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Use of Z-correlation diagrams to help classification of doubly excited states

A. Macías and A. Riera
Departamento de Química, Universidad Autónoma de Madrid, Canto Blanco, 28049-Madrid, Spain

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Taking as a benchmark the accurate calculations on ${}^{1,3}S$, ${}^{1,3}P$, and ${}^{1,3}D$ resonances under the $N=2$ threshold, carried out for two-electron systems, we present an appraisal of the practical aspects of, and equivalence between, existing schemes to classify doubly excited states. To relate properties of resonances for different values of the nuclear charge Z, we have also carried out calculations of their positions and widths for noninteger Z and have drawn the ensuing correlation diagrams. We show that however good the descriptions are they do not provide a completely general scheme to classify resonances. Furthermore, the proposed schemes are not equivalent, as is usually assumed.

I. INTRODUCTION

Doubly excited states of multicharged ions are currently receiving, from both theoretical[1–9] and experimental[10–16] viewpoints, increased attention, motivated by measurements on collisions such as

$$I^{q+}+\mathrm{He}\rightarrow(I^{**})^{(q-2)+}+\mathrm{He}^{2+}\ , \tag{1}$$

where I^{q+} is a heavy ion with an impact energy of a few keV amu^{-1}. These measurements are stimulated in turn by the increasing demand of data for nuclear fusion research and astrophysics.

Electron spectroscopy is one of the best methods[8] for studying double-capture processes like (1), since the $(I^{**})^{(q-2)+}$ ion usually decays by electron emission. This allows the study of a large number of excited ionic configurations that are otherwise unattainable by other laboratory methods, and stresses the importance and usefulness of reaching an agreement as to their classification—or at least of establishing the applicability of, and relationship between, the various labeling schemes that have been hitherto proposed. We shall see that, despite the large number of significant contributions to this subject, classification of doubly excited states is still a challenging problem, which should be distinguished from the closely related ones of achieving a physical description of the states, and of calculating their energy, or other properties.

The aim of the present work is to present an appraisal of the practical aspects of existing schemes that classify doubly excited states, and to see to what an extent they can be taken as equivalent and can be expected to be generally useful. For this purpose, a high accuracy of the resonance parameters is required, and we have refined the calculations of Ref. 3 for the lowest ${}^{1,3}S^e$, ${}^{1,3}P^o$, and ${}^{1,3}D^e$ resonances of He and heliumlike ions under the $n=2$ threshold (the most favorable case for testing any classification scheme) by including the energy shifts of our Feshbach calculations and by improving the quality of the configuration-interaction (CI) basis sets to achieve experimental accuracy (errors in positions <0.1 eV, see, e.g., Refs. 8, 10, and 14). To avoid lengthening our paper, we do not present the energy positions and widths in tabulated form; these data are available from the authors upon request.

Apart from simple energy ordering, the three mostly used notations for doubly excited states follow the suggestions of Cooper *et al.*,[17] Conneely and Lipsky,[18] and Herrick and Sinanoglu[19] and Lin.[20] Cooper *et al.*[17] were the first to show that the usual labeling $nln'l'$ for singly excited states does not adequately describe the doubly excited ones and they proposed a ± notation, $((N,n+),(N,n-))$, that was elaborated upon by Bruch *et al.*[21]

Further advances in classification schemes have either attempted to find "approximate quantum numbers"[19,20,22–28] to provide physical descriptions of the states or empirical labels[18] to achieve appropriate orderings. A common feature of the latter studies is that the analyses have been carried out for a single system at a time, usually He; as we shall see, this was an unfortunate choice. However, when one is interested in physically meaningful rather than merely empirical labels, it is obviously desirable that the wave-function characteristics be inferred from those labels—indeed, this is an implicit aim of all authors. Then one should expect that states of different atoms with the same labels share similar characteristics.

Following this line of thought, we have explicitly calculated resonance positions as continuous functions of a noninteger nuclear charge Z, much in the same way as studies on the structure of diatomic molecular states are carried out with the help of R-correlation diagrams rather than at a single internuclear distance R. This entails no difficulty in our implementation of the Feshbach approach,[3] and, as we shall see, considerably simplifies the analysis of the resonance properties. Hence, apart from improving the accuracy of our calculations with respect to Ref. 3, in the present work we plot, for the first time, our results for the resonance positions for (a large number of) heliumlike ions with noninteger nuclear charges. In Sec. II we briefly recall the main steps of our procedure since this allows us to introduce our definitions. Atomic units are used throughout.

II. DEFINITIONS

In the Feshbach theory[29] of a two-electron autoionizing resonance, the wave function is written as a sum of two components,

$$\Psi = P\Psi + Q\Psi \tag{2}$$

with $Q = 1 - P$. The usual form[30] for these operators is employed,

$$Q = Q_1 Q_2 , \tag{3}$$

where, for resonances under the $n=2$ threshold, Q_i is the projector onto the subspace spanned by all excited states,

$$Q_i = 1 - |1s(i)\rangle\langle 1s(i)| . \tag{4}$$

Insertion of (2) in the Schrödinger equation and formal solution of the ensuring coupled equations yield the energy positions in terms of the eigensolutions of the closed-channel equations,

$$(QHQ - E_n^d)Q\phi_n = 0 , \tag{5}$$

and open-channel equations

$$(PHP - E)P\chi_E = 0 , \tag{6}$$

in the form

$$\epsilon_n = E_n^d + \Delta_n \equiv E_n^d + \sum_i \frac{|\langle \phi_n | QHP | \chi_{E_i} \rangle|^2}{E_n^d - E_i} + \mathcal{P}\int \frac{|\langle \phi_n | QHP | \chi_E \rangle|^2}{E_n^d - E} , \tag{7}$$

where the principal part of the integral is assumed and we have neglected higher-order terms in QHP. The energy width is given by the golden-rule expression

$$\Gamma_n = 2\pi |\langle \phi_n | QHP | \chi_E \rangle|^2 , \tag{8}$$

with $E = E_n$. Obviously, this formalism can also be applied to a fictitious system with noninteger nuclear charge Z. In our implementation[3] of this standard theory, we write the closed- and open-channel wave functions as CI expansions over sets of configurations ψ_i, ξ_i,

$$\phi_n = \sum_i d_{in} Q\psi_i , \quad \chi_j = \sum_i c_{ij} P\xi_i , \tag{9}$$

built from a set of Slater-type orbitals (STO's). The resonance condition between open- and closed-channel energies $E_j = E_n^d$ is attained by variation of a nonlinear parameter[3] in the basics; δ-function normalization of the open-channel wave function is achieved[3] as explained in Ref. 31. Use of our discretization procedure [Eq. (9)] and of a quadrature approximation in Eq. (7) yields an expression for the energy shift,

$$\Delta_n = \sum_j \frac{|\langle \phi_n | QHP | \chi_j \rangle|^2}{E_n^d - E_j} . \tag{10}$$

As mentioned in Ref. 3, these shifts were always found to be small.

Solution of Eqs. (5) and (6) and Eqs. (7) and (8) gives the resonance parameters ϵ_n and Γ_n, together with the corresponding closed- and open-channel wave functions. To analyze the structure of these wave functions, several procedures have been employed.[19,20,23,24,27,32,33] For our purposes, we find that quantitative, easily tabulated information on the characteristics of the atomic wave functions ϕ_n is provided by the weight[3,9,18] of configurations with a given character in the expansion of Eq. (9),

$$w_n^{[k]} = \sum_i \langle d_{in}^{[k]} \psi_i^{[k]} | \phi_n \rangle = \sum_{i,j} d_{in}^{[k]} S_{ij} d_{jn}^{[k]} , \tag{11}$$

where S is the overlap matrix in the $\{\varphi_i\}$ representation and we denote the configuration character by a superscript $[k]$ (e.g., $[sp]$, $[pd]$, etc.). These weights add up to 1; they are invariant under linear transformations within the $\{\varphi_i^{[k]}\}$ manifold (in particular, they are normalization independent); they also yield[3] the contributions from a given character $[k]$ to the nth resonance energy, that is, they indicate the error involved when discarding the configurations of that character in the closed-channel expansion (9).

Further information on the resonance characteristics is provided by the contributions to the width Γ_n of configurations of a given type, or character k; equivalently, one can give the contributions[3] $y^{[k]}$ to the square root[32] of Γ_n,

$$\Gamma = 2\pi y^2 , \tag{12}$$

which are also invariant under linear transformations within the $\{\varphi_i^{[k]}\}$ manifold.

III. RESULTS

As mentioned in Sec. I, we take as a benchmark the results of our calculation on the lowest $^{1,3}S^e$, $^{1,3}P^o$, and $^{1,3}D^e$ resonance parameters of the He and heliumlike ions with integer and noninteger nuclear charge Z. For integer Z, the present results are close, but not identical, to those of Ref. 3, because experimental accuracy in the resonance positions has now been consistently achieved.

Plotting the resonance positions as functions of Z yields Z-correlation diagrams. In drawing these diagrams, we notice an obvious difference with diatomic molecular diagrams in that, while the hydrogenic $Z \to \infty$ limit is as well defined as the separated-atom $R \to \infty$ limit, the united-atom $R \to 0$ limit has no small-Z counterpart. One must then start with the hydrogenic limit $Z \to \infty$ and diminish Z.

The main advantages of considering a fictitious, nonrelativistic large-Z limit are that the wave functions are exactly written in terms of a few hydrogenic orbitals, and therefore their characteristics are clearer than for smaller Z, and that the limit is well approached by most ions. When Z decreases, because of intrashell correlations, the configuration mixings change very slowly with Z, except at small Z, where avoided crossings (as pointed out in Ref. 19) can appear: in their neighborhood, due to intershell correlations, the closed-channel wave functions interchange their character.

