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Energies and widths of $(1s^2 3l3l')$ resonant states of C^{2+}, N^{3+}, O^{4+}, and Ne^{6+}

F. Martín, O. Mó, A. Riera, and M. Yáñez
Departamento de Química, Facultad de Ciencias, C-XIV Universidad Autónoma de Madrid,
Canto Blanco, 28049 Madrid, Spain

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We report theoretical results for autoionizing states of systems with a closed-shell core and that lie above several ionization thresholds. The energy positions and widths are given for the $(1s^2 3l3l')$ ^1S and $^{1,3}P$ resonant states of the C^{2+}, N^{3+}, O^{4+}, and Ne^{6+} ions, which are of great experimental interest at the present moment. Our results show that a generalization of the method of F. Martín *et al.* [Europhys. Lett. **4**, 799 (1987); J. Chem. Phys. **87**, 6635 (1987)] provides a very useful and simple procedure to obtain energy positions and resonance widths, as well as the contributions of the different continua to the width.

Very recently, formation of $(1s^2 nln'l')$ doubly excited states of Be-like systems in collisions between multicharged ions and gaseous targets has been reported by several experimental groups.[1-12] These authors point out the fact that no theoretical results have been reported for this kind of resonant state, presumably because of their complexity. For example, it is well known[13,14] that the widely used Feshbach approach[15] is extremely difficult to implement for a four-electron system.

On the other hand, since the core $1s^2$ electrons play an almost passive role in the structure of the $(1s^2 nln'l')$ resonant states, the use of model-potential techniques is a very promising alternative to the full-electron treatment because it permits reduction of the problem to an effective two-electron case, thus considerably simplifying the theory. Nevertheless, implementation of the Feshbach formalism, even for a two-electron Hamiltonian, for resonances (like $1s^2 nln'l'$) whose energies lie above more than one ionization threshold is still very cumbersome.

To avoid this second difficulty, we have recently proposed[16,17] a new variant of the Feshbach method, based on the addition of a pseudopotential to the Hamiltonian, which allows us to solve the closed-channel equation with essentially the same computational effort whatever the number of ionization thresholds. Application of this new method to the calculation of the resonance parameters of two-electron atomic[16] and molecular[17] systems showed its high accuracy. Besides, it is very easily implemented when a model potential is included in the Hamiltonian to describe core effects, and this is a very important asset for the present study.

Hence, and as proof of the last statement, in the present communication we present energy positions and widths for the ^1S and $^{1,3}P$ $(1s^2 3l3l')$ doubly excited states of the C^{2+}, N^{3+}, O^{4+}, and Ne^{6+} ions (of great experimental interest, see, e.g., Refs. 2, 3, and 6–9). To be self-contained, we shall first present a very brief summary of the steps involved in our method. Atomic units are used throughout in the theory.

To describe the valence states of a system consisting of a core and two valence electrons, we set up a model Hamiltonian, H_M, of the form

$$H_M = H^0(1) + H^0(2) + V_M(1) + V_M(2) + r_{12}^{-1}, \quad (1)$$

in an obvious notation, where H^0 is a hydrogenic Hamiltonian, and V_M a model potential[18] that accounts for core-valence effects:

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

with α a parameter which is chosen by fitting the exact energy of the lowest ^2S state of the ionized system.

Following standard Feshbach theory, the wave function of an autoionizing state is written as a sum of closed- and open-channel components:

$$\psi(\mathbf{r}_1,\mathbf{r}_2) = P\psi + Q\psi, \quad (3)$$

where P is a projection operator such that $P\psi \rightarrow \psi$ as r_1 or $r_2 \rightarrow \infty$, $Q = 1 - P$, and[19]

$$P = P_1 + P_2 - P_1 P_2, \quad (4)$$

where P_1 is a one-electron projection operator of the form

$$P_i = \sum_\beta |\varphi_\beta(i)\rangle\langle\varphi_\beta(i)| \quad (5)$$

with φ_β the $(1s,2s,2p)$ eigenfunctions of the one-electron

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Hamiltonian H^0+V_M whose energies lie below the doubly excited state of interest.

