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EXTENSION OF THE CONVENTIONAL AND PSEUDOPOTENTIAL FESHBACH METHODS TO THE STUDY OF "TWO ACTIVE ELECTRONS + CORE" RESONANCE STATES. APPLICATION TO $C^{2+}(1s^2 3\ell 3\ell')$ and $Ne^{6+}(1s^2 3\ell 3\ell')$ SYSTEMS

A. MACIAS, O. MO, A. RIERA, M. YAÑEZ, H. BACHAU*, P. GALAN* and F. MARTIN⁽¹⁾

Departamento de Química, Facultad de Ciencias C-XIV, Universidad Autónoma de Madrid, SP-28049 Madrid, Spain

**Laboratoire des Collisions Atomiques, CNRS ER-260, Université de Bordeaux I, F-33405 Talence, France*

Résumé - Nous étudions l'extension des méthodes "conventional-Feshbach" et "pseudopotential-Feshbach" au calcul des paramètres des résonances de systèmes à un coeur $1s^2$ et deux électrons actifs, le coeur étant décrit par un potentiel modèle. Comme application nous calculons les énergies et largeurs des résonances $1s^e$, $1,3p^0(1s^2 3\ell 3\ell')$ de C^{2+} et Ne^{6+} . L'accord entre les deux méthodes est très encourageant du point de vue de la souplesse et de la rapidité de calcul de la méthode "pseudopotential-Feshbach".

Abstract - We report an extension of the conventional and pseudopotential Feshbach methods to the calculation of resonance parameters in atomic systems with two active electrons in the presence of a closed core which is described by a model potential. As illustration, energy positions, total and partial widths are calculated for the $1s^e$, $1,3p^0(1s^2 3\ell 3\ell')$ resonances of C^{2+} and Ne^{6+} . Agreement between the two Feshbach procedures is very encouraging in view of the versatility and computational speed of the pseudopotential method

I - INTRODUCTION

In the last years charge-transfer processes for slow collisions between multiply charged ions and neutral particles have been extensively studied both theoretically and experimentally. Recently, doubly excited ions produced by double capture have received a particular interest (see for example /1,2/). Electron spectroscopy is certainly one of the best methods to study multiple capture because multiply excited states formed in this process generally decay by electron emission. Despite the large number of papers devoted to the study of doubly excited states there is an almost complete lack of theoretical and experimental results in beryllium-like ions. One must note the recent results in Ne^{6+} /2-4/ where the measurements, coupled to theoretical calculations, show that capture goes to $Ne^{6+}(1s^2 3\ell n'\ell')$ $n' \geq 3$. Recently, Martín et al /5/ have proposed a method to calculate the energies and widths of $Be(1s^2 n\ell n'\ell')$ -like ions. In this work a model potential was used to describe the $1s^2$ core and the pseudopotential-Feshbach method of Martín et al /6/ to obtain the resonance wavefunctions. Good agreement with experiments was found. However, in order to systematically apply the method, some steps involved in this kind of calculation should be analyzed in detail and in this respect that concerning the use of model potentials for the calculation of resonance states will be discussed elsewhere /7/. More specifically, although the accuracy of the pseudopotential-Feshbach method has been tested for two-electron atomic systems /8/, this point remains to be checked when model potentials are used to describe core effects. The interest of this checking lies in the fact that the new pseudopotential method is computationally much less involved than the conventional Feshbach approach when several channels are open (even when model potentials are used for the latter). One of the aims of this paper is to show explicitly, as it was done in /8/ for He-like systems, that the pseudopotential-Feshbach method gives the same results than the Feshbach one when several channels are open and model potentials are used in both. To perform this study we have chosen the $(1s^2 3\ell 3\ell')1s^e$ and $1,3p^0$ resonance states of C^{2+} and Ne^{6+} , since they can decay to either $1s^2 2s$ or $1s^2 2p$ thresholds with simultaneous emission of the fourth electron.

(1) Permanent address : Departamento de Química, Facultad de Ciencias C-XIV, Universidad Autónoma de Madrid, SP-28049 Madrid, Spain

Very recently, the resonance positions of these ions have been determined experimentally by Bordenave-Montesquieu et al /2/ and Mack and Niehaus /4/. The analysis of their spectra shows that all the states corresponding to a $(1s^2 3\ell 3\ell')$ configuration lie very close in energy and that the resolution of the peaks is limited by the natural width of each state and the post-collisional interaction profile (induced by the remaining ion). Moreover, since the $2s$ and $2p$ threshold are not degenerate in these systems, these spectra contains two different peaks associated to each resonance. These complications give, however, useful information concerning the branching ratios to each threshold. In this respect, the Feshbach method directly provides partial widths that are related with these branching ratios. A second aim of this paper is to give energy positions, total and partial widths, as well as the wavefunction characteristics for the C^{2+} and $Ne^{6+}(1s^2 3\ell 3\ell')$ resonance states to provide a further insight in the resonance structure of these systems.

