Energy differences of all these absorption bands from the first strong-absorption band agree well with those of the Rydberg states of the NO molecule from its ground state, if we shift the zero point for measuring the energy difference of each band by 0.60 eV from the center of the first absorption band toward the lower energies; this is because the absorption to the $v=0$ level of the $(\sigma_u 1s)^{-1}(\pi_g 2p)$, $^1\Pi_u$ state must appear near the threshold of the absorption band instead of its center.

With the above assignment, the present experimental absorption data are compatible with the theoretical expectations for the excited states originating from the $1s$ electron excitations. The energy value of 409.5 ± 0.1 eV is obtained for the K energy level of the nitrogen molecule, using the ionization energy of the NO molecule (9.27 eV) and the energy values where the absorption bands appear in the present experiment.

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Series Perturbations and Atomic Oscillator Strengths: The ^2D Series of Al I[*]

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A model calculation has been made of the effects of perturbations of the $3s^2nd$ series of aluminum by the $3s3p^2\,{}^2D$ term. The model employed is the traditional one of configuration interaction among the independent-particle model representations of the relevant discrete states, with Hartree-Fock functions being used to compute the necessary matrix elements. It is found that, while in the Hartree-Fock approximation the $3s3p^2$ term is bound and embedded in the $3s^2nd$ series, the configuration interaction gives rise to a new autoionizing state just beyond the series limit. This state, which is approximately 50% $3s3p^2$, is found to have most of the ^2D absorption oscillator strength ($f=1.1$). The general properties of this model of series perturbations are also discussed in some detail.

INTRODUCTION

This paper reports the results of a configuration-interaction study of the term scheme and oscillator-strength distribution in an atomic Rydberg series perturbed by a single foreign term. Such perturbations have long been familiar in atomic spectroscopy where they produce an otherwise anomalous behavior in the quantum defects and term splittings along the series. These effects are normally so striking as to clearly identify the perturbing state.[1,2]

A particularly interesting example of a perturbed series appears in the spectrum of neutral aluminum, where the $3s^2nd\,{}^2D$ series should be strongly perturbed by the ^2D term of $3s3p^2$. The feature of interest in this case is the fact that the perturber can't seem to be found. Both Hartree-Fock calculations and semi-empirical estimates of the Slater parameters place the $3s3p^2$ term in the middle of the series – between $5d$ and $6d$. However, the latest experimental data[3] (quantum defects and doublet splittings) does not provide any unambiguous identification of the perturber, suggesting that the configuration interaction is quite strong with its effects spread out over a number of the lower-lying states. The situation is sufficiently ambiguous that the suggested identification for the ^2D levels is simply that of the Rydberg series, $3d$, $4d$, etc., omitting entirely $3s3p^2$.

Of more general interest is the behavior of oscillator strengths (for the transitions originating in some given initial state) along a perturbed series. While some intensity anomalies have been noted with regard to the effects of autoionizing states,[4] relatively little attention appears to have been given to the effect of such perturbations on f values. The basic theoretical model underlying the usual interpretation of perturbed series is that of configuration interaction among the single configuration representations of the perturber and series members. This means that, at least in the vicinity of the perturber, the wave functions will be mixtures of the series and perturber configurations, which could strongly affect the f values. In fact, the oscillator strengths should probably be more sensitive than the energy levels to the extent of the configuration mixing induced by the foreign term.

The calculations reported here were originally undertaken to shed some light on the question of the level assignments in Al I. Configuration-interaction wave functions were computed using as a basis the Hartree-Fock functions for the $3s3p^2$ and for the four-lowest $3s^2nd$ states ($3d - 6d$), and neglecting any other interactions. While this ignores a substantial portion of the correlation error, the calculations are entirely within the framework of the traditional model of series perturbations and should provide at least a qualitatively reliable description of the term scheme. Since the f values for the series of transitions from the ground state have been measured experimentally,[5,6] one has a further, and perhaps more stringent, check on the general validity of the model.

