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Series perturbations in atomic spectra: Superposition-of-configurations calculations on Al I and Al II

A. W. Weiss

Institute for Basic Standards, National Bureau of Standards, Washington, D. C. 20234

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Configuration-interaction calculations, using only Hartree-Fock discrete-state configurations, are reported for the two perturbed series, $3snf\,^3F$ of Al II and $3s^2nd\,^2D$ of Al I. While good results are obtained for term values and oscillator strengths in Al II, this is not the case for Al I, where the calculations predict the $3s3p^2$ perturber to be expelled into the continuum. To study this case more closely, superposition of configurations (SOC) calculations, which include all correlation effects, were carried out on the five lowest ^2D states of Al I. These results indicate that the perturber actually remains in the discrete spectrum, but loses its identity and is smeared out over the entire series. New Rydberg orbitals are extracted from the SOC wave functions which are quite different from the Hartree-Fock but very similar to those of the Coulomb approximation. Various truncations of the SOC functions are also analyzed and the implications for the correlation problem discussed.

I. INTRODUCTION

Ever since the early pioneering work of Shenstone and Russell,[1] the phenomenon of series perturbations has been a well-recognized feature in the landscape of atomic spectroscopy.[2] The perturbations here, of course, refer to the irregularities produced in a Rydberg series by configuration interaction with a foreign configuration. The effect of this configuration interaction in term splittings and quantum defects is usually sufficiently striking to permit a reasonably unambiguous assignment of the perturber, although the wave functions in the vicinity of the perturber may be strongly mixed. This, however, is only the case if the matrix elements coupling the perturbing configuration to the series die out fairly rapidly along the series away from the perturber.

If, however, the perturber is strongly coupled to all the series members, it has a far-reaching and much more global effect on the entire spectrum, which can be quite different.[3,4] One such example of a strong perturbation occurs in Al I, where the $3s^2nd\,^2D$ series is perturbed by the ^2D term of $3s3p^2$, and a detailed calculation and analysis of the lower members of this series will be the main topic of this paper. This particular series perturbation has occasioned considerable comment in the literature, which has been directed at identifying the $3s3p^2$ term.[4-7] As we will see, this question has no answer, or at least has been incorrectly phrased, since it turns out that the $3s3p^2$ term is smeared out over the entire discrete part of the series. Such a "loss of identity" is not really unknown to spectroscopists,[8] although here it may be spread over a larger number of terms than is usually the case.

In Sec. II, by way of introduction, we describe some model calculations, including only the discrete-state configuration interaction, on the perturbed ^3F series of Al II and the ^2D series of Al I. To avoid confusion, these calculations will be referred to as configuration interaction (CI), or series perturbation, calculations as distinct from the subsequent, and more accurate variational calculations which will be called superposition of configurations (SOC).[9] The basis configurations for these CI calculations represent realistic, independent-particle model, approximations to the discrete spectral terms.

Section III contains a description of the variational SOC calculations on the lowest five ^2D terms of Al I. While each of these calculations takes a Hartree-Fock function as the initial approximation, all the other correlation configurations are obtained purely variationally. The aim in such SOC calculations is to include all the important correlation effects, to a reasonable degree of accuracy. Of course, the correlation configurations need not, and usually do not, bear much resemblance to "spectroscopic" configurations. In both Secs. II and III, f values are calculated as well as wave functions and energies. In Sec. IV, we attempt a detailed analysis of the SOC wave functions of Al I. The idea here is to extract from the wave functions as much information as possible with regard to the nature of the Rydberg states as well as the important correlation effects. Since the present calculations should be equivalent to those of a moderately extensive multiconfiguration self-consistent-field (MCSCF) approximation, these SOC functions will also be analyzed with an eye to suggesting what might be a sufficiently flexible trial function for the MCSCF procedure.

II. CONFIGURATION INTERACTION CALCULATIONS FOR Al II AND Al I

These configuration-interaction calculations on the perturbed ^3F series of Al II have been reported briefly elsewhere,[9] and they will here be described in somewhat more detail. Expansion method Hartree-Fock functions, using Slater-type basis orbitals (STO's), were computed for the $3snf\ ^3F$ terms for $n=4-8$ and for the $3p3d\ ^3F$ perturber.[10] Since both energies and matrix elements for this part of the series were well described by a n^{-2} and $n^{-3/2}$ behavior, respectively, these quantities were extrapolated for the higher terms through $13f$. It was also assumed that the off-diagonal energy matrix elements coupling the series members to each other were identically zero,[11] which should be a reasonable assumption for a nonpenetrating Rydberg series and which was borne out by direct calculation for the lower members.

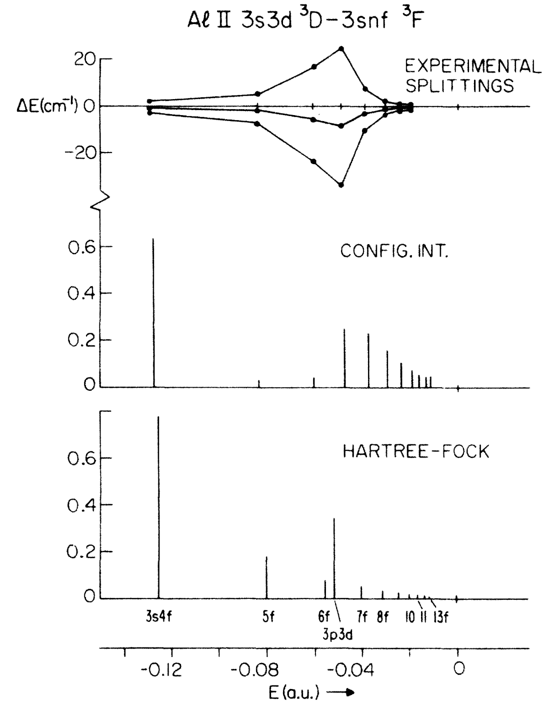

FIG. 1. Term values and oscillator strengths for the perturbed ^3F series in Al II, computed in both the HF and configuration-interaction approximation. f values are for transitions originating in the $3s3d\ ^3D$ state.

The results of the calculation are summarized in Fig. 1, which shows both the theoretical unperturbed and perturbed energies relative to the (Hartree-Fock) ionization limit, as well as the oscillator strengths for the series of transitions originating in $3s3d\ ^3D$; no configuration interaction being allowed for in this state. The experimental splittings of the J components of the ^3F terms are also shown at the top of the figure to illustrate how clearly the perturber is identified by the spectroscopic data. The CI wave functions are given in Table I. They show strong mixing of the wave functions in the vicinity of the perturber with relatively pure states for the rest of the series. There is approximately 30% of $3p3d$ mixed in with the $6f$ and $7f$ levels, with the perturber itself actually being about 30% each of $6f$, $7f$, and $3p3d$. The most obvious feature of the CI calculation is probably the asymmetric redistribution of oscillator strength in the vicinity of the perturber, which is reminiscent of the asymmetric autoionization line shapes discussed extensively by Fano and Cooper.[12] Since the interaction of a series perturber with a series is not essentially

TABLE I. The series-perturbation wave functions and oscillator strengths for the ^3F series of Al II. f values are given for transitions originating in $3s3d\ ^3D$, and energies (in a.u.) are given relative to the ionization limit.