II - METHOD

In our approach we will replace the exact four electron hamiltonian by an approximate one for the two active electrons :

$$H_M = H_M^0(1) + H_M^0(2) + \frac{1}{r_{12}} \quad (1)$$

where

$$H_M^0(i) = -\frac{1}{2} \nabla_i^2 - \frac{Z}{r_i} + V_M(i) \quad (2)$$

and V_M is a model potential which depends on the particular core considered. For the case of an $1s^2$ core, it has been shown /7/ that a convenient form that accounts for the core-valence effects is

$$V_M(i) = \frac{2}{r_i} - \frac{2}{r_i} (1 + \alpha r_i) e^{-2\alpha r_i} \quad (3)$$

with α a parameter which is chosen by fitting the exact energy of the lowest $2S$ state of the ionized system. In particular, for C^{2+} and Ne^{6+} we have used $\alpha = 3.722668$ and 6.366365 , respectively.

In the Feshbach formalism /7/, the resonant wavefunction ψ is written as a sum of a closed channel $Q\psi$ and open channel $P\psi$ components :

$$\psi = P\psi + Q\psi \quad (4)$$

where P is a projection operator such that asymptotically $P\psi = \psi$, and $Q = 1 - P$. For a two electron system, as that described by hamiltonian (1), the P operator has the form :

$$P = P(1) + P(2) - P(1)P(2) \quad (5)$$

with $P(i)$ is a one electron projection operator given by

$$P(i) = \sum_{\alpha=1}^N |\varphi_{\alpha}(i)\rangle \langle \varphi_{\alpha}(i)| \quad (6)$$

where φ_{α} are the eigenfunctions of the one electron hamiltonian H_M^0

$$H_M^0 \varphi_{\alpha} = \epsilon_{\alpha} \varphi_{\alpha} \quad (7)$$

and N is the number of states of eq. (7) whose energies lie below the doubly excited state of interest. Following the Feshbach method, the closed-channel wavefunction Φ_n can be defined as the eigensolution of

$$(QH_MQ - E_n) \Phi_n = 0 \quad (8)$$

where E_n are the resonance positions to first order in QH_MP . In practice, the solution of the projected equation (8) can be directly achieved by an extension /10/ of the truncated

diagonalization method which uses, as a basis set, two electron configurations built from the eigenfunction Φ_α of eq. (7) for $\alpha > N$.

An alternative, mathematically equivalent procedure to this conventional approach was recently proposed by Martín et al /6/ and draws on the analogy between the Feshbach /9/ and the Phillips-Kleinman pseudopotential /11/ theories. This is to solve

$$H_{eff} \Phi_n \equiv (H_M + V_{PS}) \Phi_n = E_n \Phi_n \quad (9)$$

which defines the effective hamiltonian H_{eff} and where

$$V_{PS} = M P \quad (10)$$

and M is a large arbitrary positive number. While both methods are equivalent, the advantage of the latter is that it provides the closed channel wavefunction with a much more reduced computational effort, since it does not require constructing the projected hamiltonian $QH_M Q$. The partial widths of the Φ_n resonant state corresponding to each open channel β are given by

$$\Gamma_{n\beta} = 2\pi |\langle \Phi_n | QH_M P | \chi_{E\beta} \rangle|^2 \quad (11)$$

where the open-channel wavefunction $\chi_{E\beta}$ is (to first order in $QH_M P$) the solution of

$$(PH_M P - E) \chi_{E\beta} = 0 \quad (12)$$

Then the total width can be written

$$\Gamma_n = \sum_{\beta} \Gamma_{n\beta} \quad (13)$$

To solve eq. (12) we have used the static exchange approximation for each channel β , together with the well tested discretization procedure of Macías et al /12/. Thus, the wavefunction $\chi_{E\beta}$ is written as a sum of configurations of the form $(\phi_\beta \epsilon_{n\ell m})$ with $\beta \leq N$, where ϕ_β is the one electron orbital representing the residual ion after ionization (see eq. (7)) and $\epsilon_{n\ell m}$ are Slater type orbitals (STO's).

The weights $w_n^{[k]}$ in the closed channel wavefunction of configurations of a given character $[k]$ are defined as /8/ :

$$w_n^{[k]} = \sum_{ij} c_{in}^{[k]} s_{ij} c_{jn}^{[k]} \quad (14)$$

where $c_{in}^{[k]}$ are the expansion coefficients of the closed channel Φ_n wavefunction in the representation chosen to construct it, and S is the overlap matrix in the closed channel basis.

III - RESULTS AND DISCUSSION

To obtain the resonance energies and the corresponding wavefunctions we have solved eqs. (8 and 9) in a representation of configurations built from the basis set of STO's given in Table 1. In the effective hamiltonian of eqs (9 and 10), we have chosen $M = 100$ a.u., and we have checked that the results are invariant for higher values of M. The $\epsilon_{n\ell m}$ STO basis sets employed to solve the corresponding open channel eq. (12) are those given in /8/. Table 2 presents energy positions and total widths for $1s^e$, $1,3p^0(3\ell,3\ell')$ resonance states of C^{2+} and Ne^{6+} obtained with both the pseudopotential and conventional Feshbach methods described above. The agreement between them is very good. In table 3 we present the weights in the resonant wavefunction of configurations of a given character. Those for high ℓ -df and ff- are very small, indicating the ℓ -convergence of our calculations in all cases. These results also show that each resonant state has mainly one contribution that is predominant, specially in the triplet case. This is quite different for two electron systems, where a great mixture of characters is the general rule. Finally, in table 4 we show the partial widths for these states obtained with both methods. Again, the overall agreement is very good, what can be taken as a further test of the theory.