The aluminum calculations will be described in more detail in the next section. This will be followed by a general theoretical discussion of the model. The use of Hartree-Fock functions means that the submatrix for the series is already nearly diagonal so that the full configuration interaction matrix is a bordered matrix. This simplifies the problem sufficiently so that one can draw some general conclusions about the predictions of this model.

THE Al I CALCULATIONS

The analytical, expansion method Hartree-Fock technique[7] was used to generate a set of $3s^2nd$ Rydberg states ($n = 3, 4, 5, 6$) as well as the $3s3p^2$ perturber. In this procedure, the Hartree-Fock orbitals are approximated as linear combinations of analytic basis functions,

$$\phi_{nl} = \sum C_i^{nl} \chi_i^l , \tag{1}$$

with the basis set (χ_i^l) here taken to be the usual Slater-type orbitals (STO),

$$\chi_i^l = (2\zeta_i)^{p_i+\frac{1}{2}} [(2p_i)!]^{-\frac{1}{2}} \times r^{p_i-1} e^{-\zeta_i r} Y_l^m(\theta, \varphi) . \tag{2}$$

Since the self-consistent-field procedure induces a small core relaxation in going from one state to another, the Hartree-Fock orbitals for the different D states are not quite orthonormal, and some modifications were required to get an orthonormal set suitable for the configuration-interaction calculation. The procedure adopted was to take the core and $3s$ functions from the $3s^23d$ calculation. The Hartree-Fock $4d$, $5d$, and $6d$ were then successively orthogonalized to this $3d$ and to each other. The $3p$ was the Hartree-Fock $3p$ for $3s3p^2$, Schmidt orthogonalized to the $2p$ core function. It was felt that this procedure would not give rise to any significant deviations from the Hartree-Fock for any given state, and indeed the worst case was $3s3p^2$ where the energy was raised by 0.001 a.u. (0.03 eV) above the Hartree-Fock.[8]

Such a 5-term configuration interaction is undoubtedly quite crude since it neglects the cumulative, residual correlation effects. However, this is the basic model underlying the interpretation of series perturbation effects, and it should be adequate to describe the main features of the spectrum. Since the nd series is nonpenetrating, the use of Hartree-Fock functions for purposes of computation also should not represent a severe approximation. It seems reasonable to expect at least qualitative accuracy with regard to predictions of oscillator-strength trends and identification of the dominant configuration for any particular state.

The wave functions and energies resulting from this 5×5 configuration interaction are given in Tables I and II. All the energies are given relative to the Hartree-Fock ionization limit, $3s^2\,{}^1S$ of Al II, for which $E_{\text{total}} = -241.6741$ a.u. Note that for this model, the unperturbed $3s3p^2$ state is an interloper between the third and fourth members of the Rydberg series.[9] Also given in these tables are the energies and wave functions for a 2×2 configuration-interaction calculation of the ^2P ground state

$$3s^23p + 3p^3 .$$

This latter calculation was done to maintain roughly the same level of accuracy as in the excited states, since all the f values of interest here are for transitions originating in the ground state. While the numerical results to be presented refer to this two-term ground-state function, it turns out not to be very important – the f values are not substantially changed by using simply a Hartree-Fock ground state.

TABLE I. Energies (in a.u.) and eigenvectors for $^{2}D^{e}$ states in Al I. Energies are with respect to the Hartree-Fock ionization limit.