Config.	$-E_0$	f_0	Ψ_1	Ψ_2	Ψ_3	Ψ_4	Ψ_5	Ψ_6
$3s4f$	0.1255	0.781	0.982	0.097	−0.103	0.099	−0.063	0.039
$5f$	0.0803	0.190	−0.039	0.944	0.251	−0.175	0.096	−0.055
$6f$	0.0557	0.083	0.020	−0.085	0.806	0.547	−0.178	0.085
$3p3d$	0.0516	0.349	−0.185	0.298	−0.489	0.567	−0.405	0.276
$3s7f$	0.0407	0.056	−0.013	0.044	−0.156	0.537	0.807	−0.159
$8f$	0.0313	0.039	0.010	−0.030	0.087	−0.183	0.338	0.904
$9f$	0.0247	0.029	−0.008	0.022	−0.059	0.109	−0.137	0.240
$10f$	0.0200	0.021	0.006	−0.017	0.045	−0.077	0.086	−0.106
f			0.637	0.037	0.046	0.251	0.242	0.166
$-E_{\text{calc}}$			0.1281	0.0835	0.0606	0.0476	0.0377	0.0298
$-E_{\text{expt}}$[a]			0.1296	0.0839	0.0607	0.0490	0.0391	0.0307

[a] See C. E. Moore, *Atomic Energy Levels*, Natl. Bur. Std. Circ. No. 467 (U.S. GPO, Washington, D. C., 1949), Vol. 1.

different from that of an autoionizing state embedded in a continuum, this is not particularly surprising. Asymmetric distributions of oscillator strength which cut across the continuum and discrete spectrum have also been observed experimentally.[13]

The *f* values and lifetimes for this series are given in Table II. In order to calculate lifetimes, of course, it is necessary to include all possible branchings, and we have here included the $4\,^3D$ and $5\,^3D$ as being the probably most important branches for the upper-series members. While the theoretical lifetimes for $4f$ and $7f$ may not be quite as good as desired, there is generally good agreement between the calculations and recent measurements.[14] The over-all asymmetric pattern of the *f* values is also reproduced in the march of the lifetimes.

It should be recalled that this is a model calculation, using only the Hartree-Fock for the lower ^3D states and including only the discrete series interaction for the ^3F states, and the results appear to indicate that such a model is fairly realistic. That it should be so might be expected *a priori* in this case since the system consists of nonpenetrating triplets which ought to have a very small correlation correction aside from the series perturbation. Furthermore, this is an example of a "weak" series perturbation, in the sense that the dominant effect is confined to the Rydberg states in the immediate neighborhood of the perturber.[3]

An example of a strongly perturbed series is shown in Fig. 2 which summarizes the results of exactly the same kind of calculations for the $3s^2nd\,^2D$ series of Al I. Here, the perturber is the ^2D term of $3s3p^2$ which, in the Hartree-Fock approximation, lies between $5d$ and $6d$. The configuration interaction with only the discrete series members is here strong enough to expel the perturber into the continuum with the resulting redistribution of oscillator strength as shown. The perturber composition of the predicted autoionizing state is about 50%. While the *f*-value pattern is qualitatively correct, the actual numerical values are seriously in error. The numerical results are given in Sec. III in the context of comparisons with more accurate calculations.

There are several reasons to believe that, in this case, the model calculation is seriously deficient. In the first place, since the perturber interacts strongly with the discrete series, it should also do so with the continuum, i.e., in terms of spectroscopically realistic orbitals, inclusion of continuum functions appears to be called for. Alternatively, and equivalently, from a correlation standpoint one should correct the Hartree-Fock with a set of correlation orbitals which span both the single-particle continuum basis as well as the discrete. Secondly, there are obviously important correlation terms which are missing, such as $(3p^2\,^1S)3d$. Since the *d* functions are Rydberg orbitals, fairly well removed from the $3s^2$ core, one should expect much the same kind of correlation effects as in the ground state of Al II, where there is a strong configuration mixing of the type

$$3s^2 + 3p^2.$$

In order to investigate these various effects, moderately large scale variational calculations were done for the five lowest ^2D states, and they will be described next. The idea here is to obtain a set of reasonably accurate approximations to the wave functions, which can then be analyzed in order to learn something of the structure of these strongly perturbed Rydberg states.

TABLE II. *f* values and lifetimes for $^3D-^3F$ transitions in Al II.

		f		τ (nsec)		
Transition	λ (Å)	HF	CI	HF	CI	Expt[a]
$3d\,^3D-4f\,^3F$	3588	0.815	0.678	3.32	3.98	6.4
$3d\,^3D-5f\,^3F$	2638	0.197	0.038			
$4d-$	8360	0.579	0.762	5.71	12.8	14.0
$3d\,^3D-6f\,^3F$	2326	0.085	0.048			
$4d-$	5862	0.157	0.086			
$5d-$	17480	0.900	0.585	9.01	15.7	15.0
$3d\,^3D-3p3d\,^3F$	2195	0.370	0.267	2.72[b]	3.79[b]	3.5
$3d\,^3D-7f\,^3F$	2095	0.059	0.273			
$4d-$	4589	0.092	0.047			
$5d-$	9569	0.239	0.156	10.3	3.16	5.0

[a] See Andersen *et al.* (Ref. 14); experimental uncertainties are quoted as being approximately 10%.

[b] Due to a mistake in converting from *f* to *A* these numbers are erroneously quoted in Ref. 9.

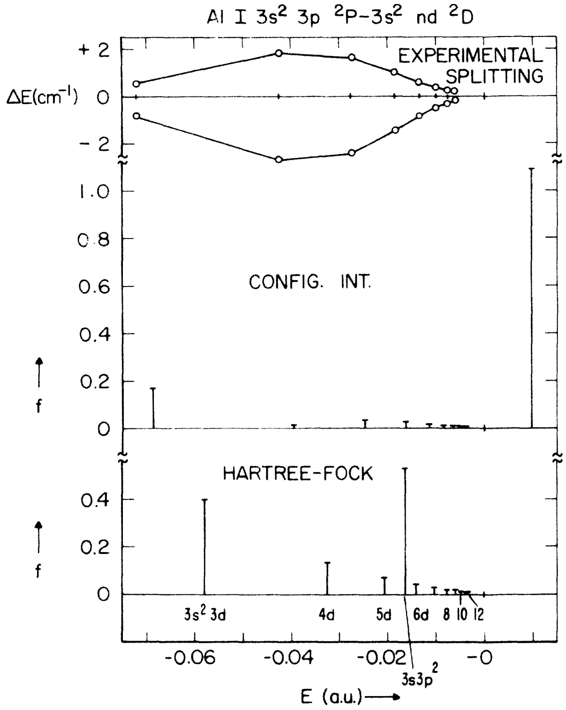

FIG. 2. Term values and oscillator strengths for the perturbed ^2D series in Al I, computed in both the HF and configuration-interaction approximations. f values are for transitions originating in the $3s^23p\ ^2P$ ground state.

