3/2}$-6 $^2S_{1/2}$	0.7585	0.740±0.050	0.7143
6 $^2P_{3/2}$-5 $^2D_{3/2}$	0.0257	0.025±0.003	0.0236
6 $^2P_{3/2}$-5 $^2D_{5/2}$	0.1535	0.140±0.015	0.1403
6 $^2P_{1/2}$-6 $^2S_{1/2}$	0.3481	0.350±0.025	0.3301
6 $^2P_{1/2}$-5 $^2D_{3/2}$	0.1179	0.105±0.010	0.1099

[a] Reference [18].
[b] Reference [24]. Semiempirical model.

TABLE III. Some lifetimes in Ba^+.

Level	This work	Experiment	Other calc.	Units
6 $^2P_{3/2}$	5.97	6.27±0.25 [a]	6.386 [b]	10^{-9} s
		6.312±0.016 [c]	6.39 [d]	10^{-9} s
6 $^2P_{1/2}$	7.54	7.74±0.40 [a]	7.993 [b]	10^{-9} s
		7.92±0.08 [e]	7.99 [d]	10^{-9} s
5 $^2D_{5/2}$	33.22	47.0±16.0 [f]	38.7 [b]	s
		32.0±5.0 [g]	37.2 [d]	s
5 $^2D_{3/2}$	73.94	79.8±4.6 [h]	85.5 [b]	s
			83.7 [d]	s

[a] Reference [18].
[b] Reference [24]. Semiempirical model.
[c] Reference [19].
[d] Reference [25]. Relativistic many-body calculations.
[e] Reference [20].
[f] Reference [21].
[g] Reference [22].
[h] Reference [23].

Now that the pseudopotential $U(r)$ in Eq. (2) is completely defined, we turn to the resolution of the three-body system. The Hamiltonian of the system A is then written

$$H=-\frac{1}{2}\Delta(1)+U(1)-\frac{1}{2}\Delta(2)+U(2)+\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}-\frac{\alpha}{r_1^2 r_2^2}f(r_1)f(r_2)\cos(\hat{\mathbf{r}}_1\cdot\hat{\mathbf{r}}_2). \tag{8}$$

The last term in Eq. (8) is a three-body polarization potential [3,9], the importance of which has been pointed out in Ref. [26]. The problem is then to solve the Schrödinger equation

$$H|\Psi\rangle=E|\Psi\rangle. \tag{9}$$

To proceed, we build a basis set of numerical two-electron wave functions for any given parity π and total angular momentum J in the self-consistent mean-field Hartree-Fock approximation. Let $\psi_\Omega^{n_1l_1n_2l_2}$ be one of these wave functions characterized by the two-electron configuration $n_1l_1n_2l_2$ and a set of quantum numbers Ω. In the nonrelativistic case (i.e., excluding the spin-orbit interaction) the Russell-Saunders LS coupling scheme is appropriate so that $\Omega=(\pi LMSM_S)$. The energy levels are therefore J independent and we use our nonrelativistic pseudopotential. In the semirelativistic case, we adopt the jj coupling scheme $\Omega=(\pi j_1j_2JM_J)$ along with the j-dependent pseudopotential and add the quantum numbers j_1 and j_2 to characterize the configuration completely. We can also carry out calculations where **L** and **S** are coupled to give **J**, and the spin-orbit interaction is treated as a perturbation in a way we will detail later on.

In the Hartree-Fock approximation the two-electron wave function is written as a combination of products of single particle functions as follows:

$$\psi_\Omega^{n_1l_1n_2l_2}=\mathcal{A}([\phi_1\phi_2]_\Omega), \tag{10}$$

where

$$\phi_a=|n_al_a\rangle|l_am_a\rangle|s_am_{s_a}\rangle \quad a\in\{1,2\} \tag{11}$$

is a one-electron spin orbital factorized in its radial, angular, and spin parts. To fulfill the Pauli exclusion principle, the antisymmetrization operator $\mathcal{A}$ equals $\mathbb{1}$ for equivalent electrons and $(1/\sqrt{2})(\mathbb{1}-\mathcal{P})$ for nonequivalent electrons, where $\mathcal{P}$ interchanges the electron space coordinates. The brackets in Eq. (10) indicate that the spin orbitals are coupled according to Ω. The only unknown components to be calculated are the two radial functions $\langle \mathbf{r}|n_a l_a\rangle=(1/r)P_a(r)$. They are the solutions of a two-equation system obtained by means of a variational principle. By requiring that a small variation of the solution of Eq. (9) leaves the energy stationary, we find that each equation of the system has the following form in LS coupling:

$$\left[-\frac{1}{2}\frac{d^2}{dr^2}+\frac{l_a(l_a+1)}{2r^2}+U_{l_a}(r)+V^{\mathrm{HF}}(r)-\epsilon_a\right]P_a(r)=0 \tag{12}$$

with

$$U_{l_a}(r)=-\frac{Z-N}{r}+V^{\mathrm{LR}}(r)+V^{\mathrm{SR}}_{l_a}(r) \quad a\in\{1,2\}. \tag{13}$$

In jj coupling, $V^{\mathrm{SR}}_{l_a}$ is replaced by the j-dependent pseudopotential $V^{\mathrm{SR}}_{l_a j_a}$ defined in Eq. (6) and P_a then becomes a j-dependent function. The Hartree-Fock potential operator V^{HF} is explicitly defined by

$$V^{\mathrm{HF}}(r)P_a(r)=\sum_k C^k_\Omega Y_k(b,b,r)P_a(r)+\sum_k E^k_\Omega Y_k(a,b,r)P_b(r), \tag{14}$$

where

$$Y_k(a,b,r)=\int_0^\infty \sigma_k(r,s)P_a(s)P_b(s)ds, \quad a,b\in\{1,2\} \tag{15}$$

and

$$\sigma_k(r,s)=\frac{r^k}{s^{k+1}}-\delta_{k1}\frac{\alpha}{r^2s^2}f(r)f(s) \quad (r\leqslant s) \tag{16a}$$

$$=\frac{s^k}{r^{k+1}}-\delta_{k1}\frac{\alpha}{r^2s^2}f(r)f(s) \quad (r\geqslant s). \tag{16b}$$

The Hartree-Fock potential Eq. (14) is the sum of two terms, the Coulomb potential and the exchange potential. C^k_Ω and E^k_Ω are the corresponding angular coefficients, which are given by elementary angular algebra according to Ω. To derive the system of Eqs. (12), we require the usual normalization and orthogonality constraints on the radial functions so that a Lagrange multiplier appears whenever $l_1=l_2$, $n_1\neq n_2$ in LS coupling, and $l_1=l_2$, $j_1=j_2$, $n_1\neq n_2$ in jj coupling. We also require that the radial functions have the correct number of nodes $n-l-1-K_l$ in the pseudopotential sense (K_l is the number of l orbitals in the core) and the correct asymptotic behaviors at origin and infinity. We recall that any fictive core state is automatically excluded from the solutions in our pseudopotential framework. The system of coupled equations (12) is solved by means of standard numerical techniques until self-consistency is reached [1,27]. We use the Numerov method with the same logarithmic grid of r values for all functions to optimize the computational time. Treating the exchange potential explicitly makes the equations inhomogeneous: numerical instabilities may occur but they have always been overcome in our calculations.

A basis set $\{\psi^m_\Omega\}$ is built for any possible two-electron configurations $m=n_1l_1n_2l_2$ (respectively, $n_1l_1j_1n_2l_2j_2$) belonging to a given symmetry $\Omega=\ {}^{2S+1}L^\pi$ (respectively, J^π) by successive self-consistent resolutions of the above system (12). Practically, we restrict the number of such configurations to a large number M_Ω, generally around 1000 per symmetry. It is important to recall that in the present approach a semiempirical effective potential that describes the e-A^{2+} interaction is taken as an l-dependent pseudopotential that cannot support any core bound state. However, l-dependent model potentials that support core bound states have been often used in various studies (see, e.g., [5,8]). In principle, there is no difficulty using such model potentials to construct the Hartree-Fock basis set for the two active electrons. However, because of the unrealistic core bound states, which are predicted by the model potential, the Hartree-Fock valence orbitals would have to be orthogonal to these core orbitals. These orthogonality constraints prevent us from using a model potential in the present Hartree-Fock approach.

