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Comparison of multichannel-quantum-defect theory and multiconfiguration-Hartree-Fock wave functions for alkaline-earth atoms

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Multiconfiguration-Hartree-Fock wave functions for 1S and 1D states in Ca I and Sr I are compared with wave functions based on a multichannel-quantum-defect analysis. Discrepancies are found for all of the four series studied. In all cases the discrepancies pertain to perturbers which probably are located in the continuum.

The application of tunable lasers to spectroscopy has led to a renewed interest in the properties of Rydberg states.

Long series of levels have been analyzed using the multichannel-quantum-defect theory (MQDT) introduced by Seaton¹ and elaborated by Lu and Fano.^{2,3} The principal advantage of this method is that one or more Rydberg series can be described by a small set of parameters. In the absence of core polarization a single unperturbed Rydberg series can be described by a single parameter, the quantum defect, and two interacting series with three parameters, the quantum defects of the two series, and the (properly normalized) strength of the interaction between them. Before the introduction of laser spectroscopy, MQDT was applied^{3,4} to Rydberg series in the rare gases where the discrete series associated with the two series limits $^2P_{3/2}$ and $^2P_{1/2}$ are interlacing in the region below the lowest limit $^2P_{3/2}$. The interactions between the series consequently reveal themselves at several places along the series, particularly in Ar,⁴ but knowledge of the quantum defects and the interaction parameters is enough to identify all these places.

The spectra investigated using laser techniques so far have been mainly two-electron spectra in the alkaline earths. The Rydberg series in these spectra are also perturbed, but the perturbations are rather different from those in the rare-gas spectra. The different ionization limits (associated with p^6p and p^6d in particular) are due to differences in the electrostatic interaction, instead of the spin-orbit interaction, and are therefore fairly widely spaced even in light atoms. This means that the discrete Rydberg series going to the lowest limit p^6s are perturbed by only a few levels and in most cases by only one level of another series going to a higher limit. In addition, the perturbing level often will be of the type nl^2 that formally can be described as belonging to the Rydberg series $nl'n'l$ but generally is a rather atypical

member of the series with, for example, a distinctly different quantum defect. To give an example, the Ca series $4snl$ going to the lowest limit $3p^64s$ is perturbed primarily by the $3d^2$ and $4p^2$ configurations which can be viewed as the lowest terms in the $3dnd$ and $4pnp$ series going to the second ($3p^63d$) and third ($3p^64p$) limits, respectively. However, at most $3d^2$ and $4p^2$ will be below the $4s$ ionization limit. The physical problem is therefore one of a Rydberg series interacting with one or several unrelated single terms located below or above the ionization limit corresponding to the series.

The parameters in the MQDT description can in principle be obtained from *ab initio* calculations. Recently Mies has described⁵ how to calculate the MQDT parameters from variational wave functions for the case of a single perturber of the type nl^2 located above the Rydberg series of interest. However, most applications of the theory have used a parametric approach in which the MQDT parameters are obtained by fitting to experimental data. For this type of application there is a distinct difference between the rare-gas and the alkaline-earth spectra. In the rare-gas spectra, as mentioned earlier, perturbations between the interacting series occur at several places along the series. Consequently, when the MQDT parameters are determined by fitting, they are determined from a number of levels from each interacting series. Furthermore, the lowest level of each series is usually discarded because its quantum defect is significantly different from that assigned to the rest of the series. In the alkaline earths, on the other hand, the MQDT parameters related to the perturbing series (term) are determined, in the best case, from the position of *one* level as well as from the effect on the perturbed series. However, if the perturber is above the ionization limit its characteristics are determined exclusively from the perturbed series. This obviously makes the interpretation of

the data less clearcut, and some knowledge of important perturbations is valuable.

One way of checking the adequacy of the MQDT representation would be to compare the fitted MQDT parameters with theoretical predictions. Another possibility, explored here, is to compare the MQDT wave functions with *ab initio* wave functions obtained from variational calculations. The explicit MQDT wave functions can be obtained from the MQDT parameters. However, for the present purpose it is only necessary to know which basis functions were included in the MQDT analysis in order to describe the pertinent series.