III. SOC CALCULATIONS OF THE ^2D STATES

The method used for correlating the wave functions for these states is the same as has already been used extensively for other atomic excited states.[15] Superposition-of-configuration (SOC) functions were calculated which included all single- and double-excitation configurations (plus a few triples) found to be of any importance for minimizing the energy. Each state is treated completely independently of the others, with the sole criterion for choosing configurations and parameters being to minimize the energy of the appropriate root of the secular equation. Thus, for example, for the $3s^25d$ state the wave function was designed to minimize the 3rd root of the matrix eigenvalue problem with no reference to any of the other states.

The main problem which arises in such a calculation concerns the determination of a suitable set of virtual orbitals for the SOC expansion, and the procedure used here was the usual pseudonatural-orbital (PSNO) technique.[16] Starting with a conventional expansion method Hartree-Fock function, based on Slater-type functions, one augments the basis and does a SOC calculation on just one pair in the Hartree-Fock field of the remainder of the atom. The full augmented basis, sequentially orthonormalized, is used in this initial calculation. This is followed by a two-particle natural orbital transformation to generate the PSNO's which form an optimally ordered set of correlation orbitals for the three-electron correlation problem—core correlation effects being neglected. Since each state is treated independently, these sets of virtual orbitals are, in principle, different from state to state.

For the lowest ^2D state, $3s^23d$, the Hartree-Fock basis set consisted of 7-s, 3-p, and 3-d Slater-type functions. This was augmented to $\{8s, 6p, 4d, 1f\}$, the added functions were varied to minimize the SOC energy of the $3s3d\ ^1D$ pair, and the PSNO's were generated by the natural orbital transformation on this pair. The $3snd\ ^1D$ pair was, in fact, used for the PSNO's of all the D states, for the obvious reason that it includes the important $3s3p^2$ perturber. Actually the choice of this pair may not be crucial since one uses the full augmented basis, and the PSNO's from another pair would simply have the effect of spreading the $3s3p^2$ perturbation over a number of configurations of the type $3spp'$.

The end result of this process was a set of SOC wave functions ranging in length from 46 to 50 configurations for the five lowest states. The computed total energies are shown in Table III, which

TABLE III. SOC calculated energies for the ground (^2P) and the lowest five ^2D states of Al I. The numbers in parenthesis represent the total number of configurations in the wave functions.

Function	$-E$	Function	$-E$	Function	$-E$
$3s^23p$	241.8766	$3s^23\boldsymbol{d}$	241.7321	$3s^24d$	241.7067
$3s^23p+3p^3$(2)	241.8934	$3s^2\boldsymbol{n}d+3s3p^2$(4)	241.7476	$3s^2\boldsymbol{nd}+3s3p^2$(6)	241.7172
SOC(35)	241.9311	$(3s^2+\boldsymbol{pp}')\,^1\boldsymbol{S}\boldsymbol{nd}+3s3p^2$(14)	241.7648	$(3s^2+\boldsymbol{pp}')\,^1\boldsymbol{S}nd+3s3p^2$(17)	241.7484
		SOC(50)	241.7847	SOC(46)	241.7554
$3s^24\boldsymbol{d}$	241.7067	$3s^25\boldsymbol{d}$	241.6948	$3s^26\boldsymbol{d}$	241.6884
$3s^2\boldsymbol{n}d+3s3p^2$(5)	241.7009	$3s^2\boldsymbol{n}d+3s3p^2$(7)	241.6920	$3s^2\boldsymbol{nd}+3s3p^2$(8)	241.6864
$(3s^2+\boldsymbol{pp}')\,^1Sn\boldsymbol{d}+3s3p^2$(14)	241.7330	$(3s^2+\boldsymbol{pp}')\,^1Sn\boldsymbol{d}+3s3p^2$(19)	241.7265	$(3s^2+\boldsymbol{pp}')\,^1\boldsymbol{S}nd+3s3p^2$(22)	241.7226
SOC(48)	241.7402	SOC(48)	241.7313	SOC(46)	241.7258

TABLE IV. Theoretical and observed term energies (in a.u.) for the ${}^2D$ terms of Al I. The column labeled SOC refers to the 4th function of Table III. For the first two columns term values are computed relative to the Hartree-Fock $3s^2\,{}^1S$ limit of Al II (−241.6741) and for the last two they are relative to the correlated $3s^2$ limit (−241.7143) of Ref. 17.

	HF	$3s^2nd+3s3p^2$	$(3s^2+pp')\,{}^1Snd$ $+3s3p^2$	SOC	Expt.[a]
$3s^2\,7d$	−0.0104	−0.0123	−0.0083	−0.0115	−0.0134
$6d$	−0.0143	−0.0179	−0.0122	−0.0170	−0.0187
$5d$	−0.0207	−0.0268	−0.0187	−0.0259	−0.0275
$4d$	−0.0326	−0.0431	−0.0341	−0.0411	−0.0426
$3d$	−0.0580	−0.0735	−0.0505	−0.0704	−0.0722
$3s^23p$	−0.2025			−0.2168	−0.2196

[a] See Eriksson and Isberg (Ref. 5).

also includes the results of a comparable calculation on the ground state, $3s^23p$. The ground state was also calculated here since we are interested in f values as well as the energies and wave functions, and in this case the $3s3p\,{}^1P$ pair was used as the generator of the PSNO's.

In addition to these variational wave functions, several sets of smaller SOC functions were also computed which incorporate only certain specific effects. The second functions in Table III include only the $3s3p^2$ perturber and the Rydberg-like terms, namely the Hartree-Fock $3s^2nd$ and the variational terms of the same form. This is thus a kind of "exact," or complete, series perturbation, since the effect on each state of the remainder of the Rydberg terms, both discrete and continuum, are included in the $3s^2nd$ correlation terms. The third function, in addition to the series and the perturber, includes the most important single correlation correction, namely the $3p^2$ correlation of the $3s^2$ electrons. Actually, this function includes a number of configurations of the form $(npn'p\,{}^1S)nd$, the higher np terms and cross terms being necessary to make up for the fact that the p-type PSNO's were generated from the $sd\,{}^1D$ pair rather than from $3s^2\,{}^1S$.

It should be noted that both the 2nd and 3rd D states start with the Hartree-Fock $3s^24d$ as the initial approximation. A SOC function was also computed for the 3rd state starting with the HF $3s^25d$, and it ended up as essentially the same SOC wave function. However, it was found that the largest HF component for this state was the $4d$, as it was also for the 2nd. This indicates the first novel result of this study, namely that, in terms of the Hartree-Fock composition, the D series should be designated $3d$, $4d$, $4d$, $5d$, $6d$, etc., although for the lower states the HF component is not particularly large.