In practice, to achieve clear correlation graphs, it is more useful to draw

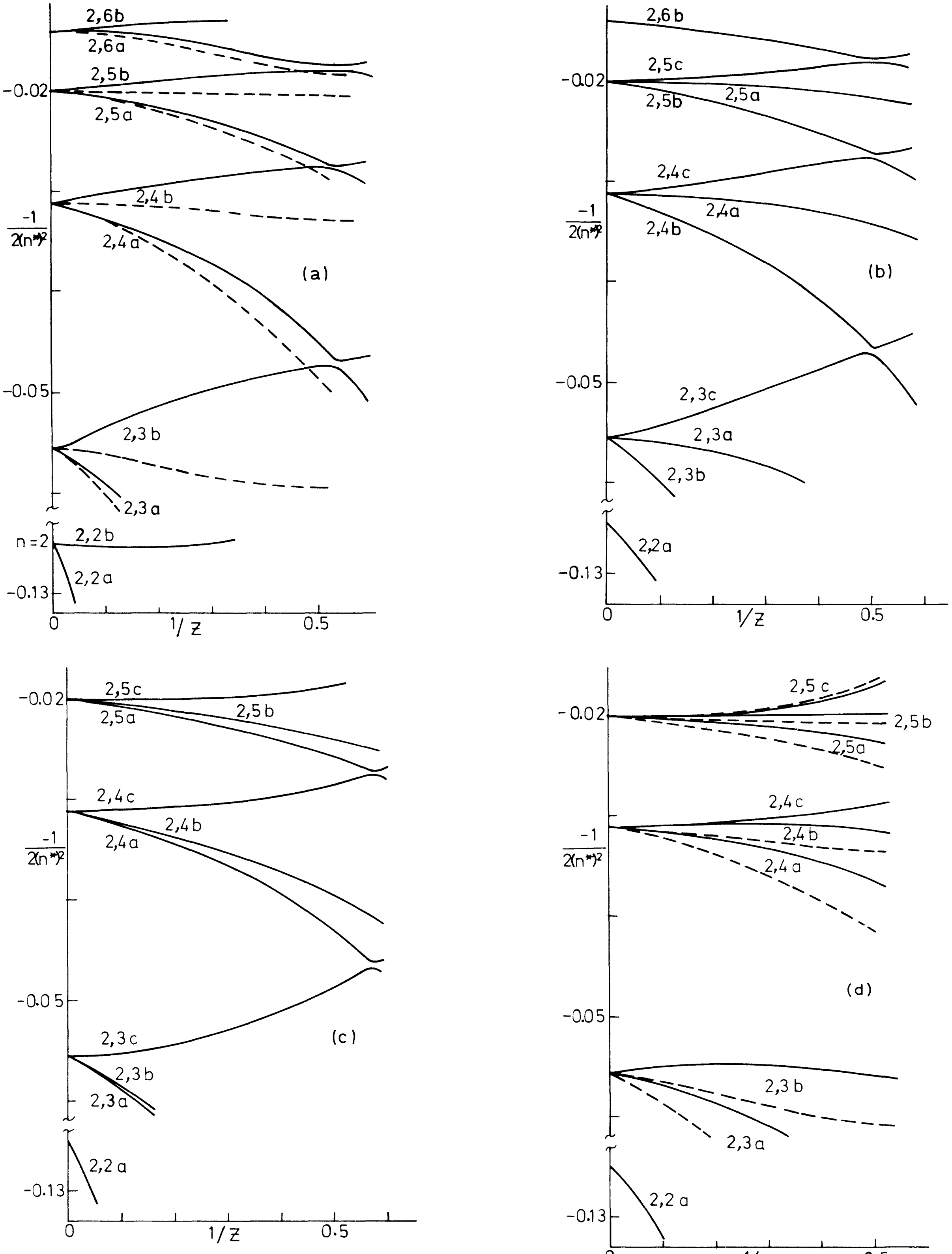

FIG. 1. (a) Plot of $-1/2(n^{*2})$ [see Eq. (13) in text] vs $1/Z$ for fractional Z. ——, ${}^1S^e$ states; — — —, ${}^3S^e$ states. (b) Plot of $-1/2(n^{*2})$ [see Eq. (13) in text] vs $1/Z$ for fractional Z and for ${}^1P^o$ states. (c) Plot of $-1/2(n^{*2})$ [see Eq. (13) in text] vs $1/Z$ for fractional Z and for ${}^3P^o$ states. (d) Plot of $-1/2(n^{*2})$ [see Eq. (13) in text] vs $1/Z$ for fractional Z. ——, ${}^1D^e$ states. — — —, ${}^3D^e$ states.

TABLE I. Weights $w^{[k]}$, defined according to Eq. (10) of text, corresponding to configurations of the type, or character k, and making up the closed-channel wave functions. (a) $^{1,3}S^e$ states. (b) $^{1,3}P^o$ states. [Notice that $(2,na)^3P$ and $(2,nb)^3P$ are not energy ordered (see Refs. 3 and 26)]. (c) $^{1,3}D^e$ states.

(a) $^{1,3}S^e$ states

					$^1S^e$					$^3S^e$			
	$(N,n\alpha)$	K	T	A	$w^{[ss']}$	$w^{[pp']}$	$w^{[dd']}$	$w^{[ss']}$	$w^{[pp']}$	$w^{[dd']}$	K	T	A
He	(2,2a)	1	0	1	0.721	0.279	0.000						
	(2,2b)	−1	0	1	0.329	0.635	0.036						
	(2,3a)	1	0	1	0.613	0.385	0.001	0.647	0.353	0.000	1	0	−1
	(2,3b)	−1	0	1	0.506	0.490	0.004	0.382	0.615	0.003	−1	0	−1
	(2,4a)	1	0	1	0.483	0.516	0.001	0.599	0.401	0.000	1	0	−1
	(2,4b)	−1	0	1	0.614	0.384	0.015	0.419	0.580	0.001	−1	0	−1
	(2,5a)	1	0	1	0.381	0.618	0.000	0.573	0.427	0.000	1	0	−1
	(2,5b)	−1	0	1	0.638	0.362	0.000	0.437	0.563	0.000	−1	0	−1
	(2,6a)	1	0	1	0.360	0.639	0.000	0.561	0.439	0.000	1	0	−1
	(2,6b)	−1	0	1	0.501	0.497	0.002	0.435	0.565	0.000	−1	0	−1
	(2,7a)							0.575	0.425	0.000	1	0	−1
	(2,7b)							0.410	0.589	0.001	−1	0	−1
O^{6+}	(2,2a)	1	0	1	0.760	0.239	0.000						
	(2,2b)	−1	0	1	0.240	0.757	0.003						
	(2,3a)	1	0	1	0.721	0.279	0.000	0.672	0.328	0.000	1	0	−1
	(2,3b)	−1	0	1	0.280	0.718	0.001	0.329	0.671	0.000	−1	0	−1
	(2,4a)	1	0	1	0.700	0.300	0.000	0.654	0.346	0.000	1	0	−1
	(2,4b)	−1	0	1	0.300	0.699	0.001	0.347	0.653	0.000	−1	0	−1
	(2.5a)	1	0	1	0.690	0.310	0.000	0.644	0.356	0.000	1	0	−1
	(2,5b)	−1	0	1	0.310	0.689	0.000	0.356	0.644	0.000	−1	0	−1
	(2,6a)	1	0	1	0.684	0.316	0.000	0.639	0.361	0.000	1	0	−1
	(2,6b)	−1	0	1	0.316	0.684	0.000	0.361	0.639	0.000	−1	0	−1
	(2,7a)							0.637	0.363	0.000	1	0	−1
	(2,7b)							0.363	0.637	0.000	−1	0	−1

(b) $^{1,3}P^o$ states

					$^1P^o$					$^3P^o$			
	$(N,n\alpha)$	K	T	A	$w^{[sp]}$	$w^{[pd]}$	$w^{[df]}$	$w^{[sp]}$	$w^{[pd]}$	$w^{[df]}$	K	T	A
He	(2,2a)	0	1	1	0.909	0.090	0.000	0.986	0.014	0.000	1	0	1
	(2,3b)	1	0	−1	0.933	0.067	0.000	0.766	0.234	0.000	0	1	−1
	(2,3a)	0	1	1	0.822	0.178	0.000	0.948	0.052	0.000	1	0	1
	(2,3c)	−1	0	0	0.712	0.286	0.002	0.334	0.663	0.003	−1	0	−1
	(2,4b)	1	0	−1	0.466	0.533	0.001	0.696	0.304	0.000	0	1	−1
	(2,4a)	0	1	1	0.808	0.192	0.000	0.935	0.065	0.000	1	0	1
	(2,4c)	−1	0	0	0.746	0.253	0.001	0.382	0.617	0.001	−1	0	−1
	(2,5b)	1	0	−1	0.444	0.555	0.001	9.675	0.325	0.000	0	1	−1
	(2,5a)	0	1	1	0.803	0.197	0.000	0.927	0.073	0.000	1	0	1
	(2,5c)	−1	0	0	0.517	0.482	0.001	0.398	0.601	0.001	−1	0	−1
O^{6+}	(2,2a)	0	1	1	0.992	0.008	0.000	0.999	0.001	0.000	1	0	1
	(2,3b)	1	0	−1	0.952	0.048	0.000	0.800	0.200	0.000	0	1	−1
	(2,3a)	0	1	1	0.905	0.095	0.000	0.964	0.036	0.000	1	0	1
	(2,3c)	−1	0	0	0.144	0.855	0.001	0.236	0.764	0.000	−1	0	−1
	(2,4b)	1	0	−1	0.937	0.063	0.000	0.767	0.233	0.000	0	1	−1
	(2,4a)	0	1	1	0.879	0.121	0.000	0.948	0.052	0.000	1	0	1
	(2,4c)	−1	0	0	0.185	0.815	0.000	0.285	0.715	0.000	−1	0	−1
	(2,5b)	1	0	−1	0.930	0.070	0.000	0.754	0.246	0.000	0	1	−1
	(2,5a)	0	1	1	0.866	0.134	0.000	0.940	0.060	0.000	1	0	1
	(2,5c)	−1	0	0	0.204	0.796	0.000	0.306	0.694	0.000	−1	0	−1

