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CHARACTERISTICS OF THE HELIUM-LIKE $1S^e(3\ell, n\ell')$ AUTOIONIZING STATES

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Résumé - Les états doublement excités des ions héliumoides du type $I^{(Z-2)***}$ situés sous le seuil d'ionisation $N = 3$ sont analysés à partir de la classification DESB (doubly excited symmetry basis). On examinera plus particulièrement les relations entre les caractéristiques du diagramme d'énergie et les propriétés des résonances.

ABSTRACT - Doubly excited states of the helium-like ions $I^{(Z-2)***}$ below the $N = 3$ ionization threshold are analysed in terms of DESB (doubly excited symmetry basis) classification. Emphasis will be put on the relations between the energy diagram features and the resonance properties.

I - INTRODUCTION

In the course of several years we have carried out a program of calculations of resonances for two-electron atomic systems using the projection-operator formalism /1,2/. Our attention for diecited heavy ions was spurred by measurements of states that are populated during collisions of the type :

where I^{Z+} is a fully stripped ion of charge Z .

There is now evidence /3,4/ that the states of the type $I^{(Z-2)+}(n\ell, n'\ell')$ with $n, n' \geq 2$ are populated during these processes. The knowledge of the resonance parameters as well as correlation patterns is crucial for the interpretation of double electron capture experiments. It must also be stressed that, generally, several continua are open for the autoionization. In this case, the calculation of branching ratios (for which almost nothing is known) can be necessary, as in the Lyman X ray spectroscopy experiments /4/. Besides the collisional study of reaction (1), the knowledge of the resonance patterns of the doubly excited ions $I^{(Z-2)***}$ has become a subject of considerable interest.

The final objective of our work is the study of the $(3\ell n\ell')$ resonances of the helium isoelectronic series for $Z = 2 - 10$ a.u. and the calculation of their energies and corresponding partial widths. In this paper we will put the attention in a partial aspect of this general study : the classification problems and the correlation patterns of these resonant states.

For the classification we adopt the doubly excited symmetry basis (DESB), where the K and T quantum numbers are defined /5/, and as correlation patterns we use the mean value of $\cos\theta_{12}$, where θ_{12} is the angle between the two electrons.

As illustration we present our results for the $1S^e He(3\ell n\ell')$ isoelectronic series which will allow us to discuss some features whose validity is general for other symmetries. Before, we will give a brief recall of the theory.

Atomic units will be used unless otherwise stated.

II - THEORY

2.1 - The conventional-Feshbach approach

This method has been widely developed in the literature /6/. Briefly we give here the main aspects of this approach. We consider the problem of two electrons moving in the field of a charge Z . We have to solve the Schrödinger equation

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$$(H - E) \Psi = 0 \quad (2)$$

where H is the non-relativistic hamiltonian of the system. In the Feshbach formalism, the unshifted energy E_s of the resonant state $\chi_s^{L,S}$ is given by

$$(QH - E_s) \chi_s^{L,S} = 0 \quad (3)$$

where L and S are respectively the total angular momentum and the total spin. Q is a projection operator defined by :

$$Q = 1 - P \quad (4)$$

$$\text{with } P = P_1 + P_2 - P_1 P_2 \quad (5)$$

$$\text{and } P_i = \sum_{n=1}^{N-1} \sum_{\ell=0}^{n-1} \sum_{m=-\ell}^{\ell} |\Phi_{n\ell m}(r_i)\rangle \langle \Phi_{n\ell m}(r_i)| \quad (6)$$

N specifies the hydrogenic threshold just above the series of autoionizing states considered, and $\Phi_{n\ell m}(r_i)$ is the hydrogenic function for the electron i . The non-resonant part of the wavefunction representing the system after autoionization is given by :

$$(PH - E_s) \chi_c^{L,S} = 0 \quad (7)$$

In equation (7) all the second-order polarization effects are neglected. The width of the resonant state $\chi_s^{L,S}$ is given by the golden rule formula :

$$\Gamma = 2\pi \left| \langle \chi_c^{L,S} | PHQ | \chi_s^{L,S} \rangle \right|^2 \quad (8)$$

where $\chi_c^{L,S}$ is normalized to the energy scale.