C. CI calculations

So far the Hartree-Fock approximation based upon an independent particle scheme neglects the major part of the correlation between the two valence electrons. This can to some extent be accounted for by configuration mixing, i.e., by writing the most general correlated solution of Eq. (9) as a linear combination of the just above calculated single configuration states (we drop the Ω subscript):

$$|\Psi\rangle=\sum_{m=1}^{M}\lambda^m\psi^m. \tag{17}$$

Solving Eq. (9) is therefore equivalent to solving the following generalized eigenvalue problem

$$(\mathcal{H}-E\mathcal{O})\Lambda=0 \tag{18}$$

with $\mathcal{H}_{m,m'}=\langle\psi^m|H|\psi^{m'}\rangle$, $\mathcal{O}_{m,m'}=\langle\psi^m|\psi^{m'}\rangle$, and $\Lambda_m=\lambda^m(m,m'\in\{1,\ldots,M\})$. After the diagonalization, the eigenvalues provide the energy spectrum of a given symmetry. The corresponding eigenfunctions are obtained by projection onto the uncorrelated basis set. Therefore, the value of the dominant mixing coefficient λ^m allows the identification of the states and of their perturbers in terms of the single configuration Hartree-Fock wave functions. Perturbed states are those for which several configurations appear with weights of comparable magnitudes.

In the LS coupling scheme, the spin-orbit interaction can be added as a perturbation before the diagonalization. To proceed, we join all configurations of those symmetries ${}^{2S+1}L^\pi$ that may give the same total angular momentum J^π

(e.g., to calculate the $J=1^o$ states we mix the $^1P^o$, $^3P^o$, and $^3D^o$ states). We then add the following spin-orbit terms to the Hamiltonian matrix elements $\mathcal{H}_{m,m'}$:

$$\langle \psi^m | V^{\mathrm{SO}}_{l_1}(r)\mathbf{l}_1\cdot\mathbf{s}_1 + V^{\mathrm{SO}}_{l_2}(r)\mathbf{l}_2\cdot\mathbf{s}_2 | \psi^{m'} \rangle, \tag{19}$$

where $V^{\mathrm{SO}}_{l_a}$ is defined in Eq. (7). Comparisons between the results provided by this LSJ coupling scheme and those by the jj coupling scheme allow one to appreciate the eventual nonperturbative effects of the spin-orbit interaction.

D. Calculation of atomic properties

We now have a knowledge of the atomic structure through the correlated wave functions and the energy positions of the states. We will further characterize the states by determining their stability and their decay modes. Two atomic properties are implied in the calculation of lifetimes: the radiative decay rate if the system emits one photon and the autoionization linewidth if the system emits one electron. In this subsection, we describe the principle of their calculations.

1. Radiative decay rates

We restrict our approach to the electric dipole approximation. As already noted, the electric dipole operator **D** has to be consistently modified as a result of the polarization effect [11]:

$$\mathbf{D}=\mathbf{r}_1\left[1-\frac{\alpha}{r_1^3}f(r_1)\right]+\mathbf{r}_2\left[1-\frac{\alpha}{r_2^3}f(r_2)\right] \tag{20}$$

with the notations of Eq. (3). We hereafter employ the gauge length form. Choosing two states $|\Psi_1\rangle$ and $|\Psi_2\rangle$ of energies $E_1 \geqslant E_2$ belonging to symmetries with opposite parities, the spontaneous dipole transition probability W and the oscillator strength F for the transition $1\rightarrow 2$ are defined by

$$W=\frac{4}{3}\frac{1}{g_1}\frac{(E_1-E_2)^3}{c^3}S, \tag{21}$$

$$F=\frac{2}{3}\frac{1}{g_1}(E_1-E_2)S. \tag{22}$$

c in Eq. (21) is the speed of light and equals the inverse of the fine-structure constant in atomic units, i.e., $c\approx 137$. g_1 is the degree of degeneracy of the state $|\Psi_1\rangle$. The line strength S is given by the reduced matrix element

$$S=|\langle \Psi_1 || \mathbf{D} || \Psi_2 \rangle|^2 \tag{23a}$$

$$=\left|\sum_{m=1}^{M_1}\sum_{m'=1}^{M_2}\lambda_1^m\lambda_2^{m'}\langle \psi_1^m || \mathbf{D} || \psi_2^{m'} \rangle\right|^2. \tag{23b}$$

The spontaneous radiative lifetime of the state $|\Psi_1\rangle$ is then $\tau_r = 1/(\Sigma W)$ where the sum runs over all accessible states $|\Psi_2\rangle$ according to the selection rules.

2. Autoionization linewidths

So far we have neglected the interaction of the states with the continua. Not only the continua induce a shift of the energy levels, but also actual autoionizing states or resonances have been treated as quasibound states. This can be circumvented perturbatively as developed by Fano [28]. The continua, however, are still coupled neither to each other nor to any quasibound state. The formula for the linewidth (full width at half maximum) of an autoionizing state according to the Fermi "golden rule" is then

$$\Gamma_c = 2\pi |\langle \Psi_a | H - E_a\mathbb{1} | \Psi_c \rangle|^2 \tag{24a}$$

$$=2\pi\left|\sum_{m=1}^{M_a}\lambda_a^m\langle \psi_a^m | H - E_a\mathbb{1} | \Psi_c \rangle\right|^2. \tag{24b}$$

In these expressions $|\Psi_a\rangle$ is an autoionizing state of the system A above the first ionization threshold with an energy E_a. Theoretical $|\Psi_a\rangle$ and E_a are known from Sec. II C. $|\Psi_c\rangle$ is an open channel of autoionization expressed as

$$|\Psi_c\rangle = \mathcal{A}([\phi_b\phi_c]_\Omega), \tag{25}$$

where ϕ_b is a one-electron bound state belonging to the discrete spectrum of A^+ with an energy ε_b, and ϕ_c is a one-electron continuum wave function to be determined. These two spin orbitals are coupled according to Ω in order to provide the symmetry of $|\Psi_a\rangle$. With the notations of Eq. (11), the radial part of the continuum wave function is the solution of the following equation:

$$\left[-\frac{1}{2}\frac{d^2}{dr^2}+\frac{l_c(l_c+1)}{2r^2}+U_{l_c}(r)+V^{\mathrm{HF}}(r)-\frac{k^2}{2}\right]P_c(r)=0. \tag{26}$$

$V^{\mathrm{HF}}(r)$ has the same form as in Eq. (14) and contains the radial part of ϕ_b. $k^2/2$ is the energy of the free electron so that $E_a=\varepsilon_b+k^2/2$. A Lagrange multiplier is added when necessary in Eq. (26). The integration of Eq. (26) is carried out by means of a procedure given by Barnett *et al.* [29]. The knowledge of $P_c(r)$ completely determines Γ_c in Eqs. (24) and other derived properties as the autoionization lifetime $\tau_a = 1/(\Sigma_c\Gamma_c)$ where the sum runs over all open channels $|\Psi_c\rangle$. We also have a direct determination of the branching ratios into the various open channels.

III. RESULTS IN NEUTRAL BARIUM

We have applied our model to neutral barium. As it is a heavy alkaline-earth atom ($Z=56$), we are likely to appreciate relativistic and correlation effects. The excitation energies of the core electrons are supposed to be much larger than those of the valence electrons so that our model can be applied confidently. Besides, there is no experimental evidence of quartet states in the spectrum of Ba$^+$. Barium is also interesting in that it has a number of doubly excited states below the first ionization limit that perturb the $6snl$ Rydberg series. Moreover, a large number of experiments and theoretical calculations have been carried out so that we have numerous data to compare with.