As a conclusion, our generalization of the pseudopotential method of Martín et al /6/ to treat this kind of resonant states gives results for positions and total widths as well as partial resonance widths that are comparable with those obtained with the conventional

partitioning technique (where the truncated diagonalization method is used). These results are achieved with a considerably smaller effort than all the alternative methods that have been hitherto proposed.

Table 1 - STO basis set used in the calculation of the closed channel wavefunction. All configurations are included. The STO functions are defined as

$$\varphi_{n\ell m} = N r^{n-1} e^{-(Z-1.7)\zeta_i r} Y_{\ell}^m(\theta, \varphi)$$

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

Table 2 - Energies and widths of the $1s^e$, $1,3p^0(1s^2, 3\ell, 3\ell')$ states of Ne^{6+} and C^{2+}

a) Pseudopotential-Feshbach approach

b) Conventional-Feshbach approach

		$-E(a.u.)$			
		Ne^{6+}		C^{2+}	
		a	b	a	b
$1s^e$	(3,3a)	7.0834	7.0816	1.7421	1.7412
	(3,3b)	6.6420	6.6332	1.5428	1.5382
$1p^0$	(3,3a)	6.8269	6.8282	1.6220	1.6235
	(3,3b)	6.3861	6.3765	1.4336	1.4306
$3p^0$	(3,3a)	6.9633	6.9685	1.6848	1.6888
	(3,3b)	6.5772	6.5715	1.5133	1.5104

Table 2 -

		$\Gamma(eV)$			
		a	b	a	b
$1s^e$	(3,3a)	0.0882	0.0917	0.0453	0.0877
	(3,3b)	0.6068	0.6156	0.3498	0.5012
$1p^0$	(3,3a)	0.3244	0.3423	0.2540	0.2986
	(3,3b)	0.1546	0.1363	0.0907	0.0862
$3p^0$	(3,3a)	0.0978	0.0948	0.0879	0.0927
	(3,3b)	0.0529	0.0547	0.0428	0.0435

Table 3 - Weights of the configurations of a given character used in the CI expansion of the closed-channel wavefunction (see eq. 14) for Ne^{6+}

		w[sp]	w[pd]	w[df]	w[ss]	w[pp]	w[dd]	w[ff]
$1p^0$	(3,3a)	0.770	0.230	0.000				
	(3,3b)	0.224	0.752	0.024				
$3p^0$	(3,3a)	0.958	0.042	0.000				
	(3,3b)	0.042	0.953	0.005				
$1s^e$	(3,3a)				0.875	0.125	0.000	0.000
	(3,3b)				0.081	0.605	0.314	0.000

Table 4 - Partial widths $\Gamma_{n\alpha}$ (in eV) for the resonant states of table 2, corresponding to $\alpha = 2s\epsilon s$, $2p\epsilon p$ (for $1S^e$ symmetry) and $2s\epsilon p$, $2p\epsilon s$ and $2p\epsilon d$ (for $1, 3P^o$ symmetry) continua. (a) and (b) as in table 2

		$\Gamma_{2s\epsilon p}$		$\Gamma_{2p\epsilon s}$		$\Gamma_{2p\epsilon d}$	
		a	b	a	b	a	b
Ne^{6+}	$1P^o$ (3,3a)	0.1146	0.1164	0.1635	0.1837	0.0463	0.0422
	(3,3b)	0.0030	0.0016	0.0102	0.0091	0.1414	0.1256
	$3P^o$ (3,3a)	0.0452	0.0429	0.0479	0.0472	0.0047	0.0047
	(3,3b)	0.0038	0.0038	0.0152	0.0166	0.0339	0.0343
C^{2+}	$1P^o$ (3,3a)	0.0865	0.1055	0.1404	0.1641	0.0271	0.0290
	(3,3b)	0.0025	0.0010	0.0041	0.0036	0.0840	0.0816
	$3P^o$ (3,3a)	0.0359	0.0392	0.0502	0.0511	0.0018	0.0024
	(3,3b)	0.0035	0.0036	0.0088	0.0085	0.0306	0.0314

		$\Gamma_{2s\epsilon s}$		$\Gamma_{2p\epsilon p}$	
		a	b	a	b
$Ne^{6+} 1S^e$	(3,3a)	0.0872	0.0906	0.0010	0.0011
	(3,3b)	0.0570	0.0659	0.5498	0.5497
$C^{2+} 1S^e$	(3,3a)	0.0438	0.0782	0.0015	0.0095
	(3,3b)	0.0474	0.0634	0.3224	0.4378

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