(c) $^{1,3}D^e$ states

			$^1D^e$						$^3D^e$				
	$(N,n\alpha)$	K	T	A	$w^{[pp']}$	$w^{[sd]}$	$w^{[pf]}$	$w^{[pp']}$	$w^{[sd]}$	$w^{[pf]}$	K	T	A
He	(2,2a)	1	0	1	0.925	0.074	0.001						
	(2,3a)	1	0	1	0.697	0.290	0.013	0.745	0.250	0.005	1	0	−1

TABLE I. (*Continued.*)

		$^1D^e$						$^3D^e$				
	$(N,n\alpha)$	K	T	A	$w^{[pp']}$	$w^{[sd]}$	$w^{[pf]}$	$w^{[pp']}$	$w^{[sd]}$	$w^{[pf]}$	K	T A
	(2,3*b*)	0	1	0	0.312	0.584	0.104	0.257	0.658	0.085	0	1 0
	(2,4*a*)	1	0	1	0.634	0.340	0.026	0.692	0.290	0.018	1	0 −1
	(2,4*b*)	0	1	0	0.369	0.548	0.083	0.304	0.582	0.114	0	1 0
	(2,4*c*)	−1	0	0	0.005	0.104	0.891	0.007	0.136	0.856	−1	0 0
	(2,5*a*)	1	0	1	0.630	0.350	0.020	0.677	0.303	0.020	1	0 −1
	(2,5*b*)	0	1	0	0.370	0.609	0.021	0.334	0.620	0.046	0	1 0
	(2,5*c*)	−1	0	0	0.029	0.048	0.923	0.026	0.123	0.851	−1	0 0
O^{6+}	(2,2*a*)	1	0	1	0.995	0.005	0.000					
	(2,3*a*)	1	0	1	0.645	0.353	0.002	0.806	0.194	0.000	1	0 −1
	(2,3*b*)	0	1	0	0.357	0.635	0.008	0.194	0.801	0.005	0	1 0
	(2,4*a*)	1	0	1	0.598	0.388	0.014	0.749	0.241	0.010	1	0 −1
	(2,4*b*)	0	1	0	0.269	0.524	0.207	0.249	0.695	0.066	0	1 0
	(2,4*c*)	−1	0	0	0.134	0.088	0.778	0.002	0.075	0.923	−1	0 0
	(2,5*a*)	1	0	1	0.581	0.398	0.021	0.725	0.260	0.015	1	0 −1
	(2,5*b*)	0	1	0	0.296	0.551	0.153	0.272	0.637	0.091	0	1 0
	(2,5*c*)	−1	0	0	0.124	0.050	0.826	0.003	0.103	0.894	−1	0 0

TABLE II. Same as in Table I, in the $Z \to \infty$ limit. For comparison, the DESB weights are given in parentheses.

	$^1S^e$		$^3S^e$	
	$w^{[ss']}$	$w^{[pp']}$	$w^{[ss']}$	$w^{[pp']}$
(2,2*a*)	0.774	0.226		
	(0.750)	(0.250)		
(2,2*b*)	0.226	0.774		
	(0.250)	(0.750)		
(2,3*a*)	0.748	0.252	0.682	0.318
	(0.667)	(0.333)	(0.667)	(0.333)
(2,3*b*)	0.252	0.748	0.318	0.682
	(0.333)	(0.667)	(0.333)	(0.667)
(2,4*a*)	0.731	0.269	0.669	0.331
	(0.625)	(0.375)	(0.635)	(0.375)
(2,4*b*)	0.269	0.731	0.331	0.669
	(0.375)	(0.625)	(0.375)	(0.625)
(2,5*a*)	0.723	0.277	0.663	0.337
	(0.600)	(0.400)	(0.600)	(0.400)
(2,5*b*)	0.277	0.723	0.337	0.663
	(0.400)	(0.600)	(0.400)	(0.600)
(2,6*a*)	0.718	0.282	0.659	0.341
	(0.583)	(0.417)	(0.583)	(0.417)
(2,6*b*)	0.282	0.718	0.341	0.659
	(0.417)	(0.583)	(0.417)	(0.583)
(2,7*a*)			0.657	0.343
			(0.571)	(0.429)
(2.7*b*)			0.343	0.657
			(0.429)	(0.571)

		$^1P^o$			$^3P^o$	
	$w^{[2snp]}$	$w^{[2pns]}$	$w^{[2pnd]}$	$w^{[2snp]}$	$w^{[2pns]}$	$w^{[2pnd]}$
(2,2*a*)	1.000	0.000	0.000	1.000	0.000	0.000
	(1.000)	(0.000)	(0.000)	(1.000)	(0.000)	(0.000)
(2,3*b*)	0.469	0.488	0.043	0.279	0.534	0.187
	(0.556)	(0.370)	(0.074)	(0.222)	(0.593)	(0.185)
(2,3*a*)	0.392	0.503	0.105	0.543	0.419	0.038
	(0.222)	(0.593)	(0.185)	(0.556)	(0.370)	(0.074)

TABLE II. (*Continued.*)

	$^1P^o$			$^3P^o$		
	$w^{[2snp]}$	$w^{[2pns]}$	$w^{[2pnd]}$	$w^{[2snp]}$	$w^{[2pns]}$	$w^{[2pnd]}$
(2,3*c*)	0.139	0.008	0.853	0.179	0.047	0.774
	(0.222)	(0.037)	(0.741)	(0.222)	(0.037)	(0.741)
(2,4*b*)	0.462	0.484	0.054	0.270	0.509	0.221
	(0.5625)	(0.3125)	(0.125)	(0.125)	(0.625)	(0.250)
(2,4*a*)	0.356	0.503	0.141	0.510	0.442	0.048
	(0.125)	(0.625)	(0.250)	(0.5625)	(0.3125)	(0.125)
(2,4*c*)	0.182	0.013	0.805	0.221	0.049	0.730
	(0.3125)	(0.0625)	(0.625)	(0.3125)	(0.0625)	(0.625)
(2,5*b*)	0.458	0.483	0.059	0.259	0.508	0.233
	(0.560)	(0.280)	(0.160)	(0.080)	(0.640)	(0.280)
(2,5*a*)	0.342	0.502	0.156	0.503	0.442	0.055
	(0.080)	(0.640)	(0.280)	(0.560)	(0.280)	(0.160)
(2,5*c*)	0.200	0.016	0.784	0.238	0.050	0.712
	(0.360)	(0.080)	(0.560)	(0.360)	(0.080)	(0.560)

	$^1D^e$			$^3D^e$		
	$w^{[2pnp']}$	$w^{[2snd]}$	$w^{[2pnf]}$	$w^{[2pnp']}$	$w^{[2snd]}$	$w^{[2pnf]}$
(2,2*a*)	1.000	0.000	0.000			
	(1.000)	(0.000)	(0.000)			
(2,3*a*)	0.627	0.373	0.000	0.821	0.179	0.000
	(0.667)	(0.333)	(0.000)	(0.667)	(0.333)	(0.000)
(2,3*b*)	0.373	0.627	0.000	0.179	0.821	0.000
	(0.333)	(0.667)	(0.000)	(0.333)	(0.667)	(0.000)
(2,4*a*)	0.602	0.387	0.011	0.760	0.231	0.009
	(0.525)	(0.4375)	(0.0375)	(0.525)	(0.4375)	(0.0375)
(2,4*b*)	0.342	0.417	0.241	0.238	0.696	0.066
	(0.450)	(0.375)	(0.175)	(0.450)	(0.375)	(0.175)
(2,4*c*)	0.056	0.196	0.748	0.002	0.073	0.925
	(0.025)	(0.1875)	(0.7875)	(0.025)	(0.1875)	(0.7875)
(2,5*a*)	0.592	0.391	0.017	0.736	0.250	0.014
	(0.448)	(0.480)	(0.072)	(0.448)	(0.480)	(0.072)
(2,5*b*)	0.318	0.326	0.356	0.261	0.649	0.090
	(0.504)	(0.240)	(0.256)	(0.504)	(0.240)	(0.256)
(2,5*c*)	0.089	0.284	0.627	0.003	0.101	0.896
	(0.048)	(0.280)	(0.672)	(0.048)	(0.280)	(0.672)

$$\frac{-1}{2(n^*)^2}=\frac{1}{(Z-1)^2}\left[\epsilon+\frac{Z^2}{2N^2}\right] \tag{13}$$

with $N=2$, as a function of Z^{-1}, then the energy itself. As $Z\to\infty$ we have

$$n^*=n-\mu=n-\frac{\sigma}{Z}+\cdots , \tag{14}$$

with μ the quantum defect, and

$$\frac{-1}{2(n^*)^2}=-\frac{1}{2n^*}-\frac{\sigma}{n^3Z}+\cdots . \tag{15}$$

It will be noticed that scaled Z-correlation diagrams such as those provided by (13) are closely related to the n^* diagrams of the pioneer article of Herrick and Sinanoglu[19] (see also Ref. 34). The novelty of our approach with respect to that reference is that calculations are actually carried out for noninteger Z; and this fact, together with the much higher accuracy of our parameters, permits us to precisely localize the avoided crossings and thus discuss character interchange in a quantitative way.