We have calculated the energy positions of even- and odd-parity states with total angular momentum J ranging from 0 to 4. In most cases, we have restricted the basis sets to all series converging below the $7p$ ionization threshold, so that our results are certainly reliable concerning the $6snl$, $5dnl$, and $6pnl$ series. In the literature, extensive data about series lying above the $7p$ ionization threshold are scarce. One can find almost extensive experimental data and MQDT studies (associated or not with the R-matrix theory) of the $6snl$, $5dnl$, and $6pnl$ series. In general, they provide energy positions and autoionization linewidths. Fewer data are available for the $7snl$, $6dnl$, $4fnl$, and $7pnl$ series. In order to shorten the presentation of our calculations, we focus on the $J=0$ even-parity and $J=1$ odd-parity states of the bound $6snl$ series and of the autoionizing $5dnl$ series. We present our results concerning the symmetrical ns^2, $7p^2$, and $6d^2$ configurations as well. The calculations not reported in this paper for other symmetries and for other series, the $6pnl$ series in particular, show about the same overall agreement with experimental measurements. These unpublished calculations are available upon request from the authors.

Data are given at 1-cm^{-1} precision, which may be considered as our method precision limit presently. We follow the experimental order for the relative positions of the levels so that eventual misplacements may occur in the reported theoretical values. The energies are given with respect to the experimental ground state, which lies at 122 721.15 cm^{-1} [30,31] below the double-ionization limit. Level designations, however, come from our calculations if not stated otherwise. They are in most cases identical to the labels assigned by the MQDT analyses generally connected to the experimental measurements in the papers cited as references, and often confirmed by more sophisticated R-matrix studies. Again, in order to shorten the tables, high-lying members of a given series are not all presented but written from five to five.

A. Bound $6snl$ series

For the bound states we give the results for our two possible coupling schemes. Barium bound states are traditionally written in the LS notation we follow here, though it has appeared that some perturbers are better described in the jj coupling scheme. Bound doubly excited states are underlined in the tables.

1. $J=0$ even-parity states

TABLE IV. Energy positions (cm^{-1}) of the bound $J=0$ even-parity levels of barium. Level designations come from our calculations.

Level	This work		Experiment
	LSJ	jj	
$6s^2$ ^1S	280	173	0
$5d^2$ ^3P	24 713	24 575	23 209 [a]
$5d^2$ ^1S	26 393	26 506	25 874 [b]
$6s7s$ ^1S	29 447	29 321	28 230 [a]
$6s8s$ ^1S	34 656	34 597	34 371 [c]
$6p^2$ ^3P	35 836	35 878	34 494 [a]
$6s9s$ ^1S	37 326	37 308	37 234 [c]
$5d6d$ ^3P	38 192	38 059	37 676 [a]
$6s10s$ ^1S	38 677	38 737	38 664 [c]
$5d6d$ ^1S	39 258	39 333	38 924 [c]
$6s11s$ ^1S	39 791	39 783	39 672 [c]
$6s12s$ ^1S	40 289	40 281	40 234 [c]
$6s13s$ ^1S	40 650	40 645	40 618 [c]
$6s14s$ ^1S	40 912	40 909	40 892 [c]
$6s15s$ ^1S	41 107	41 104	41 093 [c]
$6s16s$ ^1S	41 256	41 253	41 245 [d]
$6s17s$ ^1S	41 371	41 369	41 362 [d]
$5d7d$ ^3P	41 851	41 673	41 441 [d]
$6s18s$ ^1S	41 463	41 460	41 468 [d]
$6s19s$ ^1S	41 537	41 533	41 535 [d]
$6s20s$ ^1S	41 598	41 593	41 596 [d]
$6s25s$ ^1S	41 782	41 784	41 781 [d]
$6s30s$ ^1S	41 870	41 871	41 870 [d]
$6s35s$ ^1S	41 919	41 920	41 919 [d]
$6s40s$ ^1S	41 949	41 949	41 949 [d]
$5d7d$ ^1S	42 539	42 680	42 371 [e]

[a] Reference [17].
[b] J. Vergès, private communication cited in Ref. [33].
[c] Reference [32].
[d] Reference [33].
[e] Reference [34].

Table IV presents the energy positions of the $J=0$ even-parity states below the first ionization threshold at 42 034.90 cm^{-1} [31]. Experimental data come from several papers [17,32–34]. These calculations were carried out with about 860 configurations in LSJ coupling (including all series below the $7g$ threshold) and 680 in jj coupling (all series below the $9p_{3/2}$ threshold) in order to reach the best estimation for the barium ground state. The jj coupling scheme appears the most efficient for this purpose: 122 548 cm^{-1} instead of 122 721 cm^{-1} for the experimental ground state. Adding more configurations has negligible effects on the ground state and on the high-lying members of the $6sns$ series. Conversely, the results in LSJ coupling are not much affected if we include all series below the $9p$ threshold in the calculation only. For the perturbers, as they are low-lying members of series converging to higher ionization thresholds, it is important to include high-lying series in the calculation in order to decrease their energy with respect to the ground state. These remarks about the design of our basis sets are applicable to all our calculations. The observations and the MQDT analysis of Aymar *et al.* [33], confirmed by the R-matrix study of Greene and Aymar [35], are quite well reproduced for the $6sns$ $(n\geqslant 16)$ series, which is almost pure (more than 95%). Six doubly excited bound states are identified. The $5d^2$ $^1S_0$ $(5d_{5/2}^2)$ state is strongly mixed to the $6s7s$ state: these two levels have about 45% of $6s7s$ and 35% of $5d^2$ characters, the first one having a little more of $5d^2$ character. We then follow experiment [17] to assign these two levels. Though better defined (40%) and dominant, the $5d6d$ $^1S_0$ $(5d_{5/2}6d_{5/2})$ labeled state contains a significant percentage of $6s10s$ and $6s11s$ characters (40%) as also predicted by the MQDT analysis of Aymar *et al.* [33]. The $5d7d$ $^1S_0$ $(5d_{5/2}7d_{5/2})$ state is spread out over the $6sns(n\geqslant 12)$ series but does not perturb it strongly. It is found just above the first ionization limit as found experimentally [34]. The $6p^2$ $^1S_0$ $(6p_{3/2}^2)$ state is not bound and lies much higher in energy: at 49 044 cm^{-1} in LSJ coupling and 48 641 cm^{-1} in jj coupling, i.e., higher than the $5dnd$ series. This state was experimentally measured at about 44 800 cm^{-1} [36]. This was confirmed by Greene and Aymar [35]. The triplet perturbers are well defined and predicted at the right place, except the $5d7d\ {}^3P_0\ (5d_{3/2}7d_{3/2})$ state which is found around $n=28$ in LSJ coupling and $n=22$ in jj coupling, while experiment found it around $n=18$ [33].