$^{2}D^{e}$	$-H_{ii}$	ψ_1	ψ_2	ψ_3	ψ_4	ψ_5
$3s^{2}3d$	0.0580	0.8748	0.3728	−0.1543	0.0824	−0.2553
$3s^{2}4d$	0.0325	−0.1727	0.8185	0.4444	−0.1328	0.2919
$3s^{2}5d$	0.0207	0.1062	−0.2330	0.8119	0.4024	−0.3368
$3s^{2}6d$	0.0142	−0.0748	0.1292	−0.2415	0.8869	0.3645
$3s3p^{2}$	0.0165	0.4336	−0.3467	0.2476	0.1647	0.7767
	$-E_i$	0.0682	0.0386	0.0240	0.0158	−0.0048

It is clear from Tables I and II, that a fairly severe mixing of the configurations is indicated for each eigenfunction. It is also somewhat interesting to see to what extent the $3s^{2}nd$ Rydberg states are intermixed; since the submatrix for these terms is already very nearly diagonal, this is all brought about by their interaction with the $3s3p^{2}$ interloper. Although the identity of the ^{2}D levels may be somewhat questionable, it is possible to pick out a single configuration which is dominant for each state. This model thus supports the normal Rydberg-series assignments for at least the first four ^{2}D levels.

The oscillator strengths for transitions from the ground state to these levels are given in Table III, for both the Hartree-Fock and configuration-interaction wave functions, and compared with the experimental values.[5,6] The configuration-interaction f values are computed using the two-configuration ground-state approximation as well as the five-term D-state functions. In every case the theoretical energies have been used, although this is not a significant factor. It is clear that, while it underestimates the f values for the higher terms, the configuration interaction does give the correct qualitative behavior for the series.

The effects of configuration interaction on both the energy levels and f values are displayed in Fig. 1. Here energy is plotted along the abscissa, and oscillator strength along the ordinate. The Hartree-Fock scheme gives a normal, well-behaved Rydberg series, with the $3s3p^{2}$ interloper embedded in it between $n = 5$ and 6. When these terms are allowed to interact, however, all but one of the states are depressed in energy and with diminished f values, while the highest level floats off the top carrying most of the oscillator strength with it. The topmost level is here predicted to lie about 0.13 eV above the ionization limit.

The configuration interaction has thus effectively removed the $3s3p^{2}$ perturbing term from the discrete spectrum and produced an autoionizing state which, while predominantly $3s3p^{2}$, contains a significant admixture of each of the series members (see Table I). It is interesting to note in passing that this calculation bears some resemblance to the schematic model of collective states in nuclear-physics,[10] although the single-configuration basis is rather different in the two cases.

While an obviously important question now arises concerning the interaction of the autoionizing state with the continuum, we will concentrate next on the general properties of this simple model of series perturbations and its implications for the discrete spectrum.

DISCUSSION OF THE MODEL

The basic model considers only a single Rydberg series perturbed by a single foreign term. The wave function for each state is supposed to be a linear superposition of the unperturbed, independent-particle configurations,

$$\psi_n = \sum_{j=0}^{N} C_{nj}\Phi_j \ , \tag{3}$$

TABLE II. Energies (in a.u.) and eigenvectors for $^{2}P^{\circ}$ states in Al I. Energies are with respect to the Hartree-Fock ionization limit.

$^{2}P^{\circ}$	$-H_{ii}$	Φ_1	Φ_2
$3s^{2}3p$	0.2025	0.9821	−0.1882
$3p^{3}$	−0.2382	0.1882	0.9821
	$-E_i$	0.2193	−0.2550

TABLE III. Calculated and measured oscillator strengths for transitions from the ground state $3s^{2}3p\ ^{2}P$ of Al I to the ^{2}D levels. The experimental values for the series (Ref. 6) have been normalized to a lifetime measurement (Ref. 5) of the lowest level.