Our Z-correlation diagrams are displayed in Figs. 1(a) ($^{1,3}S$ states), 1(b) (^1P), 1(c) (^3P), and 1(d) ($^{1,3}D$). This information is complemented in Table I [(a) ($^{1,3}S$), (b) ($^{1,3}P$), (c) ($^{1,3}D$)] with that of the weights [Eq. (11)] of configurations of a given type making up the closed-channel wave functions of He and O^{6+} (as a representative for ions with $Z>2$). In addition, the $Z\to\infty$ limit of the weights is given in Table II. Width contributions $y_n^{[k]}$ are presented in Tables III [(a) ($^{1,3}S$), (b) ($^{1,3}P$), and (c) ($^{1,3}D$)]. As we shall see, those properties are sufficient for our discussion on classification schemes, although of course many other ones can be calculated to describe the resonance structure. To label resonances, the Conneely-Lipsky (see Sec. V) notation is employed. In Table I we have also included the Herrick-Sinanoglu-Lin (see Sec. VI) notation, according to the usual equivalence scheme,[20,6] although, as we shall argue below, this

TABLE III. Contributions $y^{[k]}$ to square root of resonance widths [Eq. (11)] corresponding to configurations of character $[k]$, (a) $^{1,3}S^e$ states, (b) $^{1,3}P^o$ states (triplets not energy ordered), (c) $^{1,3}D^e$ states. Powers of ten are indicated by numbers in square brackets.

(a) $^{1,3}S^e$ states

		$^1S^e$				$^3S^e$			
		$y^{[ss']}$	$y^{[pp']}$	$y^{[dd']}$	Y	$y^{[ss']}$	$y^{[pp']}$	$y^{[dd']}$	Y
He	(2,2*a*)	1.838[−2]	8.598[−3]	−1.658[−4]	2.681[−2]				
	(2,2*b*)	−3.172[−3]	1.060[−2]	−6.978[−4]	6.733[−3]				
	(2,3*a*)	1.067[−2]	3.935[−3]	1.28[−6]	1.461[−2]	5.787[−4]	4.540[−4]	−7.45[−6]	1.025[−3]
	(2,3*b*)	−4.002[−4]	4.792[−3]	−2.814[−4]	4.111[−3]	−1.060[−4]	3.295[−4]	−1.353[−5]	2.100[−4]
	(2,4*a*)	6.684[−3]	1.917[−3]	3.650[−5]	8.637[−3]	4.015[−4]	3.057[−4]	−4.56[−6]	7.027[−4]
	(2,4*b*)	1.384[−4]	3.330[−3]	−1.849[−4]	3.284[−3]	−7.337[−5]	2.388[−4]	−9.65[−6]	1.558[−4]
	(2,5*a*)	4.586[−3]	1.025[−3]	4.403[−5]	5.656[−3]	2.850[−4]	2.131[−4]	−3.11[−6]	4.950[−4]
	(2,5*b*)	1.705[−4]	2.634[−3]	−1.429[−4]	2.661[−3]	−5.092[−5]	1.964[−4]	−7.33[−6]	1.381[−4]
	(2,6*a*)	3.764[−3]	7.622[−4]	3.588[−5]	4.563[−3]	2.365[−4]	1.226[−4]	−2.44[−6]	3.567[−4]
	(2,6*b*)	−7.112[−4]	3.025[−3]	−1.916[−4]	2.122[−3]	8.632[−5]	−7.670[−5]	8.10[−6]	1.773[−5]
	(2,7*a*)					2.921[−4]	4.470[−4]	−3.32[−6]	7.357[−4]
	(2,7*b*)					−3.807[−5]	6.644[−4]	−1.386[−5]	6.125[−4]
O^{6+}	(2,2*a*)	2.290[−2]	1.043[−2]	−2.401[−5]	3.331[−2]				
	(2,2*b*)	−1.067[−2]	1.880[−2]	−1.497[−4]	7.980[−3]				
	(2,3*a*)	1.551[−2]	7.284[−3]	−4.77[−6]	2.279[−2]	8.572[−4]	7.042[−4]	−2.19[−6]	1.559[−3]
	(2,3*b*)	−7.096[−3]	1.190[−2]	−7.820[−5]	4.724[−3]	−4.753[−4]	9.286[−4]	−7.25[−6]	4.461[−4]
	(2,4*a*)	9.773[−3]	4.717[−3]	−9.62[−7]	1.449[−2]	6.815[−4]	5.790[−4]	−1.59[−6]	1.259[−3]
	(2,4*b*)	−4.789[−3]	7.920[−3]	−4.953[−5]	3.082[−3]	−3.835[−4]	7.421[−4]	−5.47[−6]	3.531[−4]
	(2,5*a*)	6.848[−3]	3.349[−3]	8.77[−8]	1.020[−2]	5.219[−4]	4.489[−4]	−1.17[−6]	9.697[−4]
	(2,5*b*)	−3.472[−3]	5.682[−3]	3.444[−5]	2.175[−3]	−2.990[−4]	5.733[−4]	−4.13[−6]	2.701[−4]
	(2,6*a*)	5.139[−3]	2.527[−3]	1.78[−7]	7.667[−3]	4.101[−4]	3.560[−4]	−8.78[−7]	7.653[−4]
	(2,6*b*)	−2.659[−3]	4.323[−3]	−2.597[−5]	1.637[−3]	−2.379[−4]	4.564[−4]	−3.21[−6]	2.153[−4]
	(2,3*a*)					3.306[−4]	3.089[−4]	−6.97[−7]	6.388[−4]
	(2,3*b*)					−1.931[−4]	4.193[−4]	−2.68[−6]	2.236[−4]

(b) $^{1,3}P^o$ states

		$^1P^o$				$^3P^o$			
		$y^{[sp]}$	$y^{[pd]}$	$y^{[df]}$	Y	$y^{[sp]}$	$y^{[pd]}$	$y^{[df]}$	Y
He	(2,2*a*)	1.334[−2]	1.510[−3]	−7.12[−6]	1.484[−2]	7.158[−3]	−5.675[−5]	−1.51[−6]	7.099[−3]
	(2,3*b*)	8.658[−4]	−9.852[−5]	−2.34[−6]	7.649[−4]	3.256[−4]	2.469[−4]	−2.27[−6]	5.703[−4]
	(2,3*a*)	6.279[−3]	6.995[−4]	−5.22[−6]	6.973[−3]	3.686[−3]	3.699[−5]	−1.14[−6]	3.722[−3]
	(2,3*c*)	2.118[−4]	−9.139[−5]	−1.114[−5]	1.093[−4]	3.075[−4]	−2.537[−4]	5.31[−6]	5.913[−5]
	(2,4*b*)	5.439[−4]	−1.211[−5]	8.02[−6]	5.399[−4]	2.186[−4]	1.500[−4]	−1.07[−6]	3.675[−4]
	(2,4*a*)	4.110[−3]	4.528[−4]	−3.33[−6]	4.559[−5]	2.262[−3]	4.079[−5]	−8.72[−7]	2.302[−3]
	(2,4*c*)	1.350[−4]	−6.887[−5]	8.79[−6]	5.735[−5]	2.345[−4]	−1.998[−4]	3.97[−6]	3.865[−5]
	(2,5*b*)	3.825[−4]	−1.572[−5]	6.03[−6]	3.728[−4]	1.552[−4]	1.079[−4]	−8.26[−7]	2.623[−4]
	(2,5*a*)	2.966[−3]	3.462[−4]	−2.67[−6]	3.310[−3]	1.547[−3]	3.221[−5]	−7.11[−7]	1.579[−3]
	(2,5*c*)	3.494[−5]	2.18[−6]	−8.80[−6]	2.832[−5]	−1.791[−4]	1.794[−4]	−3.31[−6]	2.96[−6]
O^{6+}	(2,2*a*)	2.379[−2]	1.278[−4]	−5.85[−6]	2.391[−2]	7.106[−3]	−6.088[−5]	−4.14[−7]	7.045[−3]
	(2,3*b*)	9.416[−4]	1.637[−4]	−6.58[−7]	1.105[−3]	4.316[−4]	5.086[−4]	−4.56[−7]	9.398[−4]
	(2,3*a*)	1.536[−2]	3.199[−4]	2.90[−6]	1.568[−2]	4.528[−3]	1.529[−4]	−2.10[−7]	4.681[−3]
	(2,3*c*)	3.138[−3]	−6.979[−4]	1.417[−5]	2.455[−3]	−9.178[−4]	9.678[−4]	−1.95[−6]	4.800[−5]
	(2,4*b*)	7.383[−4]	1.311[−4]	2.02[−7]	8.692[−4]	3.624[−4]	3.825[−4]	−2.23[−7]	7.446[−4]
	(2,4*a*)	9.892[−3]	2.606[−4]	−1.30[−6]	1.015[−2]	2.811[−3]	1.423[−4]	−1.04[−7]	2.953[−3]
	(2,4*c*)	2.338[−3]	−5.268[−4]	8.83[−6]	1.820[−3]	7.115[−4]	−6.872[−4]	1.06[−6]	2.539[−5]
	(2,5*b*)	5.674[−4]	1.002[−4]	−5.13[−8]	6.675[−4]	2.827[−4]	2.892[−4]	−1.24[−7]	5.717[−4]
	(2,5*a*)	7.002[−3]	2.040[−4]	−6.91[−7]	7.205[−3]	1.962[−3]	1.139[−4]	−5.60[−8]	2.076[−3]
	(2,5*c*)	1.770[−3]	−3.954[−4]	5.99[−6]	1.381[−3]	5.453[−4]	−5.074[−4]	6.59[−7]	3.859[−5]

(c) $^{1,3}D^e$ states

		$^1D^e$				$^3D^e$			
		$y^{[pp']}$	$y^{[sd]}$	$y^{[pf]}$	Y	$y^{[pp']}$	$y^{[sd]}$	$y^{[pf]}$	Y
He	(2,2*a*)	2.022[−2]	2.810[−4]	−1.331[−4]	2.037[−2]				
	(2,3*a*)	9.977[−3]	8.224[−5]	−1.190[−4]	9.940[−3]	−4.041[−4]	4.578[−4]	8.76[−6]	6.246[−5]
	(2,3*b*)	1.332[−3]	1.430[−4]	1.147[−4]	1.589[−3]	1.303[−4]	9.231[−4]	2.071[−5]	1.074[−3]