We have studied the ss'^1S_0 and sd^1D_2 series in Ca I and Sr I. These series have been analyzed using MQDT by Armstrong *et al.*⁶ and by Esherick,⁷ respectively. They conclude that for the $4sns^1S_0$ series in Ca (Ref. 6) and the $5sns^1S_0$ series in Sr (Ref. 7) only interactions with the $4p^2^1S_0$ term and the $5p^2^1S_0$ term, respectively, are important. In a later paper,⁸ Wynne and Armstrong have concluded that it is possible to describe the 1S series to the same accuracy by assuming interactions between ss'^1S_0 and $d^2^1S_0$ only. We have chosen to use the original MQDT interpretations here, but we note that this choice has no influence on our conclusions since both MQDT interpretations disagree with the multiconfiguration-Hartree-Fock (MCHF) results, as we will see later.

For the $4snd^1D_2$ series in Ca, Armstrong *et al.*⁶ found interactions with $3d5s$, $3d^2$, and $4p^2$ to be important,⁶ while in Sr the equivalent interactions must be included except for $4d^2$ which Esherick found to have a negligible influence.⁷ This means that a 1D wave function in Ca can be written as a linear combination of $4snd + 3d5s + 4p^2 + 3d^2$ components. However, it was found⁶ that a substantial part of the $3d^2$ basis state is above the ionization limit and no bound state is identified as $3d^2^1D_2$. In Sr Esherick found⁷ an autoionizing resonance 450 cm^{-1} above the ionization limit which he tentatively identified as $4d^2^1D_2$, but he noted that its interaction with the $5snd^1D$ series appeared to be 10 times smaller than the $4snd \leftrightarrow 3d^2$ interaction in Ca. However, no other indication of a $4d^2^1D$ admixture was found⁷ in Sr I.

We have carried out nonrelativistic multiconfiguration-Hartree-Fock calculations for the lowest

states in these series using the program MCHF77.⁹ In this approach the wave function is expanded in terms of certain configuration-state functions and both selected orbitals and mixing coefficients determined variationally.¹⁰ Owing to the importance of configuration interaction for these series, it was not possible to use the same expansion in all cases, and Table I shows the expansions used for Ca I $4sns^1S_0$, those for Sr I 1S_0 being slightly longer. The reason for the use of different expansions above and below the perturber (conventionally^{6,11} labeled $4p^2^1S_0$) is that for levels below, both the perturber and its associated series ($4pnp$) will be pushing the $4sns$ levels down, but for levels above, the perturber itself will be pushing up while its associated series ($4pnp$) will be pushing down. The calculations were carried out using a frozen-core approximation in which the inner orbitals as well as the $4s$ orbital were taken from a HF calculation for $3p^64s$ in Ca II. Other orbitals, too, were fixed at HF values obtained using a frozen core from the $3p^64s$ HF calculation. These are underlined in Table I. All other orbitals were determined variationally.

The calculations for the 1D series are much more difficult, and only the lowest states have been calculated. The difficulties are connected with the extreme sensitivity of the d orbital to screening, particularly in Ca. The mean radius of the $3d$ orbital in Ca II $3p^63d$ is only half as large as for Ca I $3d^2^1D$, and the mean radius of the $3d$ orbital in Ca I $4s3d^1D_2$ is between these values.

The results of the calculations are given in Table II. Since individual mixing coefficients are basis dependent, Table II shows the sum of squares of the eigenvector compositions of the calculated levels for different angular couplings. For comparison the configurations included in the MQDT analysis are shown also.

Considering the results for the $4sns^1S_0$ series in Ca I (Table II), we see that the MCHF calculations predict that $4p^2$ and $3d^2$ are mixed about equally into the series except for the lowest state (excluded from the MQDT analysis). The third eigenvalue is found to have primarily $4p^2$ character as expected,^{6,11} but the $3d^2$ component, omitted from the MQDT analysis, is nearly equally large. This is in agreement with calculations by Friedrich and Trefftz¹² and by Nesbet and

TABLE I. MCHF eigenvector expansions for $(4sns + 4p^2)^1S$ states in Ca I. Fixed orbitals from HF calculations for Ca II are underlined.