	$3s^{2}3d$	$3s^{2}4d$	$3s^{2}5d$	$3s^{2}6d$	$3s3p^{2}$
Hartree-Fock	0.398	0.132	0.072	0.042	0.530
Configuration Interaction	0.165	0.007	0.028	0.021	1.060
Experiment	0.175	0.044	0.120	0.098	

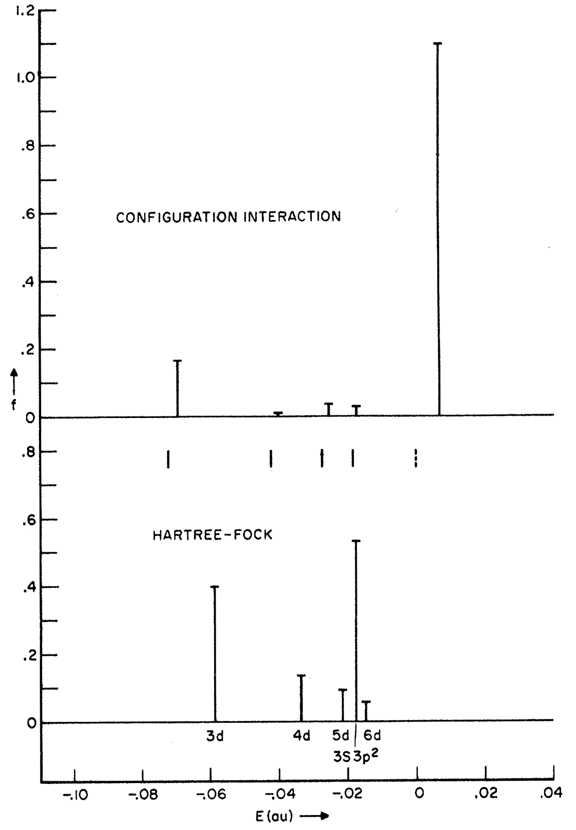

FIG. 1. The energy levels and oscillator strengths for Al I computed with and without configuration interaction. The observed level positions are also indicated.

where the summation can go over any desired number of Rydberg states. The Φ_j are furthermore supposed to be Hartree-Fock, single-configuration functions, and the C_{nj} are the coefficients of the nth eigenvector of the energy matrix. The convention will be adopted here that Φ_0 refers to the perturber, and $\Phi_j (j > 0)$ to the Rydberg terms.

In a Hartree-Fock representation of a single-series electron outside-closed shells, the matrix elements between series members vanish almost exactly.[11] To be more precise, the matrix element between a Hartree-Fock wave function and a single excitation function vanishes identically. If we then assume that core relaxation is negligible and that the Hartree-Fock functions for the individual series members form an orthonormal set, we have the following simplification. The matrix elements over the full Hamiltonian $\mathcal{H}$ are given by,

$$H_{ii} = \langle \Phi_i | \mathcal{H} | \Phi_i \rangle = \epsilon_i$$

$$H_{ij} = \langle \Phi_i | \mathcal{H} | \Phi_j \rangle = 0, \quad i \neq j \neq 0 \tag{4}$$

$$H_{0j} = \langle \Phi_0 | \mathcal{H} | \Phi_j \rangle = V_{0j} \,,$$

with ϵ_i being the unperturbed energies. Since one can, without loss of generality, take the wave functions to be real, these matrices are symmetric.

The configuration-interaction problem then is that of solving the eigenvalue problem,

$$\sum_{j=0}^{N} H_{ij} C_{nj} = E_n C_{ni} \,, \tag{5}$$

for the bordered matrix (4). In this case, the eigenvalue Eq. (5) becomes,

$$\epsilon_0 C_{n0} + \sum_{j=1}^{N} V_{0j} C_{nj} = E_n C_{n0} \,, \tag{6a}$$

$$V_{0j} C_{n0} + \epsilon_j C_{nj} = E_n C_{nj} \,. \tag{6b}$$

Equation (6b) gives the coefficients,

$$C_{nj} = C_{n0} V_{0j} / (E_n - \epsilon_j) \,, \tag{7}$$

where C_{n0} has become a normalization factor. Substituting (7) into (6a) gives a formal solution for the eigenvalues,

$$E_n = \epsilon_0 + \sum_{j=1}^{N} V_{0j}^2 / (E_n - \epsilon_j) \,. \tag{8}$$

This equation can be solved graphically by plotting the left- and right-hand sides as separate functions of a continuous variable E (in place of E_n) and finding the intersections of these curves. The right side of (8) gives a set of tangent-like curves which go to ± ∞ at the locations of the unperturbed Rydberg levels ϵ_j, and the left side is simply the straight line $Y = E$. The values of E where they intersect are then the eigenvalues E_n.