The term values predicted by these various approximations are shown in Table IV and compared with the spectroscopic ones. For the Hartree-Fock and complete series perturbation, the energies are computed relative to the HF limit, i.e., the $3s^2\,{}^1S$ state of Al II. For the third and fourth functions, the term values are computed relative to the correlated $3s^2\,{}^1S$ limit.[17] The term values for the final SOC wave functions are accurate to within 300–400 cm^{-1}, which appears to be the range of accuracy generally attainable by such calculations.[15,17] It is interesting, and perhaps significant, that the much simpler complete series perturbation calculation gives term values, relative to the HF limit, which are equally as accurate, and sometimes better. The complete

TABLE V. Most important configurations in the 50-term wave function for the lowest ${}^2D$ state.

Configurations	Coeff.
$3s^23d$	0.7985
$3s3p^2$	0.4605
$3s^2d_1$	−0.3022
$(3p^2\,{}^1S)3d$	−0.1602
$(3p4p\,{}^1S)3d$	−0.0893
$3s(3p4f\,{}^3D)$	−0.0650
$(3p^2\,{}^1S)d_1$	0.0582
$3s^2d_2$	−0.0577
$(3p^2\,{}^3P)d_1$	−0.0567
$(3p^2\,{}^3P)d_2$	−0.0535
$(3p^2\,{}^3P)3d$	0.0333
$(4p^2\,{}^1S)3d$	−0.0300
$(3p4p\,{}^1S)d_1$	0.0269
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series perturbation with the single important $pp'\,{}^1S$ correlation, however, predicts the term scheme very poorly, somewhat worse in fact than the Hartree-Fock. Moreover, this is not simply a matter of shifting the limit, since the shift required to get the lowest state right would grossly distort the upper ones, and vice versa.

While there seems to be little point to publishing the full wave functions for all these states, it is instructive to display the most important terms for one state just to get an idea of what kind of configurations are significant. This is done in Table V, which gives, for the lowest ${}^2D$ state, the configurations with coefficients greater in magnitude than 0.025. To avoid confusion with the Rydberg orbitals the PSNO-correlation d orbitals are labeled d_1, d_2, etc. The $3s3p^2$ perturber is mixed strongly into the wave function as is the remainder of the Rydberg series, as exemplified by the $3s^2d$ type of terms. Also, the $pp'\,{}^1S$ correlation of $3s^2$ is an important part of the wave function. However, there are additionally significant contributions from configurations which should probably be interpreted as correlating the $3s3p^2$ perturber. The configuration $3s(3p4f\,{}^3D)$, when referred to $3s^23d$, represents a valence-Rydberg triplet correlation effect which should be very small. Indeed, when the $3s3p^2$ perturber is omitted from the wave function, the contribution of this term diminishes considerably, and terms like $(3p^2\,{}^3P)d$ drop out altogether, even though they may belong to the same complex.[18]

In addition to the term values, the f values provide another check on the accuracy of the wave functions, and these results are shown in Table VI. Fortunately, there are reliable experimental data for the entire series—a lifetime measurement on the lowest state[19] and relative values for the series members.[20] Table VI also includes, under the column headed " Series perturbation," the f values computed with the wave function discussed in Sec. II, and which includes only the discrete series members. Thus, the only difference between the second and third set of f values is effectively the addition of $3s^2kd$ continuum functions. It should be noted also that the approximation to the ground state changes across Table VI, in order to remain roughly consistent with the level of approximation of the series-state calculations. The Hartree-Fock $3s^23p$ was used for the first set of f values (HF), the two-configuration function, $3s^23p+3p^3$, was used for the next three, and the full 35-configuration ground state was used with the final SOC ${}^2D$ functions.

The accuracy of the SOC functions reported here appears to be satisfactory for calculating oscillator strengths. Indeed, the level of agreement, judged by past calculations, may well be fortuitous, particularly for the $3p$-$4d$ transition which appears to involve considerable cancellation. The discrete series perturbation calculations, except for the lowest state, give poor results, although the qualitative behavior of the f values is predicted correctly. The complete series perturbation calculations also give the correct qualitative behavior and even approach quantitative accuracy for the series as a whole. Adding to the latter wave functions just the domi-

TABLE VI. Oscillator strengths for the transitions $3s^23p\,{}^2P$-$3s^2nd\,{}^2D$ of Al I. In the first column of f values, the ground state is approximated by the Hartree-Fock, in the next three columns by the 2-term function in Table III, and the final calculated values use the full 35-term approximation. The rows labeled $l.$ and $v.$ refer to the length and velocity forms, respectively.

Transition		λ(Å)	HF	Series perturbation[a]	$3s^2nd+3s3p^2$	$(3s^2+pp')\,{}^1Snd$ $+3s3p^2$	SOC	Expt.[b]
$3s^23p\,{}^2P-3s^23d\,{}^2D$	$l.$	3086	0.406	0.171	0.149	0.296	0.179	0.175
	$v.$		0.346		0.052	0.186	0.161	
$-3s^24d$	$l.$	2572	0.139	0.008	0.053	0.016	0.045	0.044
	$v.$		0.105		0.051	0.007	0.042	
$-3s^25d$	$l.$	2370	0.076	0.033	0.084	0.000	0.121	0.120
	$v.$		0.048		0.063	0.002	0.111	
$-3s^26d$	$l.$	2266	0.043	0.029	0.060	0.007	0.102	0.098
	$v.$		0.028		0.042	0.007	0.092	
$-3s^27d$	$l.$	2208	0.029	0.018	0.040	0.004	0.073	0.066
	$v.$				0.028	0.004	0.068	

[a] Discrete states only.
[b] See Budick (Ref. 19) and Penkin and Shabanova (Ref. 20).

TABLE VII. Dominant composition of various approximate wave functions for the lowest ^2D states of Al I. The series perturbation column refers to the model calculation discussed in Sec. II. The remaining columns are functions 2, 3, and 4 of Table III.