2.2 - The pseudopotential Feshbach approach

In this approach the equation (3) is replaced by /7/ :

$$(H + M P - P^S E_s) P^S \chi_s^{L,S} = 0 \quad (9)$$

where M is an arbitrary large positive number. Martín et al /7/ have pointed out that the solutions of eq. (9) and (3) are equivalent when $M \rightarrow \infty$ (see /8/ for a comparison between both methods). When non-hydrogenic orbitals are used as basis functions the pseudopotential-Feshbach approach is much faster than the resolution of eq. (3). In this work we will use eq. (9) and $P^S \chi_s^{L,S}$ will be denoted $\chi_s^{L,S}$ for simplicity.

2.3 - The open channel wavefunction

To calculate the open channel wavefunction $\chi_c^{L,S}$ in eq. (7), we use the static exchange approximation :

$$\chi_c^{L,S} = \frac{1}{\sqrt{2}} \mathcal{A} \left[\Phi_{n_1 \ell_1}(1) F_{\ell_2}(2) \mathcal{Y}_{\ell_1 \ell_2}^{L,S}(1,2) \right] \quad (10)$$

where $\mathcal{A}$ is the antisymmetrization operator, $\Phi_{n\ell}$ the final hydrogenic state for the ion, ℓ_2 the angular momentum of the ejected electron and $\mathcal{Y}_{\ell_1 \ell_2}^{L,S}(1,2)$ is the usual angular part for the two electron system /1/. The function F_{ℓ_2} is expanded in a basis of Slater-type orbitals (STO). Then the eq. (7) is solved through a diagonalization method and the normalization of the continuum function $\chi_c^{L,S}$ is achieved according to the well tested discretization method of Macias et al /9/.

2.4 - The DESB classification

The DESB configuration mixing has been established by Wulfman /10/. Herrick and Sinanoglu /5/ have introduced the quantum numbers K and T through the form :

$$|(Nn) \text{ } ^{KT} 2s+1 L^\pi\rangle = \sum_{\ell, \ell'} |N\ell, n\ell'; L\rangle D_{N\ell n\ell'}^{KT L^\pi}, \quad (11)$$

$|N\ell, n\ell'; L\rangle$ is related to the usual hydrogenic configurations and

$$D_{N\ell n\ell'}^{KT L^\pi} = g_\pi (-1)^{\ell'} [(n+K+T)(n+K-T)(2\ell+1)(2\ell'+1)]^{1/2}$$

$$M \begin{Bmatrix} (N-1)/2 & (n-1)/2 & (n-1+T+K)/2 \\ (N-1)/2 & (n-1)/2 & (n-1+T-K)/2 \\ \ell & \ell' & L \end{Bmatrix} \quad (12)$$

M is a normalization factor and g_π "selects" the states of a given symmetry, the quantity in braces is a 9j coefficient. The quantum number K is proportional to $\langle r_i \cos \theta_{12} \rangle$ where r_i refers to the inner electron. The positive value of K corresponds in general to the position of the electrons on the opposite side of the nucleus, the negative value of K corresponds to electrons on the same side. The number T^2 describes the relative orientation of the orbits of the electrons, and it is proportional to the square of $\langle L \cdot r_i \rangle$.

The $\chi_s^{L,S}$ states are classified according to the procedure of Robaux /11/, expanding $\chi_s^{L,S}$ in the $|(Nn) \text{ } ^{KT} 2s+1 L^\pi\rangle$ basis :

$$\chi_s^{L,S} = \sum_{K,T,n,N} a_{KT}^{Nn} |(Nn) \text{ } ^{KT} 2s+1 L^\pi\rangle \quad (13)$$

In order to classify the $1S^e$ states, we shall first develop $\chi_s^{L,S}$ on a basis of configurations $|N\ell, n\ell'; L\rangle$ with $3 \leq N \leq 4$ and $3 \leq n \leq 5$. Then we determine the coefficients a_{KT}^{Nn} in expansion (13) and the label (K,T) will be given according to the larger coefficient b_{KT} determined by :

$$b_{KT} = \sum_{n,N=3} |a_{KT}^{Nn}|^2 \quad (14)$$

III- RESULTS AND DISCUSSION

The secular equation for the effective hamiltonian (9) was set up for the $1S^e$ symmetry in a representation of configurations built from the basis set of STO's given in Table 1. We have used $M = 500$ a.u. and we have checked that our results are invariant in the range $100 \leq M \leq 1000$. In table 2 we present the energies and widths of the $1S^e(3\ell n\ell')$ resonant states of the He atom and these are compared with previous calculations /12-16/.