TABLE III. (*Continued.*)

		$^1D^e$				$^3D^e$			
		$y^{[pp']}$	$y^{[sd]}$	$y^{[pf]}$	Y	$y^{[pp']}$	$y^{[sd]}$	$y^{[pf]}$	Y
	(2,4*a*)	6.496[−3]	3.951[−5]	−8.464[−5]	6.451[−3]	−2.793[−4]	3.048[−4]	7.67[−6]	3.322[−5]
	(2,4*b*)	9.839[−4]	1.129[−4]	8.201[−5]	1.179[−3]	9.894[−5]	6.520[−4]	1.535[−5]	7.663[−4]
	(2,4*c*)	4.386[−5]	2.80[−6]	−2.188[−5]	2.479[−5]	3.26[−6]	1.37[−6]	−2.18[−6]	2.45[−6]
	(2,5*a*)	4.684[−3]	2.989[−5]	−8.496[−5]	4.629[−3]	−2.009[−4]	2.106[−4]	1.407[−5]	2.381[−5]
	(2,5*b*)	4.800[−4]	7.911[−5]	9.324[−5]	6.524[−4]	7.098[−5]	4.842[−4]	3.343[−5]	5.886[−4]
	(2,5*c*)	7.134[−4]	−3.501[−5]	−1.762[−4]	5.022[−4]	−1.761[−5]	2.193[−4]	8.552[−5]	2.872[−4]
O^{6+}	(2,2*a*)	3.273[−2]	1.761[−4]	−3.604[−5]	3.287[−2]				
	(2,3*a*)	1.833[−2]	−4.792[−4]	−4.597[−5]	1.780[−2]	9.727[−4]	−9.662[−4]	1.21[−6]	7.76[−6]
	(2,3*b*)	1.051[−2]	8.510[−4]	4.586[−5]	1.141[−2]	4.474[−4]	2.146[−3]	−5.26[−6]	2.588[−3]
	(2,4*a*)	1.145[−2]	−4.170[−4]	−2.584[−5]	1.101[−2]	−7.486[−4]	7.607[−4]	6.24[−6]	1.834[−5]
	(2,4*b*)	5.713[−3]	5.840[−4]	7.227[−5]	6.369[−3]	3.881[−4]	1.445[−3]	1.469[−5]	1.848[−3]
	(2,4*c*)	4.302[−3]	3.201[−4]	−4.931[−5]	4.573[−3]	1.773[−5]	2.992[−4]	−6.655[−5]	2.504[−4]
	(2.5*a*)	7.991[−3]	−3.294[−4]	−1.747[−5]	7.644[−3]	−5.602[−4]	5.806[−4]	7.25[−6]	2.766[−5]
	(2,5*b*)	4.222[−3]	4.638[−4]	5.870[−5]	4.745[−3]	3.058[−4]	1.043[−3]	1.653[−5]	1.365[−3]
	(2,5*c*)	2.980[−3]	2.160[−4]	−4.963[−5]	3.147[−3]	1.674[−5]	2.677[−4]	−5.860[−5]	2.259[−4]

equivalence cannot hold in all cases.

In light of those resonance properties, we now pass to analyze the practical aspects of proposed classification schemes.

IV. THE ± NOTATION

According to the notation of Cooper *et al.*[17] as generalized by Bruch *et al.*,[21] we have the approximate structures:

State	Configuration mixing	State	Configuration mixing
$(2,n+)^1S^e$	$(2sns+2pnp)$	$(2,n+)^3S^e$	$(2sns+2pnp)$
$(2,n-)^1S^e$	$(2sns-2pnp)$	$(2,n-)^3S^e$	$(2sns-2pnp)$
$(2,n+)^1P^o$	$(2snp+2pns)$	$(2,n+)^3P^o$	$(2snp+2pns)$
$(2,n-)^1P^o$	$(2snp-2pns)$	$(2,n-)^3P^o$	$(2snp-2pns)+2pnd$
$(2,nc)^1P^o$	$2pnd$	$(2,nc)^3P^o$	$(2snp+2pns)-2pnd$
$(2,n-)^1D^e$	$(2pnp-2snd)$	$(2,n-)^3D^e$	$(2pnp-2snd)$
$(2,n+)^1D^e$	$(2pnp+2snd)$	$(2,n+)^3D^e$	$(2pnp+2snd)$
$(2,nc)^1D^e$	$2pnf$	$(2,nc)^3D^e$	$2pnf$

Although it is well known[18,21,3] that configuration mixing contributions are rarely 1:1, the ± notation is still employed[6] for the sake of completeness. Nevertheless, when weight ratios are closed to 1:0 than to 1:1, the advantage of this classification, compared to the usual atomic orbital notation, is not obvious. We see from Table I that, at least for $Z>2$, the notation $2s^2$, $2p^2$, $2s3s$, etc. is often more appropriate to roughly describe the wave-function structures than the $2s^2\pm 2p^2$, $2s3s\pm 2p3p$ counterparts.

Since the Cooper notation is still employed, and to our knowledge the limitation in the reasoning of Ref. 17 has not been quantitatively exposed, it is instructive to do so for the simplest case of the lowest two ^1S resonances of the He atom. The usual atomic-orbital notation, which applies to the singly excited Rydberg series, would be $2s^2,2p^2$, where the $2s,2p$ orbitals can be taken, to a first approximation, as hydrogenlike. The reasoning then goes that the electron interaction, however small, removes the (near) degeneracy between the $2s^2$ and $2p^2$ levels, yielding the $2s^2+2p^2$ and $2s^2-2p^2$ combinations. The same argument would apply, to a greater extent, to more excited (i.e., more hydrogenlike) states.

It will be noticed that the preceding argument is really of an asymptotic nature, that is, that it refers to the $Z\rightarrow\infty$ hydrogenic limit; it would be expected to apply to He insofar as this limit is approximately fulfilled. However, the reasoning fails even in the $Z\rightarrow\infty$ hydrogenic limit, as can be seen from Table II: in the $\{(2s^2)^1S,(2p^2)^1S\}$ manifold, the Hamiltonian matrix can be written as

$$\underline{H}=-\frac{Z^2}{4}\begin{bmatrix}1 & 0\\ 0 & 1\end{bmatrix}+Z\begin{bmatrix}0.1504 & 0.0507\\ 0.0507 & 0.2168\end{bmatrix}. \tag{16}$$

In the $Z\rightarrow\infty$ limit diagonalization of H yields the (energy-ordered) eigenvectors corresponding to the lowest $^1S^e$ resonances,

$$\begin{bmatrix}0.8796\\ 0.4756\end{bmatrix},\quad\begin{bmatrix}-0.4756\\ 0.8796\end{bmatrix} \tag{17}$$

and the coefficients in (17) are not equal to $\pm(\frac{1}{2})^{1/2}$ because the difference between the diagonal Hamiltonian matrix elements is of the same order as the interaction term.

To be fair to the pioneer article of Cooper *et al.*,[17] it should be mentioned that the semiquantitative illustration given there is (approximately) correct. They treated the case of the $\{2s3p,2p3s\}$ ^1P manifold, in which the Hamiltonian matrix reads

$$\underline{H}=-\frac{13Z^2}{36}\begin{bmatrix}1 & 0\\ 0 & 1\end{bmatrix}+Z\begin{bmatrix}0.0928 & 0.0198\\ 0.0198 & 0.0899\end{bmatrix} \tag{18}$$

and the eigenvectors

$$\begin{bmatrix} 0.6803 \\ -0.7329 \end{bmatrix}, \quad \begin{bmatrix} 0.7329 \\ 0.6803 \end{bmatrix} \tag{19}$$

are very close to $\pm(\frac{1}{2})^{1/2}$, as surmised by Cooper *et al.* It will be noticed that the square of the coefficients in (19) does not exactly coincide with the $w^{[2snp]}, w^{[2pns]}$ weights for the second and third states in Table II, because the $2p3d$ configuration, not considered in Eq. (18), or in Ref. 17, interacts with the $2s3p$ and $2p3s$ ones. A more complete treatment in the $Z \rightarrow \infty$ limit yields the coefficients, in the $\{2s3p, 2p3s, 2p3d\}$ manifold:

$$\begin{bmatrix} 0.6849 \\ -0.6985 \\ -0.2079 \end{bmatrix}, \quad \begin{bmatrix} 0.6257 \\ 0.7097 \\ -0.3238 \end{bmatrix}, \quad \begin{bmatrix} 0.3734 \\ 0.0920 \\ 0.9231 \end{bmatrix}. \tag{20}$$

To sum up, the main objection to the ± notation is that in general the reasoning of Ref. 17 does not, even approximately, apply (see Table I), and is therefore not useful for a classification scheme.

V. THE $(N,n\alpha)$ NOTATION

The $(N,n\alpha)$ notation of Conneely and Lipsky,[18] with N $(=2)$ and n the "inner" and "outer" electron quantum numbers, respectively, and $\alpha = a,b,c$ is at present the most often one used for resonances under the $N=2$ threshold, because those authors made a careful analysis of the wave functions, reduced widths, and quantum defects for a large number of resonance states. The classification is based on the empirical relationship (13) defining the effective quantum number n^*. However, the fact that the quantum defect $\mu = n - n^*$ often turns out to be negative casts strong doubts upon its physical interpretation.[35] Accordingly, the classification scheme is also based upon the explicit examination of the wave-function structure and of the corresponding reduced widths.[18]

In fact, both quantum defects and wave-function structures are closely interrelated: when the former are appreciably negative, one finds avoided crossings in the Z-correlation diagrams, where the character of the corresponding a,b,c series is exchanged.[18,19] When a crossing occurs near an integer value of Z, the labeling of the resonance is not an easy matter, and most of the difficulties encountered by Conneely and Lipsky[18] were due to the fact that their empirical classification was based on an isolated study for He, and that for resonances under the $N=2$ threshold most pseudocrossings occur in the neighborhood of $Z=2$ (see Fig. 1).