2. $J=1$ odd-parity states

Table V presents the energy positions of the $J=1$ odd-parity states below the first ionization threshold. Experimental data come from Refs. [17,37,38]. We have used about 600 configurations in both calculations (all series below the $7p$ threshold). There are two $6snp$ series converging to the first ionization limit. These series are perturbed by eleven bound doubly excited states. For the states presented here, the persisting disagreement between our two calculations (LSJ and jj coupling schemes) along the series reflect the large mixing between the perturbers and the members of the series. In our calculations, the series are better characterized in LSJ coupling than in jj coupling because the admixture between $6s_{1/2}np_{1/2}$ and $6s_{1/2}np_{3/2}$ is very large due to the competition between configuration mixing and spin-orbit effects. We recall that in LSJ calculations, spin-orbit effects are treated perturbatively so that this treatment may be questionable here. Higher in the energy spectrum, jj labeled states tend to be pure and the discrepancies between the two calculations are damped as expected theoretically. Notations in Table V come from the MQDT study of Ref. [37], which have been confirmed by hyperfine structure measurements [39]. R-matrix calculations for the $J=1$ odd-parity states can be found in Ref. [40]. Our two calculations cannot account for the crossing of the quantum defects between the singlet and triplet states observed experimentally in Refs. [37,38] around $n=23$. Our triplet states compare well with experiment for $n\geqslant 15$, whereas our singlet states seem to converge more slowly towards the experimental values. This is certainly due to the perturbers: the ${}^1P$ term perturbers are spread out over a large energy range and perturb mainly the $6snp\ {}^1P$ series. In particular, this is the case of the $5d8p\ {}^1P$ state, which lies astride the first ionization limit [41]. It is found above the first ionization limit in both coupling schemes and we have calculated an autoionization linewidth of about 240 cm^{-1}. Besides, the $6snp\ {}^3P$ series is less perturbed. We give our jj labels for the $5d4f$ perturbers, which differ from those of the MQDT analysis of Ref. [37]: $5d4f\ {}^3D$ is closer to $5d_{3/2}4f_{5/2}$, $5d4f\ {}^3P$ to $5d_{5/2}4f_{5/2}$, and $5d4f\ {}^1P$ to $5d_{5/2}4f_{7/2}$.

TABLE V. Energy positions (cm^{-1}) of the bound $J=1$ odd-parity levels of barium. Level designations come from Refs. [37,38].

Level	This work		Experiment [a]
	LSJ	jj	
$6s6p\ {}^3P$	12 683	13 014	12 637 [b]
$6s6p\ {}^1P$	19 617	18 638	18 060 [b]
$5d6p\ {}^3D$	24 724	24 797	24 192 [b]
$5d6p\ {}^3P$	26 435	26 526	25 704 [b]
$5d6p\ {}^1P$	29 702	29 521	28 554 [b]
$6s7p\ {}^3P$	30 946	30 988	30 816 [b]
$6s7p\ {}^1P$	33 748	33 828	32 547 [b]
$6s8p\ {}^3P$	35 720	35 736	35 669
$6s8p\ {}^1P$	36 206	36 047	35 893 [b]
$5d7p\ {}^3D$	36 670	36 700	36 496
$5d7p\ {}^3P$	37 314	37 331	36 990
$6s9p\ {}^1P$	37 948	37 909	37 775
$6s9p\ {}^3P$	37 964	37 986	37 937
$5d7p\ {}^1P$	39 018	39 006	38 500
$6s10p\ {}^3P$	39 175	39 189	39 160
$6s10p\ {}^1P$	39 663	39 685	39 312
$5d4f\ {}^3D$	40 377	39 958	39 893
$6s11p\ {}^3P$	39 916	39 919	39 916
$6s11p\ {}^1P$	40 111	40 179	39 982
$6s12p\ {}^3P$	40 402	40 409	40 396
$6s12p\ {}^1P$	40 456	40 486	40 429
$5d4f\ {}^3P$	40 628	40 721	40 663
$6s13p\ {}^3P$	40 740	40 742	40 732
$5d4f\ {}^1P$	40 633	40 836	40 737
$6s13p\ {}^1P$	40 815	40 760	40 765
$5d8p\ {}^3D$	41 012	41 033	40 894
$6s14p\ {}^3P$	40 981	40 972	40 974
$6s14p\ {}^1P$	41 020	40 985	40 991
$5d8p\ {}^3P$	41 364	41 464	41 097
$6s15p\ {}^3P$	41 160	41 153	41 160
$6s15p\ {}^1P$	41 185	41 169	41 184
$6s20p\ {}^3P$	41 618	41 619	41 616
$6s20p\ {}^1P$	41 622	41 626	41 618
$6s25p\ {}^1P$	41 793	41 793	41 790
$6s25p\ {}^3P$	41 791	41 791	41 791 [c]
$6s30p\ {}^1P$	41 876	41 876	41 874
$6s30p\ {}^3P$	41 875	41 875	41 875
$5d8p\ {}^1P$	42 504	42 695	42 012 [d]

[a] Reference [37].
[b] Reference [17].
[c] Reference [38].
[d] Reference [41].

B. Autoionizing $5dnl$ series

We turn now to the autoionizing states of neutral barium, i.e., the states lying above the first ionization limit. They are characterized by an autoionization linewidth that can be calculated as described in Sec. II D 2. The $5dnl$ series are converging either to the $5d\ {}^2D_{3/2}$ or to the $5d\ {}^2D_{5/2}$ threshold lying at 46 908.75 cm^{-1} and 47 709.724 cm^{-1}, respectively [17]. It has been recognized that the jj coupling scheme is more appropriate to account for the spin-orbit splitting of the $5d$ orbital. According to this remark and since we ourselves observed large discrepancies between our LSJ calculations and experiment, we only present our jj results in the following tables. In general, one or more Rydberg series are converging to the $5d_{3/2}$ limit and are interacting with each other and also with the low-lying members of

TABLE VI. Energy positions and widths (cm^{-1}) of the autoionizing $J=0$ even-parity levels of barium below the $5d\ ^2D_{5/2}$ threshold. Level designations come from our calculations.

Level	This work		Experiment [a]	
	Energy	Width	Energy	Width
$5d_{3/2}8d_{3/2}$	43 445	78	43 282	8.6
$5d_{5/2}8d_{5/2}$	44 236	30	44 117	6.0
$5d_{3/2}9d_{3/2}$	44 490	115	44 324	
$5d_{3/2}10d_{3/2}$	45 009	10.9	44 956	13.6
$5d_{5/2}9d_{5/2}$	45 266	59		
$5d_{3/2}11d_{3/2}$	45 462	44	45 398	11.7
$5d_{3/2}12d_{3/2}$	45 718	3.9	45 692	3.9
$5d_{5/2}10d_{5/2}$	45 862	32	45 791	6.9
$5d_{3/2}13d_{3/2}$	45 965	36	45 918	4.4
$5d_{3/2}14d_{3/2}$	46 103	9.1	46 080	
$5d_{3/2}15d_{3/2}$	46 211	0.09	46 198	
$5d_{5/2}11d_{5/2}$	46 276	24	46 222	
$5d_{3/2}16d_{3/2}$	46 336	22	46 309	
$5d_{3/2}17d_{3/2}$	46 403	8.7	46 388	
$5d_{3/2}18d_{3/2}$	46 461	2.3	46 452	
$5d_{3/2}19d_{3/2}$	46 508	0.03	46 501	
$5d_{5/2}12d_{5/2}$	46 543	5.8	46 513	3.9
$5d_{3/2}20d_{3/2}$	46 573	12.7	46 552	
$5d_{3/2}21d_{3/2}$	46 602	10.1	46 589	
$5d_{3/2}22d_{3/2}$	46 630	6.3	46 621	
$5d_{3/2}23d_{3/2}$	46 655	3.7	46 648	
$5d_{3/2}24d_{3/2}$	46 677	2.0	46 671	
$5d_{3/2}25d_{3/2}$	46 696	0.8	46 692	
$5d_{3/2}26d_{3/2}$	46 712	0.1	46 708	
$5d_{5/2}13d_{5/2}$			46 723	
$5d_{3/2}27d_{3/2}$	46 727	0.03	46 729	
$5d_{3/2}28d_{3/2}$	46 740	0.53	46 741	
$5d_{3/2}29d_{3/2}$	46 751	1.4	46 753	
$5d_{3/2}30d_{3/2}$	46 761	2.1	46 764	
$5d_{3/2}35d_{3/2}$	46 802	1.7		
$5d_{3/2}40d_{3/2}$	46 829	0.6		
$5d_{5/2}14d_{5/2}$	46 850	14	46 887	
$5d_{5/2}15d_{5/2}$	46 954	141	47 015	
$5d_{5/2}20d_{5/2}$	47 330	36	47 354	2.6
$5d_{5/2}25d_{5/2}$	47 484	15	47 494	
$5d_{5/2}30d_{5/2}$	47 560	7	47 565	
$5d_{5/2}35d_{5/2}$	47 604	1.5	47 606	
$5d_{5/2}40d_{5/2}$	47 631	0.5		

[a] Reference [42].

the series converging to the next $5d_{5/2}$ threshold. The overlapping of resonances affects the energy positions and the autoionization linewidths of the states. Note that in our approach the resonances are treated as quasibound states and should be linked to their corresponding linewidths to present their real significance.