State	Series perturbation	$3s^2nd+3s3p^2$	$(3s^2+pp')\,^1Snd+3s3p^2$	SOC
$3s^23d$	$0.86(3d)-0.18(4d)+0.45(3p^2)$	$0.76(3d)-0.33(d_1)+0.56(3p^2)$	$0.89(3d)-0.2(4d)+0.32(3p^2)$	$0.8(3d)-0.3(d_1)+0.46(3p^2)$
$3s^24d$	$0.78(4d)+0.4(3d)-0.37(3p^2)$	$0.58(4d)-0.69(d_1)-0.43(3p^2)$	$0.85(4d)-0.34(d_1)-0.3(3p^2)$	$0.6(4d)-0.6(d_1)-0.46(3p^2)$
$3s^25d$	$0.74(5d)+0.5(4d)+0.27(3p^2)$	$0.74(4d)+0.61(d_1)+0.29(3p^2)$	$0.49(4d)+0.69(d_1)+0.4(3p^2)$	$0.72(4d)+0.54(d_1)+0.36(3p^2)$
$3s^26d$	$0.75(6d)+0.52(5d)-0.19(3p^2)$	$0.74(5d)+0.64(d_1)-0.2(3p^2)$	$0.49(5d)+0.76(d_1)-0.29(3p^2)$	$0.71(5d)+0.6(d_1)-0.27(3p^2)$
$3s^27d$	$0.79(7d)+0.49(6d)+0.14(3p^2)$	$0.66(6d)-0.74(d_1)+0.15(3p^2)$	$0.43(6d)-0.82(d_1)+0.17(3p^2)$	$0.68(6d)-0.65(d_1)+0.21(3p^2)$
$\Sigma\%(3s3p^2)$	47%	65%	47%	67%

nant $3s^2$ correlations, however, proves to be somewhat disastrous. Except for the lowest-state transition, which is not too bad, the series is entirely wrong. This calculation should be quite similar to a multiconfiguration self-consistent-field (MCSCF) approximation such as used by Froese-Fischer in a study of the lowest ^2D states of the Al isoelectronic sequence,[6] and the f value reported here for that state is actually quite close to hers. While the approximation appears to be adequate for the isoelectronic ions, for the neutral atom it does not properly represent the over-all effect of the important series interactions.

IV. ANALYSIS OF THE SOC CALCULATIONS

It is of some interest next to see what other information about this strongly perturbed series may be contained in these calculations. While a variety of things may be done here, the first and most obvious is simply to examine the composition of the wave functions for different levels of approximation. This is done in Table VII, which shows the dominant configurations for the various approximations described in Sec. III.

We consider first the distribution of the perturber components along the series. The final SOC wave functions, shown in the last column, indicate that the perturber has actually been smeared out over the entire series. With no more than 21% of the perturber in any state, but with the total composition for only the lowest five adding up to 67%, it seems clear that no one state can be singled out as $3s3p^2$. In other words, the strong series interaction has essentially wiped out the $3s3p^2$ perturber, while distributing its pieces throughout the series.

The model series perturbation calculation (discrete states only), however, seriously underestimates the perturber composition, particularly for the higher series members. The total for the five lowest states is 47%, a figure which is not changed much by including the higher ones. This leaves approximately 50% of $3s3p^2$ for an autoionizing state, and which appears to be an incorrect prediction.

The relatively simple complete series perturbation functions are essentially in agreement with the large SOC calculations, spreading about 65% of the perturber over these lowest Rydberg states, although the distribution seems to be skewed somewhat towards the lower part of the spectrum. Adding to this function only the important $3s^2$ correlation terms, as shown in the third column, then grossly distorts the wave-function composition, which is also reflected in the term values and oscillator strengths discussed earlier. The total amount of the perturber is diminished and shifted higher up in the series. It is as though the strong $3s^2$ correlation term had pushed the series members down away from the $3s3p^2$ with a resultant weakening of the series couplings.

All of these wave functions also show a large admixture of Rydberg-like correlation terms, i.e., the $3s^2d_1$ terms, accompanied by a significant dilution of the relevant Hartree-Fock component. This is brought about primarily, of course, through the strong coupling with the $3s3p^2$ perturber. Here too the complete series perturbation calculation agrees with the full SOC while the other two do not. The previous comment, that the series states should be labeled 3*d*, 4*d*, 4*d*, 5*d*, etc., according to the largest HF component, should therefore not be taken too seriously, although it does reflect a large change in the Rydberg part of the wave function.

The fact that there is a strong admixture of terms such as $3s^2d$ means that one may extract a kind of natural Rydberg orbital from the SOC wave function. All such Rydberg-like configurations can be combined into one term simply by defining a new *d* orbital as a linear combination of the old ones, with the same relative weights as the individual configurations. Thus, for example, the lowest state has the structure,

$$\Psi = a_0 3s^2 3d + a_1 3s^2 d_1 + a_2 3s^2 d_2 + b_1 3s3p^2 + \cdots, \quad (1)$$

which can be rewritten

$$\Psi = b_0 3s^2 d_{\mathrm{SOC}} + b_1 3s3p^2 + \cdots, \quad (1')$$

with

$$d_{\mathrm{SOC}} = (a_0^2 + a_1^2 + a_2^2)^{-1/2} [a_0 3d + a_1 d_1 + a_2 d_2] \quad (2)$$

and

$$b_0 = (a_0^2 + a_1^2 + a_2^2)^{-1/2}. \quad (3)$$

This defines in a natural way a new 3*d* orbital which represents the Rydberg part of the SOC function. It should, moreover, be essentially the same as that calculated from an MCSCF calculation with a trial function of the form Eq. (1′), including, of course, all the other important correlation terms in Table V. That is, it should be equivalent to a *d* orbital calculated self-consistently in the field, not only of the $3s^2$ core, but also in the virtual field of the $3s3p^2$ perturber and other correlating configurations. For the case of strong couplings, such as we have here, it is not surprising that such Rydberg orbitals be quite different from the Hartree-Fock.

The form of the SOC functions, in terms of the SOC orbitals, is shown in Table VIII. Now each of the wave functions is predominantly one Rydberg-like configuration, the greatest dilution being 73% for $3s^24d$. The perturber composition, of course, remains unchanged. The SOC orbitals themselves are plotted in Fig. 3 along with the corresponding Hartree-Fock functions, for comparison. The large phase shift is, of course, due to the ubiquitous $3s3p^2$ perturber. Its effect is to shift the Rydberg orbitals further in towards the origin as one goes up the series, gradually squeezing the inner loop to almost nothing for the higher terms. In fact, the SOC 6*d* already resembles much more closely the Hartree-Fock 5*d* than 6*d*. This is also reflected in the experimental quantum defects[5] which approach 1.0 for the higher members.

Another, and very interesting comparison, can be made with the wave functions of the famous Coulomb approximation.[21] This semiempirical approximation has been widely used, and has proven eminently successful, as a method for computing *f* values. In brief, the Coulomb approximation assumes that the electron moves in the purely Coulombic field of the atom core, and all departures from this field are taken into account by inserting the experimental ionization potential in place of the hydrogenic eigenvalue in the resulting one-electron Schrödinger equation. This means that the hydrogenlike series expansion of the orbital now involves a noninteger effective quantum number n^*, and so diverges at the origin. Some sort of cutoff is then invoked for this region of space, which is unimportant for an *f* value, and this has usually been done in the expansion formulas of the transition integral. The method is thus tailor made for transitions involving Rydberg states. It should be remembered, however, that the Coulomb approximation also implies a wave function, and this aspect of the method has been discussed by Friedrich, Katterbach, and Trefftz.[22] For purposes of plotting the Coulomb-approximation functions, we have adopted their procedure, which essentially cuts off the series expansion for the orbital at negative powers of *r*.