$n = 5, 6$	$\underline{4sns} + \underline{4s^2} + \underline{5s^2} + \underline{4p^2} + \underline{4p5p} + \underline{5p^2} + \underline{3d^2} + \underline{3d4d} + \underline{4f^2} + \underline{4f5f}$
$4p^2^1S_0^a$	$4p^2 + \underline{5p^2} + \underline{3d^2} + \underline{4d^2} + \underline{5d^2} + \underline{4s5s} + \underline{4s^2} + \underline{6s^2} + \underline{4f^2} + \underline{5f^2}$
$n = 7, 8, 9$	$\underline{4sns} + \underline{4s^2} + \underline{5s^2} + \underline{5s6s} + \underline{4p^2} + \underline{5p^2} + \underline{5p6p} + \underline{3d^2} + \underline{3d4d} + \underline{4f^2} + \underline{4f5f}$

^aThird eigenvalue.

TABLE II. Compositions of $ns\ ^1S_0$ and $nd\ ^1D_2$ levels in Ca I and Sr I obtained from MCHF and MQDT calculations. The percentage compositions are obtained by adding all contributions (squared) of the same type in a given MCHF eigenvector (see Table I). The label designates the dominant component. A component labeled $4p^2$ in reality, therefore, includes contributions like $5p^2$ and $4p5p$.

		State	Composition
Ca I 1S_0	MCHF	4s5s:	96.39% 4s5s + 3.45% 4p ² + 0.16% 3d ²
		4s6s:	94.97% 4s6s + 3.60% 4p ² + 1.42% 3d ²
		4p ² :	47.46% 4p ² + 39.25% 3d ² + 13.27% 4sns
		4s7s:	95.65% 4s7s + 2.31% 3d ² + 2.04% 4p ²
		4s8s:	99.31% 4s8s + 0.35% 4p ² + 0.34% 3d ²
		4s9s:	99.68% 4s9s + 0.18% 4p ² + 0.18% 3d ²
	MQDT		4sns + 4p ²
Ca I 1D_2	MCHF	4s3d:	80.88% (4s3d + 3d5s) ^a + 17.97% 4p ² + 0.96% 4f4p + 0.15% 3d ²
	MQDT		4snd + 3d5s + 4p ² + 3d ²
Sr I 1S_0	MCHF	5s6s:	95.78% 5s6s + 3.70% 5p ² + 0.51% 4d ²
		5p ² :	49.26% 4d ² + 39.96% 5p ² + 10.63% 5sns + 0.15% 4f ²
		5s7s:	83.41% 5s7s + 9.73% 4d ² + 6.85% 5p ² + 0.02% 4f ²
		5s8s:	99.15% 5s8s + 0.45% 5p ² + 0.39% 4d ²
		MQDT	
Sr I 1D_2	MCHF	5s4d:	83.07% (5s4d + 4d6s) ^a + 15.10% 5p ² + 1.17% 5p4f + 0.65% 4d ²
	MQDT		5snd + 4d6s + 5p ²

^aThe relative size of these contributions in the MCHF wave function depends on the basis set and they have been added together.

Jones.¹³ From the fourth eigenvalue on, the $4p^2$ and $3d^2$ components are nearly equally large, and this might be the reason why it is possible to fit the energy levels in the series using only $4sns$ and $4p^2$ (or $3d^2$) basis states as found in the MQDT analysis.^{6,8} However, other quantities like transition probabilities can be expected to be sensitive to the $3d^2$ components.

The results for the $4s3d\ ^1D$ state show that the $4f4p\ ^1D$ term, also omitted in the MQDT analysis, gives a larger contribution to the $4s3d\ ^1D$ state than the included $3d^2$ term. Friedrich and Treffitz¹² and Nesbet and Jones¹³ have carried out calculations for 1D states but did not include a $4f4p\ ^1D$ term. This state is expected to be located in the continuum. Preliminary calculations for higher 1D states indicate that the $4p^2$ and $3d^2$ components for these states are closely linked in magnitude in the same way as for the 1S series, making the $3d^2$ component larger than the $4f4p$ component.