Comparison between Tables I and II shows that for O^{6+} (and, in fact, already[3] for Li^+), the closed-channel component of the resonances presents, to a good approximation, the "high-Z" structure. Comparison between Tables I (weights) and III (width contributions) shows that for $Z>2$, both of these quantities follow similar patterns.

As Z decreases, the weights and width contributions display monotonic behavior, except in the neighborhood of avoided crossings in the Z diagrams. For example, from Tables I and II, comparing $Z \rightarrow \infty$, O^{6+}, and He, one finds character (i.e., weight) mixing of the $(2,2b)^1S$ and $(2,3a)^1S$, and $(2,3b)^1S$ and $(2,4a)^1S$ resonances, and character interchange of the $(2,4b)^1S$ and $(2,5a)^1S$, $(2,5b)^1S$ and $(2,6a)^1S$, $(2,3c)^1P$ and $(2,4b)^1P$, and $(2,4c)^1P$ and $(2,5b)^1P$ states, respectively. Notice from Fig. 1(c) that the avoided crossings for ^3P states occur for $Z<2$ and therefore have no influence on Table I(b).

For resonances with mixed characters, one often finds[3] that the ordering of the weights does not correspond to that of the width contributions. Thus, for ^1S He states, which ionize yielding a $1s\epsilon s$ state, when $w^{[ss']} > w^{[pp']}$ in Table I(a), the same order is found for $y^{[ss']}$ and $y^{[pp']}$ [Table III(a)], but for the "mixed" $(2,3b)^1S$ and $(2,4a)^1S$ and partly mixed $(2,5a)^1S$ and $(2,6a)^1S$ resonances, we find that $w^{[ss']} < w^{[pp']}$ while $|y^{[ss']}| \gg |y^{[pp']}|$. The difference with ^3S states will be noticed, their energies do not exhibit pseudocrossings and their properties have a more regular behavior.

It is interesting to note that inspection of the resonance properties (energies and lifetimes) calculated at physical (integer) Z values would lead to the (hasty) conclusion that they vary smoothly with Z, with the possible exception of energy pseudocrossings, where widths, as well as any other property of the closed-channel components, would simply be interchanged at the left and right side of it, and would present a "mixed" value in the middle of the avoided crossing. However our data show that the situation is not so simple, a counterexample is provided by the $(2,3c)^1P$ and $(2,4b)^1P$ states, whose characters have been interchanged [Table I(b)] for He with respect to the positive ions, while the avoided crossing is situated at $Z=2$ (see Fig. 1) to good precision, so that one would have expected a mixed, and not interchanged, character for He. The variation of configuration weights in the neighborhood of an avoided crossing is analyzed in the Appendix, where it is shown that the closer the weights of the two states are to 1 and 0, the closer the weight crossing will be to the energy pseudocrossing position.

A related question is the following: How does the presence of an avoided crossing affect the resonance widths? This bears on the related topic: Are reduced widths, as employed by Conneely and Lipsky, useful as a further property to help the classification?

An analysis of the behavior of the widths in the neighborhood of a pseudocrossing at $Z \simeq Z_0$ is also given in the Appendix, where it is shown that a similar situation to the weights holds, in the sense that, when (and only when) the widths are strongly dissimilar outside the avoided crossing, they cross at a position that is close to Z_0.

To complement those analyses with an illustration, we shall take as specific examples two avoided crossings: (i) that between $(2.3b)^1S$ and $(2,4a)^1S$, occurring at $Z_0^{-1} \simeq 0.536$ (Fig. 1), and (ii) between $(2,3c)^1P$ and $(2,4b)^1P$, at $Z_0^{-1} \simeq 0.5$ (Fig. 2).

If we draw for integer Z the positions [Fig. 2(a) and 2(b)] and widths [Figs. 3(a) and 3(b)] of those four resonances, there seems to be a smooth variation of both properties, and the crossing of the Γ values for the P states is clearly accidental. Notice that lines are only used in both figures to help the eye, as in Herrick and Sinanoglu.[19]

However, inspection of the weights in Tables I [(a) and (b)] indicates that variation is not smooth; there is character mixing, and the explanation is seen from the pseudocrossings of Figs. 1(a) and 1(c). To see the closed-channel character variation in more detail we have drawn, as functions of fractional Z, the weights $w^{[ss]}$ and $w^{[pp]}$ for the S resonances [Fig. 4(a)] and $w^{[sp]}$ and $w^{[pd]}$ for the P states [Fig. 4(b)]. Similarly, a plot [Figs. 5(a) and 5(b)] of the resonance widths shows that they also cross, and vary quickly about the pseudocrossing position. An important practical consequence is that a small error in the wave functions can substantially affect their values for $Z=2$. According to the theory developed in the Appendix, in case (i) the weights cross for $Z>Z_0$ and the widths cross for $Z\simeq Z_0$, while for (ii) crossings are at $Z\simeq Z_0$ and $Z<Z_0$, respectively. We also see from Fig. 4(b) that the situation in case (ii) for $Z=2$ is one of character mixing, and not interchange, as could have been gathered above from Table I [(b)].

Consideration of the expressions given in the Appendix, together with the values of energies, weights, and widths for fractional Z, permits us to understand the variation with Z of the resonance properties. On the other hand, it is difficult to reach the same conclusions with the energies and lifetimes for $Z=2$ alone, while consideration of the weights provides an indication. We also notice that most information is given by the energy-correlation diagrams as functions of fractional Z. This information is complemented by the configuration weights, which are also useful to find out which basis sets must be employed in the closed-channel component calculation; on the other hand, we find that widths provide little information to classify resonances.

To conclude, for a given symmetry the Conneely-Lipsky scheme is equivalent to energy ordering. In a sense, it fails to describe resonances, since the same labels correspond, for Li^+ (O^{6+}) and He, to wave functions with widely different characteristics, yielding "adiabatic" Z diagrams. For states under the $N=3,4,\ldots$ thresh-

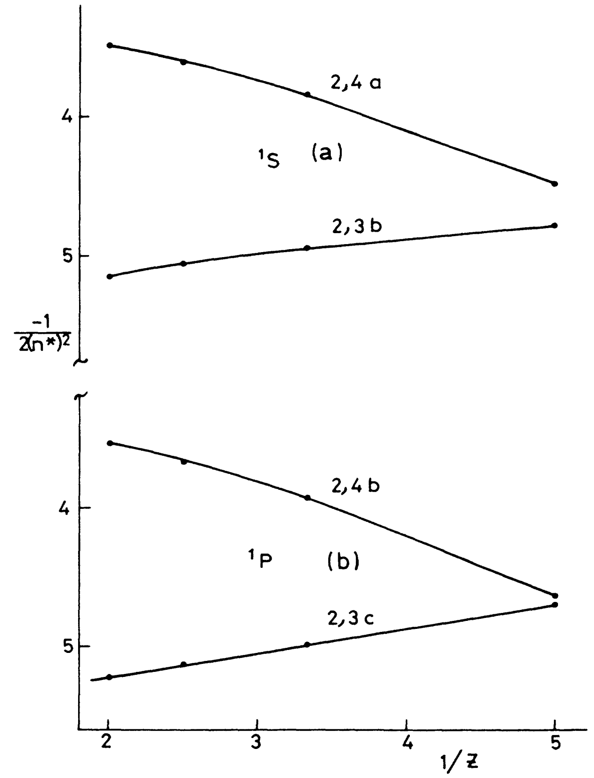

FIG. 2. Plots of $-1/2(n^{*2})$ for some ^1S (a) and ^1P (b) states of B, Be, Li, and He.

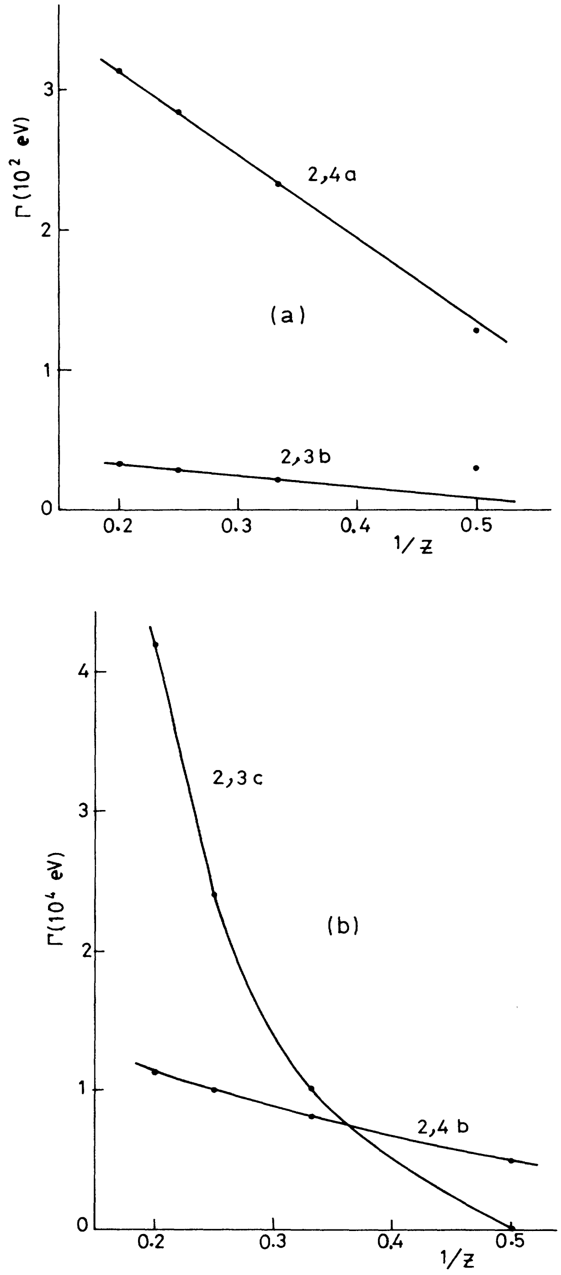

FIG. 3. (a) Plot of Γ for the same states of Fig. 2(a) (^1S states). (b) Plot of Γ for the same states of Fig. 2(b) (^1P states).

olds, more avoided crossings appear, and for larger-Z values, so that the a,b,c labeling becomes increasingly difficult to assign without the help of Z diagrams. On the other hand, widths are of little help in the classification, and because of their sensitivity to the positions of avoided crossings, if these occur in the neighborhood of an integer Z, calculations should not be performed just for single species but for a range of fractional Z values.