1. *J=0 even-parity states*

Table VI presents the energy positions and widths of the autoionizing $J=0$ even-parity states below the $5d\ ^2D_{5/2}$ threshold. Experimental data come from Ref. [42]. The basis set used was the same as for the bound states. We recall that only one CI calculation is required to explore a large part of the spectrum. In the present energy range, there are two interacting series: $5d_{3/2}n_1d_{3/2}$ and $5d_{5/2}n_2d_{5/2}$. Our calculations give the correct arrangement of the states and a satisfactory estimation of their energies. Our $6p^2\ ^1S_0$ state, however, does not appear in this energy range (as noticed above) though it ought to be here [36]. This may come from the finite size of our basis set and the lack of continuum type wave functions. The $n_2=7$–14 members of the $5d_{5/2}n_2d_{5/2}$ series are embedded in the $5d_{3/2}n_1d_{3/2}$ series and in this range of n_2 values, these states are more and more diluted in the high-lying members of the $5d_{3/2}n_1d_{3/2}$ series. The $n_2=13$ state even disappears but strongly perturbs the $5d_{3/2}n_1d_{3/2}$ states with $n_1=26$–30. The effect of this missing state, as can be observed in Table VI, is to shift the energy positions of the next calculated levels below the experimental measurements whereas the energy positions of the preceding calculated levels are lying above the experimental ones. The $5d_{5/2}14d_{5/2}$ state is correctly predicted below the second ionization limit. However, we do not practically see its influence upon the first series as we limit our calculations to the $5d_{3/2}40d_{3/2}$ state, whereas the $5d_{5/2}14d_{5/2}$ state lies around the $5d_{3/2}60d_{3/2}$ state according to experiment. The members of a same series appear strongly mixed to each other, particularly the members of the $5d_{5/2}n_2d_{5/2}$ series above the threshold. However, there is no difficulty labeling the states, except in the region of the $5d_{5/2}12d_{5/2}$ perturber concerning the $5d_{3/2}n_1d_{3/2}$ states with $n_1=18$–22. Our labels are then identical to those of Ref. [42], which come from the empirical MQDT analysis of Aymar *et al.* [43], later confirmed by the *R*-matrix study of Greene and Aymar [35]. Reference [42] gives a few experimental linewidths that are also reported in Table VI though this experiment was not designed to give accurate linewidths. These do not compare well with our results. What can be said in general is that our calculations seem to overestimate the linewidths. The most interesting point is that our results account for the interference effect between the two series as reported by Neukammer *et al.* [44] and Van Woerkom *et al.* [45]. This effect leads to the existence of long-living states near each perturber (i.e., states with very small linewidths) and to a variation of about three orders in magnitude of the linewidths around the perturbers. We refer the reader to Refs. [44,45] and to Aymar [46] for an analysis of this effect. Though our linewidths are larger than those extrapolated from Refs. [44,45], both effects are reproduced in our calculations as shown in Table VI. Above the threshold, our too large linewidths for the $5d_{5/2}n_2d_{5/2}$ series can be explained by the strong mixing between a given state with the preceding one (this mixing itself is related to the missing $5d_{5/2}13d_{5/2}$ state noticed above). The linewidths then decrease continuously as the high members of the series become pure.

2. *J=1 odd-parity states*

Table VII presents the energy positions and widths of the autoionizing $J=1$ odd-parity states below the $5d\ ^2D_{5/2}$ threshold. Experimental data come from Refs. [47,48]. We have six interacting series: $5d_{3/2}n_1p_{1/2}$, $5d_{3/2}n_2p_{3/2}$, $5d_{3/2}n_3f_{5/2}$, $5d_{5/2}n_4p_{3/2}$, $5d_{5/2}n_5f_{5/2}$, and $5d_{5/2}n_6f_{7/2}$. Members of the $5d_{5/2}n_4p_{3/2}$, $5d_{5/2}n_5f_{5/2}$, and $5d_{5/2}n_6f_{7/2}$

TABLE VII. Energy positions and widths (cm^{-1}) of the autoionizing $J=1$ odd-parity levels of barium below the $5d\ ^2D_{5/2}$ threshold. Level designations come from Refs. [47,48].

Level	This work		Experiment [a]	
	Energy	Width	Energy	Width
$5d_{3/2}5f_{5/2}$	42 425	45	42435 [b]	9.1 [b]
$5d_{3/2}9p_{3/2}$	43 007	4.0	42 954 [b]	23 [b]
$5d_{3/2}9p_{1/2}$	43 200	71	43 026	5.0, 4.6 [b]
$5d_{5/2}5f_{7/2}$	43 465	214	43 258	26
$5d_{5/2}5f_{5/2}$	43 298	3.2	43 264	20, 11 [b]
$5d_{3/2}6f_{5/2}$	43 834	2.5	43 801	1.8
$5d_{5/2}9p_{3/2}$	44 068	57	43 909 [b]	42 [b]
$5d_{3/2}10p_{3/2}$	44 160	3.8	44 126 [b]	14 [b]
$5d_{3/2}10p_{1/2}$	44 414	255	44 163 [b]	5 [b]
$5d_{5/2}6f_{7/2}$	44 709	63	44 604	0.8
$5d_{5/2}6f_{5/2}$	44 629	1.1	44 614	4.4, 2.2 [b]
$5d_{3/2}7f_{5/2}$	44 645	1.5	44 638	7.4, 4.3 [b]
$5d_{3/2}11p_{3/2}$	44 861	2.4	44 833	1.7
$5d_{3/2}11p_{1/2}$	44 897	22	44 855	0.7, 1.4 [b]
$5d_{5/2}10p_{3/2}$	45 220	81	45 008 [b]	18 [b]
$5d_{3/2}8f_{5/2}$	45 150	60	45 168	2.9, 1.8 [b]
$5d_{3/2}12p_{3/2}$	45 320	0.65	45 306	2.2
$5d_{3/2}12p_{1/2}$	45 366	53	45 309	
$5d_{5/2}7f_{5/2}$	45 454	1.8	45 437	
$5d_{5/2}7f_{7/2}$	45 490	34	45 441	7.0, 2.5 [b]
$5d_{3/2}9f_{5/2}$	45 554	11	45 535	0.7, 1.2 [b]
$5d_{3/2}13p_{1/2}$	45 645	0.8	45 626	
$5d_{3/2}13p_{3/2}$	45 647	2.5	45 637	1.4
$5d_{5/2}11p_{3/2}$	45 780	44	45 691 [b]	6.7 [b]
$5d_{3/2}10f_{5/2}$	45 820	32	45 797	1.7, 1.3 [b]
$5d_{3/2}14p_{3/2}$	45 876	0.44	45 863	2.2, 2.1 [b]
$5d_{3/2}14p_{1/2}$	45 894	22	45 869	
$5d_{5/2}8f_{5/2}$	45 982	15	45 969	1.5
$5d_{5/2}8f_{7/2}$	46 011	0.98	45 974	2.1
$5d_{3/2}11f_{5/2}$	45 993	1.4	45 991	1.8
$5d_{3/2}15p_{3/2}$	46 052	1.4	46 037	2.6
$5d_{3/2}15p_{1/2}$	46 056	3.9	46 048	
$5d_{5/2}12p_{3/2}$	46 211	31	46 134	
$5d_{3/2}12f_{5/2}$	46 142	0.3	46 139	1.8
$5d_{3/2}16p_{3/2}$	46 175	0.34	46 173	3.1
$5d_{3/2}16p_{1/2}$	46 185	7.2	46 181	
$5d_{3/2}13f_{5/2}$	46 259	2.5	46 252	1.5
$5d_{3/2}17p_{3/2}$	46 287	0.65	46 276	3.3
$5d_{3/2}17p_{1/2}$	46 292	1.7	46 286	
$5d_{5/2}9f_{5/2}$	46 345	0.54	46 334	1.8
$5d_{5/2}9f_{7/2}$	46 360	4.9	46 338	0.7
$5d_{3/2}14f_{5/2}$	46 346	0.46	46 343	1.5
$5d_{3/2}18p_{3/2}$	46 371	0.86	46 361	4.5
$5d_{3/2}18p_{1/2}$	46 376	1.2	46 371	
$5d_{3/2}15f_{5/2}$	46 419	0.24	46 416	1.3
$5d_{3/2}19p_{3/2}$	46 438	0.93	46 429	5.5
$5d_{3/2}19p_{1/2}$	46 442	0.1	46 438	
$5d_{5/2}13p_{3/2}$	46 489	7.7	46 453	
$5d_{3/2}16f_{5/2}$	46 477	0.86	46 476	1.7
$5d_{3/2}20p_{3/2}$	46 495	0.40	46 486	5.4
$5d_{3/2}20p_{1/2}$	46 500	4.2	46 495	
$5d_{5/2}10f_{5/2}$	46 605	0.78	46 598	1.2
$5d_{5/2}10f_{7/2}$	46 613	0.88	46 599	4.0
$5d_{5/2}14p_{3/2}$	46 705	1.6	46 683	
$5d_{5/2}11f_{5/2}$	46 797	0.93	46 791	0.7
$5d_{5/2}11f_{7/2}$	46 803	0.37	46 793	
$5d_{5/2}15p_{3/2}$	46 870	0.66	46 854	
$5d_{5/2}12f_{5/2}$	46 943	1.7	46 940	4.0
$5d_{5/2}12f_{7/2}$	46 947	0.79		
$5d_{5/2}16p_{3/2}$	46 998	0.81	46 987	
$5d_{5/2}13f_{5/2}$	47 056	2.0	47 055	2.3
$5d_{5/2}13f_{7/2}$	47 060	0.86		
$5d_{5/2}17p_{3/2}$	47 099	0.94	47 091	
$5d_{5/2}14f_{5/2}$	47 146	2.3	47 145	2.0
$5d_{5/2}14f_{7/2}$	47 149	0.98		
$5d_{5/2}18p_{3/2}$	47 180	1.2	47 174	
$5d_{5/2}15f_{5/2}$	47 219	2.6	47 218	1.8
$5d_{5/2}15f_{7/2}$	47 221	0.97		
$5d_{5/2}19p_{3/2}$	47 247	1.4	47 241	
$5d_{5/2}16f_{5/2}$	47 278	2.8	47 278	1.6
$5d_{5/2}16f_{7/2}$	47 280	0.94		
$5d_{5/2}20p_{3/2}$	47 301	1.5	47 297	