The graphical solution for a set of parameters representative of the earlier aluminum calculation is illustrated in Fig. 2. Here, the curves have been shifted by ϵ_0, so that the straight-line plot of the left side of (8) crosses the abscissa at ϵ_0, the location of the perturbing term. The figure is actually drawn for a five-member series, although, of course, the actual number is not important, since any number of series terms could be used. It is clear that including more, or less, terms in the series would not have changed things substantially; the highest eigenvalue would still detach itself from the series and move up into the continuum. Nor would the results have changed much if the perturber were further up in the series or just above the limit. Had it been significantly below the lowest member, however, the main effect of the interaction would have been to push it down and the lowest series members up, with the effects dying out further up in the series.

Since these results are somewhat different from the classical effect of a perturber buried in a spec-

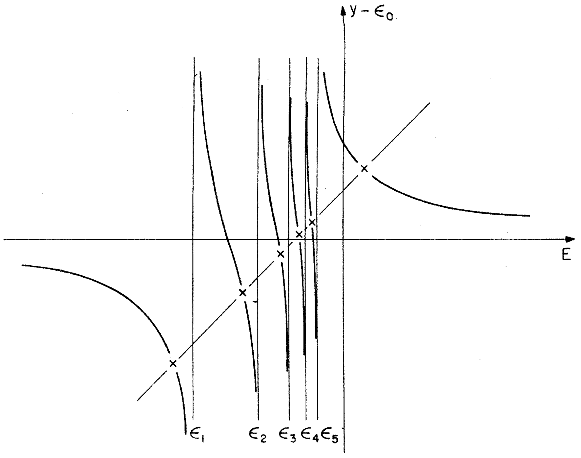

FIG. 2. The graphical solution of Eq. 8, for the case where the matrix elements are comparable to the unperturbed Rydberg level spacings. The energy scale in the figure is that of the Rydberg series under consideration.

tral series, it is of interest to examine what happens if the interactions V_{0j} are altered. In particular, if the magnitudes of the matrix elements are decreased by about an order of magnitude and made to fall off more rapidly along the series, one obtains for the graphical solution of (8) the set of curves in Fig. 3. This change in the V_{0j} results in making the curves much tighter and, in effect, wipes out the autoionizing state. The perturber now remains bound and pushes its nearest neighbors apart, with the effect dying out toward the extremes of the series, just as one normally expects from series perturbations. The identification of the perturber itself will depend on a detailed examination of the wave functions, which in the vicinity of the perturber, will probably be strong mixtures of the neighboring configurations. The important question seems to be whether or not the matrix elements are comparable in magnitude to the corresponding unperturbed-series spacings. Thus, if $|V_{0j}|$ is comparable to $(\epsilon_{j-1} - \epsilon_j)$, one has the situation depicted in Fig. 2; if it is significantly smaller one has the case of Fig. 3.

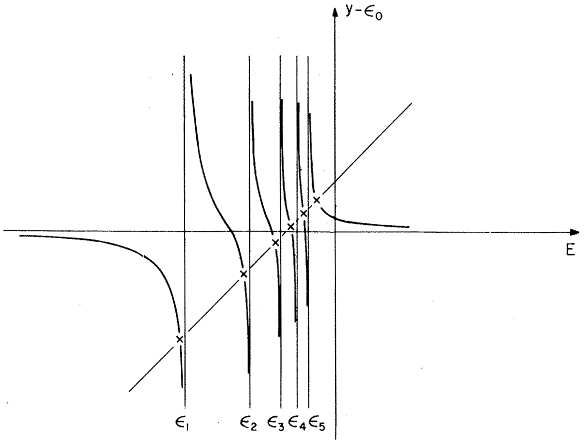

FIG. 3. The graphical solution of Eq. 8 for a set of matrix elements which are both smaller and fall off more rapidly than those for Fig. 2.