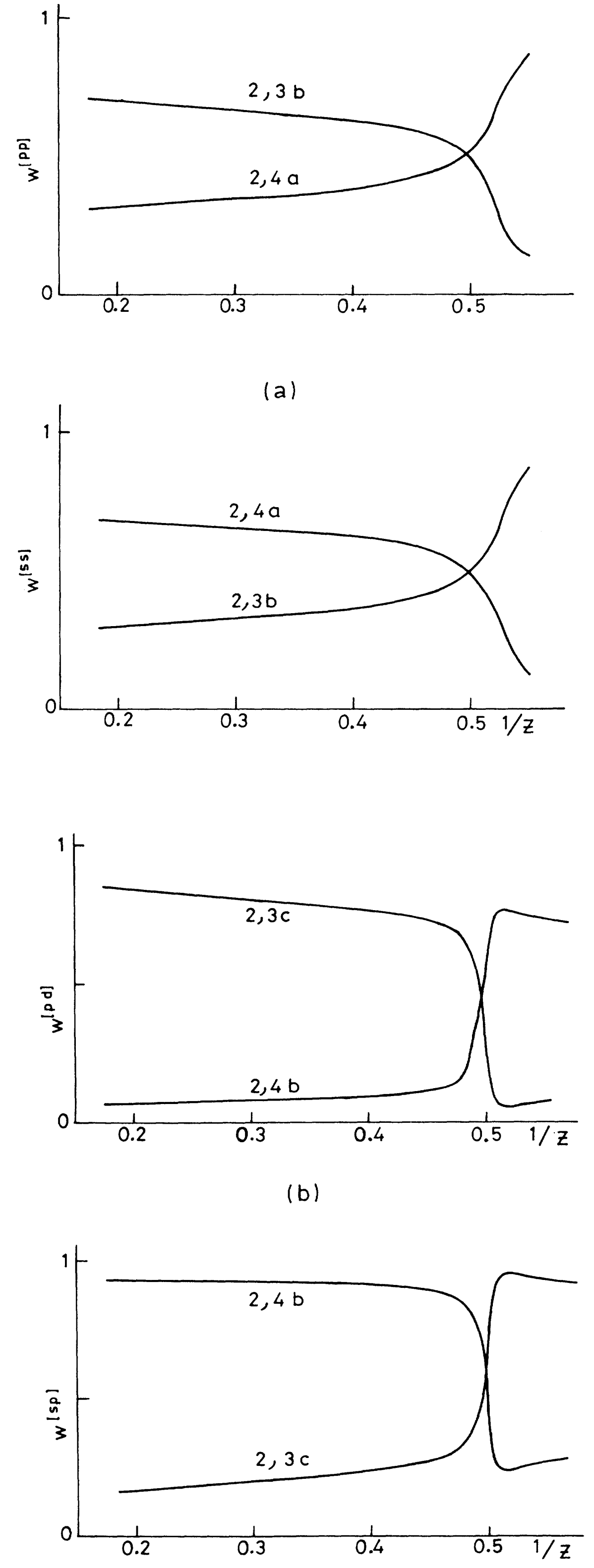

FIG. 4. (a) Weights $w^{[ss]}$ and $w^{[pp]}$ for fractional Z for ${}^1S$ states of Fig. 2(a). (b) Weights $w^{[sp]}$ and $w^{[pd]}$ for fractional Z ${}^1P$ states of Fig. 2(b).

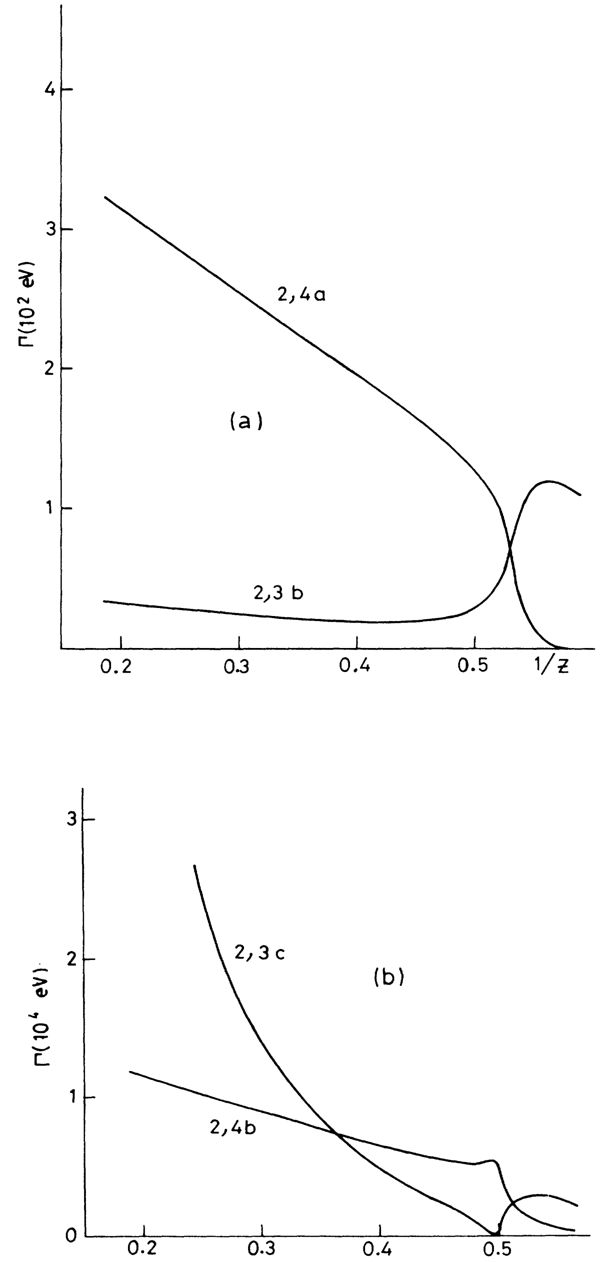

FIG. 5. (a) Values of Γ vs $1/Z$ (Z fractional) for the ${}^1S$ states of Fig. 2(a). (b) Values of Γ vs $1/Z$ (Z fractional) for the ${}^1P$ states of Fig. 2(b).

VI. THE *K*, *T*, *A* NOTATION

This was introduced in the work of Wulfman, and Herrick and Sinanoglu[19] and Lin.[20] It is noteworthy that, following different approaches, these authors arrived at essentially the same scheme. However, as we shall reason below, in practice this cannot be exactly so.

The former authors studied the problem from a group-theoretical point of view, as a symmetry breaking of the SO(4)×SO(4) group. They introduced two "approximate quantum numbers" K,T to characterize doubly-excited-state-basis (DESB) functions, which were assumed to approximate very well the Coulomb (r_{12}^{-1}) mixing between hydrogenlike configurations corresponding to the same shell (same N, different n).

Lin assumed that the closed-channel wave functions are quasiseparable in hyperspherical coordinates;[26] channel functions were then defined and used to diagonalize the Schrödinger equation at each hyperspherical coordinate R; avoided crossings in the ensuing curves were diabatised and remaining radial couplings neglected; from the properties of the channel functions and analysis of the curves, two "angular correlation" K,T (equivalent to those of Herrick and Sinanoglu) and one "radial correlation" quantum number A were introduced. In this treatment, both intershell (functions with same N, and different n) and intrashell (same N and n) correlations were considered. Since for a given symmetry species, Lin's quantum number A is determined when K and T are known;[20] both notations have been taken as identical (this can be seen from Table I, where the correspondence drawn by Lin[20] has been employed). A related scheme is the molecular picture of the atom proposed by Ezra and Berry,[26] which introduces the $v=0.5\ (N-K-T-1)$ quantum number.

We first notice that those approaches deal exclusively with the closed-channel component of the resonance wave function, and that widths were not considered in the classification, in agreement with our remarks in Sec. V.

Both SO(4) coupling coefficients and channel curves yield very useful descriptions of Feshbach resonances. Our interest here lies in how good a labeling scheme they provide. Firstly, this classification is obviously much more satisfactory than that of Sec. V because the labels are given a clear, physically intuitive interpretation. Also, it can be applied to more excited resonances than the previous method. On the other hand, since Lin[20] established a one-to-one correspondence (save for F states) between his classification and that of Conneely and Lipsky, which we have used in our tables; both schemes have been taken[6] as equivalent in practice.

However, this cannot be correct. It will be noticed from the n^* diagrams of Herrick and Sinanoglu[19] that the DESB classification aims at "diabatic" (i.e., character conserving) Z diagrams, in sharp contrast with the Conneely-Lipsky classification, which yields "adiabatic," i.e., character swapping, or even characterless (for mixed states) diagrams. Hence, the equivalences usually employed[20,6] and given in Table I cannot hold in general, and their use for the (He) doubly excited states with "mixed" character is questionable.

The applicability of the DESB approach has been critically studied by Lin and Macek[24] and Robaux,[27] who pointed out, for some He resonances, the importance of intershell correlations. Now, Lin[20] does take into account these correlations and reaches the same labeling. Since intershell correlations are most important in the avoided crossing regions of the Z diagrams, to see the correspondence between the schemes of Herrick and Sinanoglu and Lin we have to deal separately with those regions and the rest of the diagrams.