[a] Reference [47].

[b] Reference [48].

series with $n_4=9$–15 and $n_5,n_6=5$–11 are embedded in the $5d_{3/2}nl$ series converging to the second ionization limit. Our calculated energies are in reasonable agreement with the measurements of Gounand *et al.* [47] and we note a few misplaced states pertaining to the $5d_{5/2}n_4p_{3/2}$ and $5d_{5/2}n_6f_{7/2}$ series. The $5d_{3/2}n_1p_{1/2}$ and $5d_{3/2}n_2p_{3/2}$ series are mixed together and are interacting more and more as n increases. These two series are perturbed by members of the $5d_{5/2}n_4p_{3/2}$ series, the $5d_{3/2}n_1p_{1/2}$ series being the most affected one. We observe the smallest energy splitting between the $5d_{3/2}13p_{1/2}$ and $5d_{3/2}13p_{3/2}$ states. The eigenchannel R-matrix study of Gounand *et al.* [47] predicted it for $n=11$ whereas it actually occurs for $n=12$ experimentally. With the same method but with a larger basis set, Aymar predicts it well at $n=12$ [49]. This feature has been related to the perturbation by the $6p_{1/2}7s_{1/2}$ state in Ref. [48]. In our calculations, this configuration appears in the fourth position in the CI decomposition of the $5d_{3/2}n_2p_{3/2}$ states. The $5d_{3/2}n_3f_{5/2}$ series is not perturbed except the states $n_3=8$ and 10, which are strongly mixed to the $5d_{5/2}10p_{3/2}$ and $5d_{5/2}11p_{3/2}$ states, respectively. Perturbing $5d_{5/2}n_4p_{3/2}$ states are very diluted and are not clearly identified for $n_4\leqslant 12$. Above the second ionization limit, however, they become almost pure. Perturbing $5d_{5/2}n_6f_{7/2}$ states are mixed to the three $5d_{3/2}nl$ series, more than the perturbing $5d_{5/2}n_5f_{5/2}$ states. These perturbers are better described in jk coupling

TABLE VIII. Energy positions (En.) and widths (Wid.) (cm^{-1}) of the ns^2 $^1S_0$ Wannier states of barium.

n	This work [a]		This work [b]		Ref. [51]	Ref. [52]	
	En.	Wid.	En.	Wid.	En.	En.	Wid.
7	64 253	2111	64 481	898	65 000	60 575	1327±531
8	88 627	171	88 761	92	88 483	83 290	902±425
9	100 092	2632	100 215	1142	99 457	94 922	106±53
10	106 020	889			106 151	101 287	
11	110 516	704			110 277		

[a] LSJ coupling.

[b] jj coupling.

so that we follow the labels given in Refs. [47,48]. Above the second ionization limit, the two $5d_{5/2}n_5f_{5/2}$ and $5d_{5/2}n_6f_{7/2}$ series are mixed together but are identifiable (67%–30%). Extracting even general trends is difficult as far as the linewidths are concerned. They are either overestimated for most low-lying levels or underestimated for most high-lying levels. No really good agreement is then reached though they are of the same order of magnitude as the observed ones above the threshold.

C. Symmetrical ns^2, $7p^2$, and $6d^2$ configurations

Symmetrical configurations are present in our basis sets as well. These configurations are expected to exhibit large correlation effects together with large resonance profiles. We now present our results concerning the so-called Wannier ns^2 $^1S_0$ states and the $7p^2$ and $6d^2$ configurations. No experimental data are available for these configurations (though the $7p^2$ $^3P_2$ and $6d^2$ $^3F_2$ states have been identified in Ref. [50]) due to their difficult optical characterization and their very large width. We therefore compare our results with those obtained by other theoretical studies.

The Wannier ns^2 $^1S_0$ states have been studied by Aymar [51] by means of CI calculations in a finite-size box. We report her work in Table VIII as well as the work of Hahn and Nasser [52]. Hahn and Nasser used a CI method restricted to relevant configurations only. Their energies in Table VIII are their single configuration Hartree-Fock predictions and the error bars account for the variation of the linewidths as their restricted basis set is modified. We note that according to our linewidths, our energies are in good agreement with the calculations of Aymar [51]. The ns^2 states are not well defined since they are strongly mixed to other symmetrical configurations. The $7s^2$ character, in particular, can be ascribed to two successive states. To decide between the two, we have referred to our jj calculation showing that the first state is closer to the $7s^2$ character. Amazingly, the $8s^2$ resonance appears narrow compared with the others. This is probably due to the fact that this state is mainly composed of asymmetrical configurations, as $7pnp$ $(n\geqslant 8)$, contrary to the other resonances. This narrow linewidth is not confirmed by the work of Hahn and Nasser [52]. Conversely their $9s^2$ resonance is much narrower than ours. This reflects the difficulty in calculating the widths of not well characterized states since many symmetrical, but also asymmetrical, configurations are relevant. In this respect, we note that the basis sets used by Hahn and Nasser [52] and their mixing coefficients are quite different from ours.