For the study of the characteristics of these resonant states it is useful to consider the evolution of their energies with the nuclear charge Z. In this respect, it is useful to introduce the effective quantum number n^* through the usual formula :

Table 1 - STO basis set used in the calculation of closed channel wavefunctions. All $n\ell n'\ell'$ configurations with $n' < 7$ are included. The STO functions are defined as

$$\varphi_{n\ell} = N r^{n-1} e^{-\zeta_i r} Y_\ell^m(\theta, \varphi).$$

$\ell = 0$		$\ell = 1$		$\ell = 2$		$\ell = 3$	
n	ζ_i	n	ζ_i	n	ζ_i	n	ζ_i
1-3	1/3	2-3	1/3	3	1/3	4	1/4
4-6	1/5	4-6	1/5	3-6	1/5	4-6	1/5
7-9	3/20	7-9	3/20	7-9	3/20	7-9	3/20
10	1/10	10	1/10				
11	1/11						

Table 2 - Energies and widths of the $1S^e(3\ell n\ell')$ states of helium. Comparison with other calculations.

State	- E(a.u.)				
	This work	Feshbach ^a	Complex coordinate ^b	Close-coupling ^c	Feshbach (TDM) ^d
$1S^e(1)$	0.354503	0.35448	0.35354	0.3534	0.3537
$1S^e(2)$	0.316450	0.31614	0.31745	0.3167	0.3137
$1S^e(3)$	0.281510	0.28148	0.28115	0.2800	0.2798
$1S^e(4)$	0.263503	0.26304	0.26350	0.2617	0.2613
$1S^e(5)$	0.257663	0.25746	0.25737	-	0.2492
$1S^e(6)$	0.256161	0.25612	-	0.2554	0.2551
$1S^e(7)$	0.246610	0.24638	-	0.2463	0.2457
$1S^e(8)$	0.244376	0.24420	-	-	0.2400
$1S^e(9)$	0.243909	0.24386	-	0.2433	0.2432
$1S^e(10)$	0.238406	0.23836	-	-	-

State	$\Gamma(\text{eV})$				
	This work	Feshbach ^a	Complex coordinate ^b	Close-coupling ^c	Feshbach (TDM) ^d
$1S^e(1)$	0.09700	-	0.08164	0.0860	0.083
$1S^e(2)$	0.17087	-	0.18096	0.2246	0.146
$1S^e(3)$	0.04871	-	0.00014	0.0478	0.046
$1S^e(4)$	0.05731	-	0.06395	0.0688	0.037
$1S^e(5)$	0.00264	-	0.00014	-	0.00032
$1S^e(6)$	0.02232	-	-	0.0249	0.023
$1S^e(7)$	0.02573	-	-	0.0207	0.018
$1S^e(8)$	0.00295	-	-	-	-
$1S^e(9)$	0.01149	-	-	-	0.015
$1S^e(10)$	0.01333	-	-	-	-

a) Oberoi /12/

b) Ho and Callaway /13/

c) Ormonde, Whitaker and Lipsky /15/, the energies are given by Ormonde and Lipsky in /16/ (private communication)

d) Herrick and Sinanoglu /14/

$$E = -\frac{Z^2}{2N^2} - \frac{(Z-1)^2}{2n^2} \quad (15)$$

with $N = 3$. Following Macias and Riera /17/ we have varied Z continuously and we have represented $1/2n^2$ as a function of Z^{-1} (see fig. 1). In fig. 1 we give also the (K,T) label for the six lowest states in the $Z = \infty$ limit. We will focus our attention on the avoided crossings that appear in this figure. As Herrick and Sinanoglu pointed out /14/, these pseudo-crossings play a crucial role in the problem of classification. The large number of them, in the vicinity of $Z^{-1} \approx 0.5$ a.u., makes the characterization of the $1S^e(3\ell n\ell')$ resonant states of He much more difficult than for the $1S^e(2\ell, n\ell')$ resonances. In fig. 2 we have plotted $\langle \cos\theta_{12} \rangle$ as function of Z^{-1} for the six lowest states shown in fig. 1. For $Z^{-1} \leq 0.2$ a.u., this angular correlation pattern is stable and therefore no problems of classification arise there. However, as one could expect, $\langle \cos\theta_{12} \rangle$ varies rapidly in the pseudo-crossing regions. In particular, let us consider the $1S^e(3)$ state which is classified (-2,0) in the $Z = \infty$ limit. Fig. 1 shows that this resonant state interacts with the $1S^e(4)$ one at $Z^{-1} \approx 0.33$ a.u. (the exchange of character between these two states is clearly exhibited in fig. 2). When $Z^{-1} = 0.5$, the $1S^e(3)$ state is clearly classified (2,0). However, the situation is not so simple for the $1S^e(4)$ state, which presents a wide pseudo-crossing - i.e. a mixing - with the $1S^e(5)$ one in this region. This is confirmed by the comparison of the b_{KT} coefficients (eq. 14) between Ne^{8+} and He (see table 3). The presence of this