Let us first consider those avoided crossing regions. There, Herrick and Sinanoglu[19] replace, in a semiquantitative way (and from not very accurate calculations), crossing for avoided crossings in their n^* diagrams. However, since the resonance widths are smaller than the avoided crossing separations, the only physically meaningful quantities are the resonance positions given in Fig. 1, and not those of a "diabatic" diagram. Hence, we conclude that the Herrick-Sinanoglu labeling scheme breaks down for the ^1S He resonances with mixed characters discussed above. Since for higher-excited resonances more avoided crossings appear and for larger-Z values, the K,T labels become less meaningful when a larger number of ionization thresholds is involved.

On the other hand, Lin's equivalent labeling[20] is not based on DESB but on qualitative considerations of the channel function energy curves. Hence, in cases of mixed characters, where K and T lose their meaning according to our reasoning, either the same holds for Lin's K and T labels or such a classification differs from that of Herrick and Sinanoglu, and the two schemes cannot be equivalent as claimed. It is also clear that the problem is not solved by the introduction of an additional quantum number A.

We now consider the regions outside the avoided crossings. There K and T have unambiguous values, and the question is how good the approximate quantum numbers are. Herrick and Sinanoglu[19] provided an answer to this question by calculating the projection of the closed-channel wave functions over the corresponding DESB functions (see also Ref. 27). They carried out these calculations for the lowest $^{1,3}P$ He resonances (and for H^-). The results were, in general, quite good, with some exceptions that can be easily traced to the appearance of character mixing.

However, as pointed out above, He is not a good test case for approximate quantum numbers since it does not lie outside pseudocrossing regions. In Table II we have included, within parentheses, the weights of configurations of a given type corresponding to DESB states. Notice that $w^{[sp]}=w^{[2snp]}+w^{[2pns]}$.

Although the DESB weights and ours are not directly comparable for $Z<\infty$, because of our much larger bases, a perusal of Tables I and II shows that the description afforded by DESB is a good one in general. Further, we see that Lin's correspondence between the $(N,n\alpha)$ and (K,T) schemes holds for $Z=\infty$.

We also see that Lin's classification of $^1S,{}^1P$ He resonances cannot be equivalent to that of Herrick and Sinanoglu. Take, for example, the $(2,nb)^1S$ states with $n=4,5,6$: the comparison shows that, taking the overlap between our closed-channel wave functions and DESB as a criterion, these states would be approximated by DESB with $K=1$ and not with $K=-1$ as stated by Lin;[20] the opposite holds for $(2,na)$ with $n>4$; a similar criticism can be applied to $(2,nc)^1P$ states. Moreover, no distinctive K,T labels can be attached to $(2,3b)^1S$ and $(2,4a)^1S$ resonances. Of course, a definite conclusion would need a comparison of our data with the weights of Lin's $F_\mu^n(R)$ and $\phi_\mu(R;\Omega)$ functions, where R and Ω are hyperspherical coordinates, so that assignation is not based solely upon consideration of energy diagrams for the channel functions.

VII. CONCLUSIONS

As both theoreticans and experimentalists are studying increasingly excited doubly excited states, and in view of the complexity of the resonance spectra, a classification scheme is of enormous usefulness. This should be carefully distinguished from methods that provide insight on the structure of doubly excited states: many quantities, such as $\langle r_{1,2}\rangle$, $\langle r_{12}^{-1}\rangle$, $\langle\cos\theta_{12}\rangle$, etc., can be employed to describe that structure;[23,27,36–38] on the other hand, labels are usually required to take integer, or at most fractional, values, and, most importantly, to unambiguously determine a given state.

In practice, a common attitude in the assignation of labels to resonance positions is either to use energy ordering (provided no resonance is mised in the search) or eclectically employ any of the three schemes studied in the previous sections, which are mistakingly taken as equivalent.

Our main conclusion is that energy ordering together with Z diagrams is, at present, the only general solution to the classification problem, and even more so for resonances lying above several thresholds. Existing schemes can be viewed as providing a compact and physically appealing description of, and a classification for, some particular sets of resonances. Unfortunately, they do not seem to provide a general labeling. Basically, the reason is that, whatever the properties used to characterize resonances, such classification schemes cannot still hold when two states are *mixed* to an appreciable extent, so that they do not possess any definite character. Also, differences between those schemes should be taken into account.

Thus, despite its undeniable historic importance, the Cooper notation should be abandoned as a general scheme, and only be used as a rough way to characterize some doubly excited states. For resonances under the $N=2$ threshold for the He isoelectronic series, the Conneely-Lipsky labeling provides a kind of energy ordering that has an approximate physical interpretation, except for He "mixed" states (although He was paradoxically the system treated in Ref. 18). To find out which states are "mixed," energy calculations can be carried out for noninteger nuclear charges Z; also, very accurate calculations must be performed should an avoided crossing occur in the close neighborhood of an integer Z, since a small shift in its position can imply significant changes in the corresponding resonance widths (see Fig. 5). When an avoided crossing occurs close to an integer Z value, inspection of the configuration weights [Eq. (11)], together with the analysis given in the Appendix, permits one to decide whether a state is "mixed" or characters have interchanged.

In the regions free of avoided crossings, the Herrick-Sinanoglu K and T approximate quantum numbers are very useful as providing physical insight on the properties of the closed-channel component of the resonance. This scheme is not equivalent to energy ordering and therefore to the Conneely-Lipsky scheme. It breaks down at the pseudocrossings whose energy separation is larger than the sum of the corresponding widths (otherwise only an average width[27] is meaningful, and can also be defined from the "diabatic" states, whose energy positions cross). The relationship of Lin's[20] proposal to the Herrick and Sinanoglu[19] scheme requires clarification.

Finally, avoided crossings in Z-correlation diagrams, involving two or more states and wider Z ranges than in Fig. 1, become the rule, rather than the exception, for resonances above several thresholds. Then the regions where the K,T (or K,T,A) scheme holds becomes increasingly restricted and Z-correlation diagrams indispensable.

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APPENDIX

Taking a linear model[39] to describe a sharp pseudocrossing between two resonance positions E_1 and E_2 as functions of fractional nuclear charge Z, we write the two closed-channel wave functions ϕ_1 and ϕ_2 in the usual way, as linear combinations of two "diabatic" (character conserving) wave functions whose energies H_{11} and H_{22} cross at $Z=Z_0$,

$$\begin{aligned}\phi_1&=(\cos\theta)\varphi_1-(\sin\theta)\varphi_2\ ,\\ \phi_2&=(\sin\theta)\varphi_1+(\cos\theta)\varphi_2\ ,\end{aligned}\tag{A1}$$

and we assume that for $Z\simeq Z_0$

$$H_{11}-H_{22}=a\left[\frac{1}{Z}-\frac{1}{Z_0}\right]\equiv ax,\quad H_{12}=c\ .\tag{A2}$$

The rotation angle θ is then given by

$$\theta=\frac{\pi}{4}-\tfrac{1}{2}\tan^{-1}\frac{H_{22}-H_{11}}{2H_{12}}=\frac{\pi}{4}+\tfrac{1}{2}\tan^{-1}\frac{ax}{2c}\ .\tag{A3}$$

To simplify the analysis, we suppose that two configurations ψ_1 and ψ_2 (or one configuration ψ_1 and a complementary set orthogonal to it) dominate in the expansion for the diabatic wave functions. We can then write

$$\begin{aligned}\varphi_1&=(\cos\omega)\psi_1-(\sin\omega)\psi_2\ ,\\ \varphi_2&=(\sin\omega)\psi_1+(\cos\omega)\psi_3\ ,\end{aligned}\tag{A4}$$

and from (A1) and (A4) the configuration weights [Eq. (11)] are then given by

$$w^{[1]}=\cos^2(\theta+\omega),\quad w^{[2]}=\sin^2(\theta+\omega)\ . \tag{A5}$$

From (A3) and (A5) we shall have $w^{[1]}=w^{[2]}$ when

$$x=-\frac{2c}{a}\tan(2\omega)\ . \tag{A6}$$

That is, the weight crossing occurs for $Z=Z_0$ when $\omega=n\pi/2$. It takes place for $Z<Z_0$ when the configuration mixings due to the ω rotation (A4) and the θ rotation (A1) occur in the same direction and for $Z>Z_0$ in the opposite case.

The variation of the widths in the pseudocrossing is a little more complicated. Defining first the Y values [Eq. (12)] for the diabatic wave functions,

$$y_1=\langle\varphi_1|QHP|\chi_1\rangle,\quad y_2=\langle\varphi_2|QHP|\chi_2\rangle\ . \tag{A7}$$

Assuming that, for $|x|$ small, $\chi_1\simeq\chi_2$, we have for the closed-channel functions:

$$\begin{aligned}
Y_1&=(\cos\theta)y_1-(\sin\theta)y_2\\
&=\left[\frac{1}{2}\left[1-\frac{ax}{(a^2x^2+4c^2)^{1/2}}\right]\right]^{1/2}y_1\\
&\quad-\left[\frac{1}{2}\left[1+\frac{ax}{(a^2x^2+4c^2)^{1/2}}\right]\right]^{1/2}y_2\ ,\\
Y_2&=(\sin\theta)y_1+(\cos\theta)y_2\\
&=\left[\frac{1}{2}\left[1+\frac{ax}{(a^2x^2+4c^2)^{1/2}}\right]\right]^{1/2}y_1\\
&\quad+\left[\frac{1}{2}\left[1-\frac{ax}{(a^2x^2+4c^2)^{1/2}}\right]\right]^{1/2}y_2\ ,
\end{aligned} \tag{A8}$$

and the widths are given by Eq. (12). We see that $\Gamma_1=\Gamma_2$ or $Y_1=\pm Y_2$ when

$$x=\pm\frac{2cy_1y_2}{a(y_2^2-y_1^2)}\ . \tag{A9}$$

Assuming c/a small, the widths will cross for $Z\approx Z_0$ unless those of the diabatic states are similar ($y_1\simeq\pm y_2$).

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