R-matrix calculations for the $7p^2$ and $6d^2$ configurations are given in Ref. [53]. We compare them with our results in Tables IX and X, respectively. The $7p^2$ triplet states are better characterized than the singlet states, which are strongly mixed to other configurations. The $7p^2$ $^1S_0$ state, in particular, is hidden by the $6d7d$ $^1S_0$ state with a practically equal weight (30%). The $6d^2$ configurations are generally better characterized than the $7p^2$ configurations (between 57 and 88%) and the larger J is, the larger the configuration weight. Comparing now the two theoretical approaches, we observe that the best agreement is reached for the triplet states. The difference in energy positions never exceeds 350 cm^{-1} (for the $6d^2$ $^3P_0$ state), which is correct compared with the linewidths. A larger difference is found for the singlet states. However, the two theoretical results compare well, according to the calculated linewidths. Among the triplet states, the spin-orbit splittings are well reproduced by our perturbation treatment as compared with the R-matrix results.

TABLE IX. Energy positions and widths (cm^{-1}) of the $7p^2$ configuration of barium.

Term	This work		Ref. [53]	
	Energy	Width	Energy	Width
$^1S_0$	80 566	303	79 849	270
$^3P_0$	77 099	135	76 807	172
$^3P_1$	77 194	136	76 904	145
$^3P_2$	77 394	143	77 097	169
$^1D_2$	78 611	1681	78 049	368

TABLE X. Energy positions and widths (cm^{-1}) of the $6d^2$ configuration of barium.

Term	This work		Ref. [53]	
	Energy	Width	Energy	Width
$^1S_0$	73 345	2070	72 600	1300
$^3P_0$	72 471	814	72 120	930
$^3P_1$	72 542	838	72 280	860
$^3P_2$	72 683	859	72 363	800
$^1D_2$	72 814	1097	72 582	815
$^3F_2$	72 279	275	72 045	250
$^3F_3$	72 356	284	72 140	240
$^3F_4$	72 460	297	72 240	220
$^1G_4$	74 072	2158	73 260	810

D. Discussion

The preceding study has shown that our approach is able to give rather good estimations for the energy positions of the $6snl$ and $5dnl$ series, considering the complexity of the spectra and the number of series and states involved in the calculations. In most cases, the CI approach combined with Hartree-Fock wave functions allows a straightforward identification of the states. As a general trend, the energy agreement between theory and experiment increases as the principal quantum number increases, i.e., we predict the energy of very excited states quite accurately. We, however, fail to predict the positions of the low-lying states, in particular, the symmetrical ones, with the same precision. The discrepancies often reach several hundreds of cm^{-1}. We think that this comes from the lack of flexibility of our basis set, which uses numerical Hartree-Fock wave functions. For the low-lying states, our basis set is not rich enough to account for the whole correlation between them. Adding more Hartree-Fock configurations cannot solve the problem, the convergence being too slow or already reached. Another consequence is that we do not predict exactly the position of the most excited perturbers in a series. Indeed, the first perturbers are in the right place because the first members of the perturbed series are energetically well separated, while the next perturbers are often misplaced where this energy separation becomes small. Our configuration-interaction calculation, however, gives a good estimation of the mixing between the perturbers and the members of a given series and allows their labeling without ambiguity. Adding pseudostates in the form of Slater orbitals to the basis sets tends to improve the results for some low-lying states, confirming the preceding analysis. Calculations carried out with Ba^{+} wave functions alone appear well suited for the low-lying states. These calculations, however, failed in describing the high-lying Rydberg states.

Bartschat *et al.* [54] have studied the autoionizing even-parity states below the $6p$ threshold as intermediate states of photoionization from the $6s6p\ {}^1P_1$ state of barium by means of Breit-Pauli *R*-matrix calculations. Their results are of comparable accuracy to ours. We observe that our misplaced states with respect to the experimental order are identical to theirs, though the two theoretical frameworks are quite different. It was pointed out by Bartschat and Greene [55] that the discrepancies observed in this method come from the lack of continuum-continuum-like configurations in the basis set. We recall that our approach neglects the interaction with the continuum too and this may explain why our $6p^2\ {}^1S_0$ state lies so high. This remark leads to discuss the calculation of the linewidths. It seems that our first-order perturbation calculations are not reliable for every state of the investigated spectrum. Neglecting interactions with the continua and then possible destructive interferences may overestimate the widths in many cases. Too large mixing coefficients between two or more configurations with respect to the actual wave function may enlarge the calculated linewidths as well (see the $5dnd$, $J=0$, series). Very small linewidths are difficult to reproduce numerically as noticed for some long-living $5dnd$, $J=0$, states. For more accurate calculations, it is desirable to introduce the continuum in a different way.

IV. CONCLUSIONS

In this paper, we have presented a general approach that combines a pseudopotential framework with the Hartree-Fock approximation followed by CI calculations. This approach appears less accurate than empirical MQDT and eigenchannel *R*-matrix theory but possesses other advantages. Empirical MQDT sometimes requires hyperfine structure measurements to reproduce the correct singlet-triplet admixture and the identification of the perturbers is not absolutely reliable. Moreover, fitting the experimental energy levels becomes a difficult task when many channels interact. The eigenchannel *R*-matrix theory combined with MQDT has been proven to solve these problems. In this latter framework, the predictions are essentially limited by the size of the basis set required, which is often large, and the restricted size of the reaction volume. Our approach needs one CI calculation per symmetry only to provide a complete picture of an atomic or ionic spectrum over a large energy range. This can be done whatever the number of interacting series may be and without previous experimental information. Moreover, its effectiveness has been shown to calculate highly excited states of neutral barium with a reasonable accuracy. More generally, our results are in overall satisfactory agreement with the experimentally observed spectra. All Rydberg series of barium are well reproduced and their perturbers, though sometimes predicted a little too high in the series, are clearly identified. Symmetrical configurations are quite well described too. In detailed comparisons, however, there are significant disagreements. More work is certainly needed to achieve a better accuracy, in particular, for the lowest states, but also for the higher members of the series, where an accuracy of 1 cm^{-1} is not enough to predict the correct effective quantum number, though this was not the main purpose of this work. In some cases, our calculated linewidths show poor agreement with experimental data. This may be attributed either to the use of the Fermi ''golden rule,'' which does not couple the different continua, or to the energy misplacement of the perturbers. Completing and improving our basis sets and treating the continuum properly are the main directions for future investigations.

Application of this approach to the case of doubly excited states of multiply charged ion X^{q+} (Ar^{6+}, for example) is in progress. Such doubly excited states are currently produced by double-electron capture in collisions of $X^{(q+2)+}$ ions with an atomic or molecular target. This field of research is very active experimentally but often lacks data concerning the autoionizing processes, in particular, when the two electrons of X^{q+} are in closely related excitation degrees. This spectroscopic information is needed for a better understanding of ion-atom collisional mechanisms.