The resonance positions are given[15] by the eigenenergies E_n^d of the closed-channel projected Hamiltonian QH_MQ. To obtain these, and the corresponding wave functions, we draw on the analogy between the Feshbach[15] and the Phillips-Kleinman[20] pseudopotential theories, pointed out by Martín and co-workers,[16,17] and solve

$$H_{\text{eff}}\phi_n = E_n^d\phi_n \,, \tag{6}$$

where H_{eff} is an effective Hamiltonian:

$$H_{\text{eff}} = H_M + V_{ps} \tag{7}$$

and the pseudopotential V_{ps}, as shown by Martín and co-workers,[16,17] can be written in the form

$$V_{ps} = MP \tag{8}$$

where M is a large, but otherwise arbitrary, positive number.

Next, the open-channel wave function corresponding to the continuum $\chi^{E\beta\gamma}$ ($\beta\gamma = 2s\varepsilon s$, $2p\varepsilon p$, $2s\varepsilon p$, $2p\varepsilon s$, and $2p\varepsilon d$) is constructed with the well-tested discretization procedure of Macías, Martín, Riera, and Yáñez,[21] by solving

$$(P_{\beta\gamma}HP_{\beta\gamma} - E)\chi^{E\beta\gamma} = 0 \,, \tag{9}$$

TABLE I. STO basis sets and configurations used in the calculation of closed- and open-channel wave functions of a ${}^1S$ and ${}^{1,3}P$ symmetry. The definition of each STO is $\varphi_{lm}(n,l,m,r,\zeta) = N_i r^{n-1}\exp[-\zeta_i(Z-1.7)r]Y_l^m(\Theta,\phi)$, where Z is the nuclear charge. For the open-channel wave functions, α_N is the exponent of the last term of geometrical sequence of STO's with exponents $\alpha_i = \alpha_0\beta^i$, $i = 0, 1, \ldots, N$.

${}^1S$ States

Discrete

$l=0$		$l=1$		$l=2$	
n	ζ_i	n	ζ_i	n	ζ_i
1–3	$\frac{1}{3}$	2–3	$\frac{1}{3}$	3	$\frac{1}{3}$
4–6	$\frac{1}{5}$	4–6	$\frac{1}{5}$	4–6	$\frac{1}{5}$
7–9	$\frac{3}{20}$	7–9	$\frac{3}{20}$	7–9	$\frac{3}{20}$

Configurations: All $nsn's$ with $n \leq 6$ or $n' \leq 6$
All $npn'p$ with $n \leq 6$ or $n' \leq 6$
All $ndn'd$ with $n \leq 6$ or $n' \leq 6$

Continuum

$2s\varepsilon s$				$2p\varepsilon p$			
n	α_N	β	N	n	α_N	β	N
2	2.5	1.6	8	2	2.5	1.6	8
4	1.25	1.6	8	4	1.25	1.6	8

Configurations: Full configuration-interaction

${}^{1,3}P$ states

Discrete

$l=0$		$l=1$		$l=2$		$l=3$	
n	ζ_i	n	ζ_i	n	ζ_i	n	ζ_i
1–3	$\frac{1}{3}$	2–3	$\frac{1}{3}$	3	$\frac{1}{3}$	4	$\frac{1}{4}$
4–6	$\frac{1}{4}$	4–6	$\frac{1}{4}$	4–6	$\frac{1}{4}$	5–7	$\frac{1}{5}$
7–9	$\frac{1}{7}$	7–9	$\frac{1}{7}$	7–8	$\frac{1}{7}$		

Configurations: All $nsn'p$ with $n \leq 3$ or $n' \leq 3$
All $npn'd$ with $n' \leq 7$
All $ndn'f$

Continuum

$2s\varepsilon p$				$2p\varepsilon s$				$2p\varepsilon d$			
n	α_N	β	N	n	α_N	β	N	n	α_N	β	N
2	2.5	1.6	8	2	2.5	1.6	8	3	2.5	1.6	8
4	1.25	1.6	8	4	1.25	1.6	8	5	1.25	1.6	8

Configurations: Full configuration-interaction

TABLE II. Resonance energies and widths for ^1S and $^{1,3}P$ states of berylliumlike systems above the $1s^22p$ threshold.. Numbers in parentheses indicate powers of ten.