TABLE VIII. Dominant composition of the ^2D wave functions of Al I in terms of the transformed SOC *d* orbitals.

	Configurations			
Term	$3s^2nd$	$3s3p^2$	$(3p^2\ ^1S)nd$	$(3p4p\ ^1S)nd$
$3s^23d$	0.8561	0.4605	−0.1708	−0.0929
$3s^24d$	0.8543	−0.4609	−0.1787	−0.0947
$3s^25d$	0.8982	0.3647	−0.1896	−0.1028
$3s^26d$	0.9329	−0.2656	−0.1959	−0.1071

The Coulomb-approximation functions, obtained in this way for this series, are shown in Fig. 4 and compared with the Rydberg orbitals derived from these *ab initio* SOC calculations. Needless to say, the agreement is quite striking; so much so that one may be tempted to say that we have merely found an expensive way of generating the Coulomb approximation. While the Rydberg part of the wave function certainly appears to be Coulombic, it should be remembered that there is also a large admixture of the $3s3p^2$ perturber in each state, as well as all the other lesser correlation terms. Looking at this from the standpoint of the effective potential for the Rydberg orbital, the primary mechanism for shifting the orbitals from Hartree-Fock to Coulomb-like is the virtual field of the $3s3p^2$ perturber, and it seems quite remarkable that the net effect of the correlation part of the potential should be so Coulombic.

This technique of extracting a Rydberg orbital from a multiconfiguration wave function can also be used to study the truncated SOC calculations already discussed at some length. Figure 5 shows such a comparison for the lowest two states, $3s^23d$ and $3s^24d$. The Rydberg orbitals plotted here are, the Hartree-Fock, the SOC orbitals derived from the fully correlated wave functions, and those obtained from the series perturbation calculation which also include the important $3s^2$ correlations. The orbitals derived from simply the complete series perturbation calculations are very nearly the same as the final SOC orbitals, and they are not drawn here so as not to unduly confuse the picture. As can be seen, the effect of including

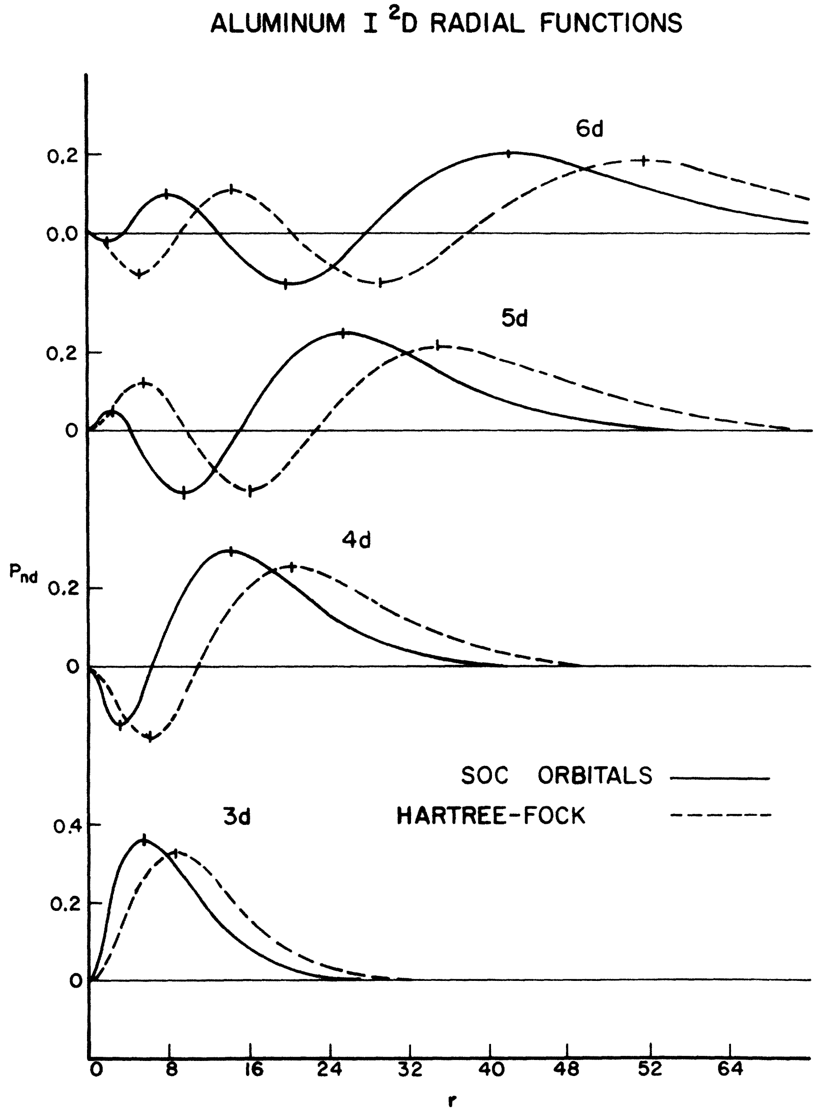

FIG. 3. Rydberg orbitals for the ^2D series in Al I. Comparison of Hartree-Fock with *d* orbitals derived from the SOC wave functions.