The results for the 1S series in Sr I (Table II) are closely analogous to the Ca I results. However, in Sr the perturber, conventionally^{7,14} labeled $5p^2\ ^1S$, turns out to have a nearly 50% $4d^2\ ^1S$ component. In the higher eigenvalues the $4d^2$ component seems to decrease somewhat faster than the $5p^2$ component, analogous to the situation in Ca.

For the $5s4d\ ^1D$ state in Sr I, it is found that the $4d^2$ component, neglected in the MQDT analysis,⁷ is larger than in the analogous $4s3d\ ^1D$ state in Ca I where $3d^2$ was included in the MQDT analysis.⁶ However, as in Ca, the $fp\ ^1D$ term, omitted in the MQDT analysis, is found to be larger than the d^2 component.

It can be concluded that disagreements exist between MQDT and MCHF wave-function compositions for all series considered here. In all these cases perturbing terms are present which have not been identified, or at least not identified with certainty, and presumably are located above or close to the ionization limit. This result seems to answer in the negative the question, raised earlier, whether it is possible to identify all perturbers from the shape of a Lu-Fano plot or from the quality of a MQDT fit. The number of branches in a Lu-Fano plot in principle determines the number of perturbers (or perturbing series). This is true if the perturbing series actually has a level in the region covered by the Lu-Fano plot but does not necessarily apply to perturbers in the continuum above the series under study.

The insensitivity to perturbers in the continuum of the MQDT fitting of levels in the bound-state region is illustrated by the procedure used in the fitting of the 1D series. It was necessary to assume that the

perturbers interact with the series but *not* among themselves.⁶ This was done in order to reduce the number of free parameters. The interaction between, for example, $3d^2$ and $4p^2$ was fixed at zero. Since this interaction in reality is very strong, an admixture of $4p^2$ in the MCHF calculation automatically gives a large $3d^2$ component. Neglect of the $3d^2 \leftrightarrow 4p^2$ interaction will necessarily give a rather different result.

In Ref. 8 it is pointed out, as mentioned already, that a MQDT fit to the 1S series in Ca I and Sr I can be carried out assuming the perturber in the bound region to be either d^2 or p^2 . The quality of the fitting is practically the same whichever choice is made, and the authors conclude that information about the continuum absorption, for example, is necessary to decide which label is the correct one. The MCHF results, on the other hand, lead to the prediction that experimental information about the continuum, if used to determine the interaction between d^2 and p^2 , will show that the bound perturber has a mixture of p^2 and d^2 character and cannot be described adequately by a single-particle label.

Alternatively it might be possible to introduce new parameters into the MQDT which can account for strongly interacting perturbors as encountered in the alkaline earths. Perhaps the energy-dependent channel-mixing angle introduced by Geiger¹⁵ in his study of $4snp, 3dnp \ ^1P_1, \ ^3P_1$ channel interactions in Ca

can be useful for this purpose.

It can be concluded that the interpretation of the alkaline-earth spectra using MQDT is much more difficult than the interpretation of the rare gases. The difficulty is related to the occurrence of perturbors in the continuum above the series under study. Since the perturbors themselves are unidentified, their characteristics must be inferred from the observed (perturbed) series. Being above the series each perturber pushes all observed levels in the same direction, making it difficult to disentangle contributions from different perturbors in the continuum as well as the effect of a perturber from an energy dependence of the quantum defect. Core polarization makes the quantum defect somewhat level dependent, particularly for the lowest levels. This effect can, to some degree, be incorporated into the MQDT analysis by allowing the quantum defect to vary with energy. However, it is difficult to verify that the energy dependence in fact is due to the influence of core polarization. We note that the energy dependence found⁷ for the 1D series in Sr I does not fall in line with the trend between Ca I and Sr I found for other series.

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