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[1] D. R. Hartree, *The Calculation of Atomic Structures* (John Wiley, New York, 1957); C. Froese Fischer, *The Hartree-Fock Method for Atoms* (John Wiley, New York, 1977).
[2] For original articles, see H. Hellmann, Acta Physicochim. URSS **1**, 913 (1935); **4**, 225 (1936); J. Chem. Phys. **3**, 61 (1935); P. Gombás, Z. Phys. **118**, 164 (1941); J. C. Phillips and L. Kleinmann, Phys. Rev. **116**, 287 (1959); **118**, 1153 (1960); B. Austin, V. Heine, and L. Sham, *ibid.* **127**, 276 (1962). For reviews, see J. N. Bardsley, Case Stud. At. Phys. **4**, 299 (1974); A. Hibbert, Adv. At. Mol. Phys. **18**, 309 (1982); L. Szasz, *Pseudopotential Theory of Atoms and Molecules* (John Wiley, New York, 1985); C. Laughlin and G. A. Victor, Adv. At. Mol. Phys. **25**, 163 (1988).
[3] C. D. H. Chisholm and U. Öpik, Proc. Phys. Soc. London **83**, 541 (1964).
[4] P. Hafner and W. H. E. Schwarz, J. Phys. B **11**, 217 (1978).
[5] C. Laughlin and J. E. Hansen, J. Phys. B **29**, L441 (1996); H. Bergeron and A. Valance, Z. Phys. D **6**, 309 (1987).
[6] E. Czuchaj, F. Rebentrost, H. Stoll, and H. Preuss, Chem. Phys. **196**, 37 (1995); W. R. Wadt and P. J. Hay, J. Chem. Phys. **82**, 284 (1985); P. A. Christiansen, Y. S. Lee, and K. S. Pitzer, *ibid.* **71**, 4445 (1979); W. H. E. Schwarz, Theor. Chim. Acta **11**, 377 (1968); A. U. Hazi and S. A. Rice, J. Chem. Phys. **45**, 3004 (1966); L. Szasz and G. McGuinn, *ibid.* **42**, 2363 (1965).
[7] M. Aymar, Phys. Rep. **110**, 163 (1984), and references therein.
[8] M. Aymar, C. H. Greene, and E. Luc-Koenig, Rev. Mod. Phys. **68**, 1015 (1996), and references therein.
[9] G. Peach, in *Atoms in Astrophysics*, edited by P. G. Burke, W. B. Eissner, D. G. Hummer, and I. C. Percival (Plenum, New York, 1983).
[10] J. E. Sienkiewicz and W. E. Baylis, J. Phys. B **20**, 5145 (1987).
[11] S. Hameed, A. Herzenberg, and M. G. James, J. Phys. B **1**, 822 (1968); I. L. Beigman, L. A. Vainshtein, and V. P. Shevelko, Opt. Spectrosc. **28**, 229 (1970); D. W. Norcross, Phys. Rev. A **7**, 606 (1973); A. Hibbert, Phys. Scr. **39**, 574 (1989); C. Laughlin, *ibid.* **45**, 238 (1992).
[12] J. P. Connerade, J. Phys. B **15**, L881 (1982).
[13] H. Silberbach, P. Schwerdtferger, H. Stoll, and H. Preuss, J. Phys. B **19**, 501 (1986); Y. S. Lee, W. C. Ermler, and K. S. Pitzer, J. Chem. Phys. **67**, 5861 (1977).
[14] L. F. Pacios and P. A. Christiansen, J. Chem. Phys. **82**, 2664 (1985); A. O. E. Animalu, Philos. Mag. **13**, 53 (1966).
[15] W. R. Johnson, D. Kolb, and K. N. Huang, At. Data Nucl. Data Tables **28**, 33 (1983).
[16] J. P. Desclaux, At. Data Nucl. Data Tables **12**, 311 (1973).
[17] C. Moore, *Atomic Energy Levels*, Natl. Bur. Stand. (U.S.) Circ. No. 467 (U.S. GPO, Washington, DC, 1958), Vol. 3.
[18] A. Gallagher, Phys. Rev. **157**, 24 (1967).
[19] H. J. Andrä, in *Beam-Foil Spectroscopy*, edited by I. A. Sellin and D. J. Pegg (Plenum, New York, 1976), Vol. 2, p. 835.
[20] P. Kuske, N. Kirchner, W. Wittmann, H. J. Andrä, and D. Kaiser, Phys. Lett. **64A**, 377 (1978).
[21] F. Plumelle, M. Desaintfuscien, J. L. Duchene, and C. Audoin, Opt. Commun. **34**, 71 (1980).
[22] W. Nagourney, J. Sandberg, and H. Dehmelt, Phys. Rev. Lett. **56**, 2797 (1986).
[23] N. Yu, W. Nagourney, and H. Dehmelt, Phys. Rev. Lett. **78**, 4898 (1997).
[24] M. Poirier, Z. Phys. D **25**, 117 (1993).
[25] C. Guet and W. R. Johnson, Phys. Rev. A **44**, 1531 (1991).
[26] H. W. van der Hart, C. Laughlin, and J. E. Hansen, Phys. Rev. Lett. **71**, 1506 (1993).
[27] D. F. Mayers and F. O'Brien, J. Phys. B **1**, 145 (1968).
[28] U. Fano, Phys. Rev. **124**, 1866 (1961).
[29] A. R. Barnett, D. H. Feng, J. W. Steed, and L. J. B. Goldfarb, Comput. Phys. Commun. **8**, 377 (1974).
[30] J. Boulmer, P. Camus, J. M. Gagné, and P. Pillet, J. Phys. B **20**, L143 (1987).
[31] H. Rinneberg, J. Neukammer, G. Jönsson, H. Hieronymus, A. König, and K. Vietzke, Phys. Rev. Lett. **55**, 382 (1985).
[32] J. R. Rubbmark, S. A. Borgström, and K. Bockasten, J. Phys. B **10**, 421 (1977).
[33] M. Aymar, P. Camus, M. Dieulin, and C. Morillon, Phys. Rev. A **18**, 2173 (1978).
[34] P. Camus, M. Dieulin, and A. El Himdy, Phys. Rev. A **26**, 379 (1982).
[35] C. H. Greene and M. Aymar, Phys. Rev. A **44**, 1773 (1991).
[36] M. Aymar, P. Camus, and A. El Himdy, J. Phys. B **15**, L579 (1982).
[37] J. A. Armstrong, J. J. Wynne, and P. Escherick, J. Opt. Soc. Am. **69**, 211 (1979).
[38] B. H. Post, W. Vassen, W. Hogervorst, M. Aymar, and O. Robaux, J. Phys. B **18**, 187 (1985).
[39] B. H. Post, W. Vassen, and W. Hogervorst, J. Phys. B **19**, 511 (1986).
[40] M. Aymar, J. Phys. B **23**, 2697 (1990).
[41] R. D. Hudson, V. L. Carter, and P. A. Young, Phys. Rev. A **2**, 643 (1970).
[42] P. Camus, M. Dieulin, A. El Himdy, and M. Aymar, Phys. Scr. **27**, 125 (1983).
[43] M. Aymar, P. Camus, and A. El Himdy, Phys. Scr. **27**, 183 (1983).
[44] J. Neukammer, H. Rinneberg, G. Jönsson, W. E. Cooke, H. Hieronymus, A. König, K. Vietzke, and H. Spinger-Bolk, Phys. Rev. Lett. **55**, 1979 (1985).
[45] L. D. Van Woerkom, J. G. Story, and W. E. Cooke, Phys. Rev. A **34**, 3457 (1986).
[46] M. Aymar, J. Phys. B **18**, L763 (1985).
[47] F. Gounand, B. Carré, P. R. Fournier, P. d'Oliveira, and M. Aymar, J. Phys. B **24**, 1309 (1991).
[48] K. Maeda, M. Aymar, K. Ueda, H. Chiba, K. Ohmori, Y. Sato, J. B. West, K. J. Ross, and K. Ito, J. Phys. B **30**, 3159 (1997).
[49] M. Aymar (private communication).
[50] J.-M. Lecomte, B. Carré, M. Telmini, H. Lagadec, P. R. Fournier, D. Porterat, and M. Aymar, J. Phys. B **28**, L655 (1995).
[51] M. Aymar, J. Phys. B **22**, 2359 (1989).
[52] Y. Hahn and I. Nasser, Z. Phys. D **27**, 203 (1993).
[53] J.-M. Lecomte, M. Telmini, M. Aymar, and E. Luc-Koenig, J. Phys. B **27**, 667 (1994).
[54] K. Bartschat, B. M. McLaughlin, and R. A. Hoversten, J. Phys. B **24**, 3359 (1991).
[55] K. Bartschat and C. H. Greene, J. Phys. B **26**, L109 (1993).