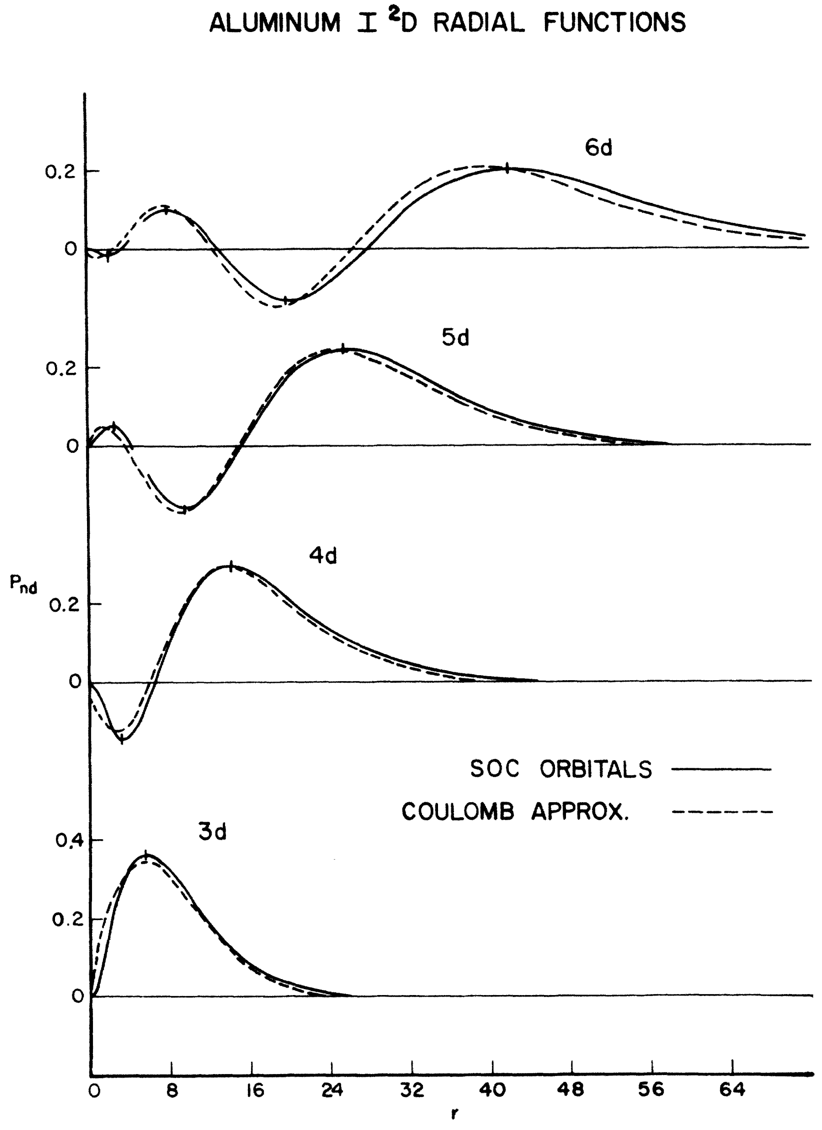

FIG. 4. Rydberg orbitals for the ^2D series in Al I. Comparison of *d* orbitals derived from SOC wave functions with those of the Coulomb approximation.

TABLE IX. Correlation energies for the $3s^2$ electrons in Al II $3s^2\,{}^1S$ and Al I $3s^23d\,{}^2D$. The notation such as $ss'3d$ means that all configurations of this general form, which were found to be important energetically, are included. It does not necessarily refer to just one configuration.

Al I	$-E$	ΔE	Al II [a]	$-E$	ΔE
$3s^23d$	241.7321	⋯	$3s^2$	241.6741	⋯
$(3s^2+ss')3d$	241.7337	0.0016	$3s^2+ss'$	241.6759	0.0018
$\cdots+(pp')\,{}^1S3d$	241.7703	0.0382	$\cdots+pp'$	241.7127	0.0386
$\cdots+(dd'+f^2)\,{}^1S3d$	241.7712	0.0391	$\cdots+dd'+f^2$	241.7143	0.0402
$\cdots+3s3p^2$	241.7755	0.0434			
50-term SOC	241.7847	0.0526			

[a] See Ref. 17.

only the partial correlation, $3s^2 + p^2$, is to shift the SOC Rydberg orbital back to somewhere in between the Hartree-Fock and the "full" SOC calculation.

Just how important the $3s^2$ correlation terms are is indicated by Table IX. This table compares the various correlation energy contributions (s^2, p^2, etc.) for the $3s^2$ electrons in $3s^2 3d$ with those of the ground state of Al II where the $3d$ electron has been completely removed. These correlation effects are quite large and, within the level of accuracy of the calculations, are essentially the same for the ion and neutral atom. These correlation energy considerations would also seem to imply that the $3s3p^2$ perturber is of relatively minor importance, which, of course, is not true. The perturber interaction is by far the dominant effect determining the basic structure of the series. Similar calculations have also been done, including a set of terms such as $3s^2 nd$, $p^2 nd$, $pp'nd$, etc., and which give similar correlation energy increments. Comparable results have also been obtained for the next-excited ^2D state, namely $3s^2 4d$.

It thus appears that if one wants to improve on the simple complete series perturbation function, it is not enough to simply add the next most important correlation effect, i.e., the correlation of the $3s^2$ core; it is also necessary to correlate the $3s3p^2$ perturber as well. Some calculations have been done on the lowest state which include these correlations but omit terms such as $(pp'\,^1S)nd$, and, not surprisingly, this also grossly distorts the picture. The $3d$ orbital derived from such a calculation is contracted even more than the full SOC Rydberg function. The effect of the $3s^2$ correlation potential seems to be nearly completely cancelled by the perturber correlations.

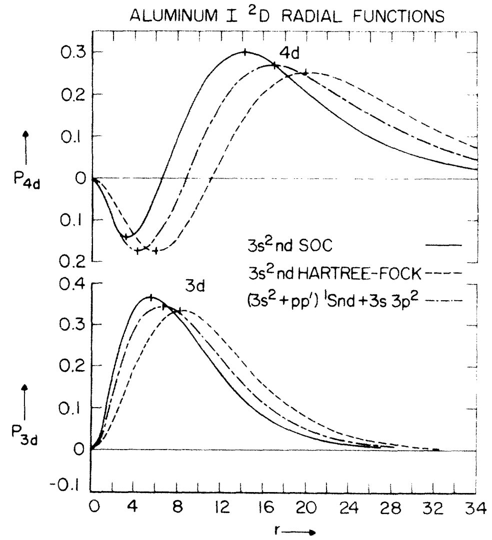

FIG. 5. $3d$- and $4d$-orbitals derived from the full SOC wave functions compared to those derived from the truncated function of the form $(3s^2 + pp')\,^1Snd + 3s3p^2$.

A few final comments can be made about the $3p$ orbitals appropriate for a multiconfiguration representation of these Rydberg states. Figure 6 compares the $3p$ PSNO derived for the $3s^2 3d$ state with the Hartree-Fock $3p$ of $3s3p^2\,^2D$ and with the optimum correlation orbital of the $3s^2\,^1S$ ion. Although they are computed in a completely independent manner, the Hartree-Fock $3p$ and the variationally derived perturber $3p$ functions are remarkably similar. Furthermore, they are both substantially different from the correlation orbital of the ion. This suggests that the optimum $3p$ orbital for correlating the ion core of $3s^2 3d$ should be somewhat different from that of the series perturber.

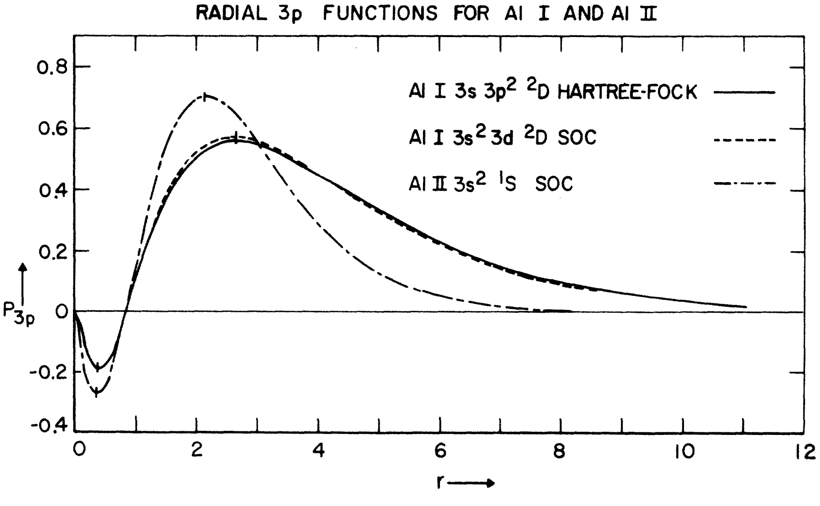

Fig. 6. $3p$ orbitals for Al I and Al II. The pseudonatural orbitals are from $3s^2 3d\,^2D$ of Al I and $3s^2\,^1S$ of Al II, and the Hartree-Fock is from $3s3p^2\,^2D$ of Al I.