	$1\,^1S$	$2\,^1S$	$1\,^1P$	$2\,^1P$	$1\,^3P$	$2\,^3P$
			$-E$ (a.u.)			
C^{2+}	1.729880	1.541509	1.621883	1.433512	1.684652	1.513232
N^{3+}	2.729287	2.481949	2.588574	2.337108	2.669746	2.445095
O^{4+}	3.952068	3.645174	3.778474	3.463913	3.878042	3.599791
Ne^{6+}	7.066473	6.639119	6.828589	6.387434	6.964866	6.577623
			Γ (eV)			
C^{2+}	0.45317(−1)	0.36976	0.22815	0.66209(−1)	0.76196(−1)	0.37109(−1)
N^{3+}	0.57567(−1)	0.45299	0.25338	0.89702(−1)	0.81489(−1)	0.42031(−1)
O^{4+}	0.68330(−1)	0.51293	0.27418	0.10954	0.85412(−1)	0.45690(−1)
Ne^{6+}	0.88144(−1)	0.60686	0.30392	0.14453	0.89977(−1)	0.51413(−1)

TABLE III. Comparison between (a) our resonance positions of Table II, with the PCI shift as given by Eq. (13); (b) the measured positions of Mack (Refs. 6 and 7) and Mack and Niehaus (Refs. 8 and 9); these authors do not state their ^1S and ^1D assignments, and therefore we give both measurements. All values in eV.

	C^{2+}		N^{3+}		O^{4+}		Ne^{6+}	
	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)
$1\,^1S$	47.2	47.3	74.4	74.4	107.7	107.7	192.5	193.6±0.3
$2\,^1S$	42.9	41.8–42.0	68.7	67.2–67.7	100.2	98.7–99.2	182.1	180.0–180.6
$1\,^1P$	44.7	···	71.1	71.4±0.5	103.3	103.8	186.5	···
$2\,^1P$	39.2	39.1	63.8	63.9	94.4	94.2	174.1	173.6

TABLE IV. Calculated partial widths (in eV), $\Gamma_{\beta\gamma}$, for the resonant states of Table II, corresponding to $\beta\gamma = 2s\varepsilon s$, $2p\varepsilon p$ (for S symmetry) and $2s\varepsilon p$, $2p\varepsilon s$, and $2p\varepsilon d$ (for P symmetry) continua. Numbers in parentheses indicate powers of ten.

		$\Gamma_{2s\varepsilon s}$	$\Gamma_{2p\varepsilon p}$	
C^{2+}	$1\,^1S$	0.43770(−1)	0.15471(−2)	
	$2\,^1S$	0.47361(−1)	0.32240	
N^{3+}	$1\,^1S$	0.56383(−1)	0.11842(−2)	
	$2\,^1S$	0.50532(−1)	0.40246	
O^{4+}	$1\,^1S$	0.67322(−1)	0.10082(−2)	
	$2\,^1S$	0.52909(−1)	0.46002	
Ne^{6+}	$1\,^1S$	0.87156(−1)	0.98810(−3)	
	$2\,^1S$	0.57021(−1)	0.54984	
		$\Gamma_{2s\varepsilon p}$	$\Gamma_{2p\varepsilon s}$	$\Gamma_{2p\varepsilon d}$
C^{2+}	$1\,^1P$	0.72785(−1)	0.13233	0.23033(−1)
	$2\,^1P$	0.18307(−2)	0.43199(−2)	0.60058(−1)
	$1\,^3P$	0.30691(−1)	0.43522(−1)	0.19825(−1)
	$2\,^3P$	0.35218(−2)	0.91620(−2)	0.24425(−1)
N^{3+}	$1\,^1P$	0.81005(−1)	0.14257	0.29804(−1)
	$2\,^1P$	0.22294(−2)	0.60008(−2)	0.81472(−1)
	$1\,^3P$	0.34806(−1)	0.43982(−1)	0.27013(−2)
	$2\,^3P$	0.36718(−2)	0.11523(−1)	0.26836(−1)
O^{4+}	$1\,^1P$	0.88917(−1)	0.14970	0.35563(−1)
	$2\,^1P$	0.22933(−2)	0.77001(−2)	0.99551(−1)
	$1\,^3P$	0.37730(−1)	0.44238(−1)	0.34444(−2)
	$2\,^3P$	0.36930(−2)	0.13329(−1)	0.28668(−1)
Ne^{6+}	$1\,^1P$	0.10340	0.15578	0.44736(−1)
	$2\,^1P$	0.19899(−2)	0.11379(−1)	0.13116
	$1\,^3P$	0.41664(−1)	0.43476(−1)	0.48370(−2)
	$2\,^3P$	0.35188(−2)	0.15963(−1)	0.31931(−1)