Fig. 1 - Variation of $1/2 N^{*2}$ versus $1/Z$.
The (K,T) label refers to DESB classification.

Fig. 2 - The mean values $\langle \cos \theta_{12} \rangle$ versus $1/Z$. The label is relative to the position of the state in the series.

Table 3 - The main coefficients b_{KT} in the DESB classification of the six lowest $1S^e$ resonant states of He. The values within parentheses are relative to the Ne^{8+} case.

(KT)	(2,0)	(0,0)	(-2,0)
State			
$1S^e(1)$	1.0 (1.0)	- -	- -
$1S^e(2)$	- -	1.0 (1.0)	- -
$1S^e(3)$	1.0 -	- -	- (1.0)
$1S^e(4)$	- (1.0)	0.8 -	0.2 -
$1S^e(5)$	- -	0.2 (1.0)	0.8 -
$1S^e(6)$	1.0 -	- -	- (1.0)

pseudo-crossing does not prevent only the classification of this state, but it also complicates the calculation of its resonance parameters. In this region, any small variation of the basis set used to determine the resonant wavefunction may introduce critical variations of the width.

Another conclusion that can be extracted from fig. 1 is that the interaction between resonant states is related directly with the (K,T) quantum numbers exchanged in the pseudo-crossing region. In general, it can be stated, in a qualitative way, that the energy separation in the avoided crossing is larger, the smaller is $| \Delta K |$.

We now examine the results presented in table 2. Our calculated energy values are in fairly good agreement with other previous calculations. In this respect, it is worth noticing that we use approximately 150 configurations. Nevertheless, we can observe in table 2 two major discrepancies for the width of the $1S^e(3)$ and $1S^e(5)$ states. These discrepancies (orders of magnitude) concern mainly the widths reported by Ho and Callaway /13/. We notice also that some values given by Herrick and Sinanoglu /14/ are in disagreement with other calculations. For instance, these authors give 0.037 eV for the width of the $1S^e(4)$ state, while the other calculations give approximately 0.06 (± 0.01) eV. Such discrepancy may be explained by the

smallness of the basis set used by Herrick and Sinanoglu. In view of the previous analysis, the pseudo-crossing between $1S^e(5)$ and $1S^e(6)$ for $Z \approx 2.0$ a.u. may explain the large difference between our results and those of Ho and Callaway /13/. Indeed, the value of the width of the $1S^e(5)$ resonant state is very sensitive to the basis set used in the calculations. It is also the case of the b_{kl} coefficients relative to this state. Therefore it is impossible to conclude definitively on the validity of our calculations for this state. However, the case of the $1S^e(3)$ autoionizing state is quite different. As mentioned above, it does not present any pseudo-crossing in the region $Z \approx 2.0$ a.u. (see fig. 1) and we have checked the stability of our results when the basis set is modified. Moreover, for this state our result is in agreement with the close coupling calculation of Ormonde et al /15/. Therefore, the value given by Ho and Callaway /13/ for the width of the $1S^e(3)$ state is questionable.

IV - CONCLUSIONS

We have analysed the properties of the $1S^e(3\ell n\ell')$ resonant states for $Z = 2 - \infty$ a.u.. The energy diagram of fig. 1 exhibits some pseudo-crossings that complicate the classification as well as the determination of the resonance parameters /14/. In the pseudo-crossing region, where the resonance states exchange their character, explicit calculations are necessary to classify the resonances. Nevertheless, the sensitivity of the results to the basis set used must be carefully checked. Outside the pseudo-crossing regions the (K,T) label may be assigned without any ambiguity. As a matter of fact, these problems exist for other symmetries and they are under investigations.

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