As it happens, one can also extract from the full SOC wave function a $3p$ orbital which is approximately optimal for correlating the $3s^2$ pair. The coefficients in the wave function of Table V are such that the wave function, which is of the form

$$\Psi = a_0 3s^2 3d + b_0 3s3p^2 + (c_0 3p^2 + c_1 3p4p + c_2 4p^2)^1S\, 3d + \cdots , \qquad (4)$$

can very nearly be rewritten

$$\Psi = a_0 3s^2 3d + b_0 3s3p^2 + c_0'(3p')^2\ {}^1S\, 3d + \cdots , \qquad (4')$$

with

$$3p' = (1 + \lambda^2)^{-1/2}(3p + \lambda 4p). \qquad (5)$$

While the relative values of the coefficients c_i are not such as to make this contraction exact, they are close enough that it makes little difference whether λ is chosen to fit the coefficient of $4p^2$ or the $3p4p$ cross term. The $3p'$ orbital obtained from fitting the cross term is compared in Fig. 7 with the correlation $3p$ orbital of Al II; the two agree quite closely, except for the very small outer loop of the $3p'$, which apparently reflects the Rydberg tail associated with this state. This seems to imply that the trial function appropriate for an MCSCF calculation should have the form of Eq. (4′) with a $3p$ and $3p'$ neither orthogonal nor identical. Alternatively, if the MCSCF is formulated with orthogonal orbitals, the trail function should then be of the form of (4), using a $4p$ orbital with a cross-term configuration to provide the flexibility to make up for the relaxation of the correlation orbitals representing different types of correlation effects. Of course, as is clear from the preceding discussion, the trial function should also not end with just the configurations of Eqs. (4) or (4′), but should also include at least the dominant $3s3p^2$ correlations, which appear to be terms such as $(3p^2)\,{}^3Pnd$. It also happens that these terms too can be collected together to yield a d' orbital, and hence a single $(3p^2)\,{}^3P\,d'$ configuration. This orbital is quite different from the Rydberg d functions, being contracted to the point where its radial dependence closely resembles that of the $3p$.

V. CONCLUSIONS

While our conclusions strictly apply only to the two Rydberg series which have been discussed, they clearly have more general implications. In summary, then, the main points are the following.

(i) In a weakly perturbed series, the perturbing term remains localized in the series, and a configuration-interaction calculation which includes only the discrete series members and the perturber is probably adequate to represent the main features of the spectrum. This was exemplified here by model calculations on the $3snf\ {}^3F$ series of Al II. In a strongly perturbed series, this does not appear to be the case, an example of which is the $3s^2nd$ series of Al I, where the embedded perturber is $3s3p^2\,{}^2D$. The same calculation predicts the perturber to be expelled into the continuum, taking along most of the oscillator strength, which is not correct. This strong coupling case appears to require a more careful treatment of correlation.

(ii) Correlated wave functions were calculated for the lower members of the Al I ${}^2D$ series by the SOC method. These calculations included, indirectly, the effects of the $3s^2kd$ continuum, as well as other correlations. The result was that most of the perturber was brought back down into the discrete spectrum losing its identity and being

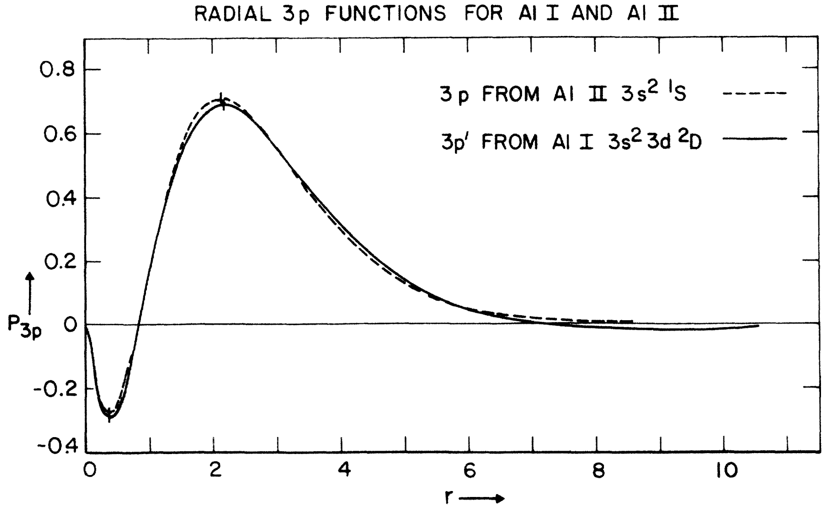

FIG. 7. The $3p$ orbitals most effective for correlating the $3s^2$ pair; comparison between Al II ground state and $3s^2 3d\,{}^2D$ of Al I.

smeared out over the entire series, with concomitant strong effects on the series as a whole. These SOC calculations were also able to satisfactorily reproduce both the term spacings and f values.

(iii) It is also possible to extract from these wave functions a Rydberg component which is quite different from the Hartree-Fock but nearly identical to that implied by the Coulomb approximation. The wave function can thus be separated as,

$$\text{Rydberg part (Coulomb approx.)} + \text{Perturber (HF)} + \text{Correlation terms.}$$

(iv) Omitting all the correlation terms also seems to give a reasonably good approximation, in terms of both level spacings and f values as well as the derived Rydberg components. Such a complete series-perturbation approach is essentially equivalent to a quantum-defect calculation. However, adding onto such a function only the important interaction,

$$3s^2 + 3p^2,$$

gives a poor approximation. The $3s^2$ correlation and the correlations of the $3s3p^2$ perturber appear to be in rather delicate balance, with their effects very nearly cancelling.

(v) The $3p$ orbital which is most effective for correlating the $3s^2$ core is also quite different from that of the perturber. Thus, the most appropriate trial function for something like an MCSCF approach would be of the form (4′) with nonorthogonal orbitals, or the more elaborate form (4) if orthogonal orbitals were used. In addition it is essential to also include some of the important perturber correlations in such a calculation.

In conclusion, while the comparatively simple "complete" series-perturbation approximation appears to represent the main features of the spectrum quite well, one should perhaps be a little cautious. The $3s^2$-$3p^2$ interaction is present and is strong, and its adverse effect is only cancelled out by the addition of terms which appear to represent correlation corrections for the perturbing configuration.

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