where

$$P_{\beta\gamma} = |\varphi_\beta(1)\rangle\langle\varphi_\beta(1)| + |\varphi_\beta(2)\rangle\langle\varphi_\beta(2)| - |\varphi_\beta(1)\rangle\langle\varphi_\beta(1)| \otimes |\varphi_\beta(2)\rangle\langle\varphi_\beta(2)| \,, \tag{10}$$

and where, following usual practice, we neglect the optical potential part of the open-channel-projected Hamiltonian.

The partial widths are obtained by the golden-rule–like expression[22]

$$\Gamma_{\beta\gamma} = 2\pi |\langle\phi_n|QHP_{\beta\gamma}|\chi^{E\beta\gamma}\rangle|^2 \text{ for } E = E_n^d \,, \tag{11}$$

and the total width is given by

$$\Gamma = \sum_{\beta,\gamma} \Gamma_{\beta\gamma} \,. \tag{12}$$

The secular equation for the effective Hamiltonian (7), with $M = 100$ a.u. in Eq. (9), was set up, for each ${}^1S$, ${}^{1,3}P$ symmetry, in a representation of configurations built from the basis set of Slater-type orbitals (STO's) given in Table I. This table also contains the STO basis employed to solve the corresponding open-channel equations (9). The values of the parameter α in the model potential of Eq. (2) for C^{2+}, N^{3+}, O^{4+}, and Ne^{6+} are 3.7300, 4.4054, 5.0736, and 6.3943, respectively.

Our calculated resonance positions and total widths are presented in Table II. The only reported experimental work on these resonances that we are aware of is that of Bordenave-Montesquieu and co-workers[2,3] for Ne^{6+} and of Mack and co-workers[6–9] for C^{2+}, N^{3+}, O^{4+}, and Ne^{6+}. Our resonance positions for ${}^1S$ and ${}^1P$ symmetries are compared with those of Mack and co-workers[6,7] in Table III; we notice that those experimental outcomes are affected by the postcollisional interaction (PCI) between the target, with charge Q, and the emitted electron.[23] Accordingly, in Table III we have modified the energy positions E_n^d of Table II to include the PCI shift, as given by

$$\Delta E = Q\Gamma/2v \tag{13}$$

(in a.u.), where v is the collision velocity (=0.37, 0.38, 0.52, and 0.43 for C^{2+}, N^{3+}, O^{4+}, and Ne^{6+}, respectively, in the experiments of Mack and Niehaus). Agreement between theory and experiment is quite encouraging in all cases. It is excellent for all resonances, except for the $2\,{}^1S$ positions that are 1 eV below those of experiment; we note that this quantity is roughly equal to the corresponding PCI shift.

Finally, since partial widths [Eq. (11)] provide additional information to characterize the different resonant states in collisions between multicharged ions and inert gases,[2,3,8,9,24] they are presented in Table IV for the ${}^1S$ and ${}^{1,3}P$ ($1s^2 3l3l'$) resonances treated in the present work.

As a conclusion, our generalization of the method of Martín and co-workers[16,17] to treat resonant states of systems with a closed-shell core and whose energies lie above several ionization thresholds provides an accurate procedure to obtain positions and total as well as partial resonance widths, with a considerably smaller effort than all potentially alternative methods.

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