One can get some idea of the effect on the oscillator strengths now by substituting the wave functions (Eqs. 3 and 7) into the expression for the transition moment

$$D_{0n} = \langle \psi_0' | \vec{r} | \psi_n \rangle \ , \tag{9}$$

where ψ_0' is the ground-state wave function. This gives

$$D_{0n} = C_{n0} \left(d_{00} + \sum_{j=1}^{N} V_{0j} d_{0j} / (E_n - \epsilon_j) \right) \ , \tag{10}$$

where d_{00} and d_{0j} are the transition moments from the ground state to the perturber and series members, respectively. If now one makes the dipole approximation for the interaction matrix elements, i.e., supposes that they can be approximated by a product of the transition moments,

$$V_{0j} \simeq \lambda d_{00} d_{0j} \ , \tag{11}$$

then the transition moment (9) becomes

$$D_{0n} = C_{n0} d_{00} \left(1 + \lambda \sum_{j=1}^{N} d_{0j}^{\,2} / (E_n - \epsilon_j) \right) . \tag{12}$$

If $\lambda > 0$, then for the highest eigenvalue all the terms in (12) add up coherently, enabling the topmost state to collect a large portion of the oscillator strength. Conversely, for the lowest state the entire sum over the Rydberg terms in (12) is negative, and one can expect a severe cancellation in the oscillator strength. This means that if the perturber were originally below the series, it would lose oscillator strength to the series.

It should be noted here that the conclusions with regard to the energy levels are independent of the dipole approximation. This latter approximation is only important for the predictions concerning the oscillator strengths, and here all that one really needs is that the phase of the matrix elements V_{0j} match those of the transition moments d_{0j} according to Eq. (11). The validity of the dipole approximation appears to depend on the series being a nonpenetrating one, so that the series electron is radially far removed from the rest of the atom. This is discussed in the Appendix for the case $3s3p^2 + 3s^2nd$.

Some experimental support for these conclusions for the case of a perturbing state lying below a nonpenetrating series is shown in Table IV. This table compares Hartree-Fock calculations with some recent measurements of f values for tran-

TABLE IV. *f* values for some transitions involving low-lying series perturbers.

Transition	Atom	Hartree-Fock	Expt.
$2s^22p\,^2P - 2s2p^2\,^2D$	B I	0.339	0.048[a]
	C II	0.274	0.114[a]
$2s^22p^2\,^3P - 2s2p^3\,^3D$	C I	0.286	0.076[a], 0.091[b]
	N II	0.240	0.109[a]
$2s^22p^5\,^2P - 2s2p^6\,^2S$	Ne II	0.161	0.035[c]
$3s^23p\,^2P - 3s3p^2\,^2D$	Si II	0.451	< 0.006[d]
$3s^23p^2\,^3P - 3s3p^3\,^3D$	Si I	0.419	0.068[d]
	P II	0.410	0.008[d]
$3s^23p^5\,^2P - 3s3p^6\,^2S$	Ar II	0.227	0.009[e]

[a] See Lawrence and Savage (Ref. 12).
[b] See Boldt (Ref. 13).
[c] See Hinnov (Ref. 14).
[d] See Savage and Lawrence (Ref. 15).
[e] See Lawrence (Ref. 16).

sitions in first- and second-row atoms and ions which connect the ground state with low-lying valence excited states.[12–16] In every case the excited state has a nonpenetrating series above it with which it can interact, and in every case the *f* value is significantly smaller than predicted by the single-configuration approximation, which is in agreement with the above conclusions.

The importance of the nonpenetrating property of the series electron appears to be well illustrated by the ^2S series in carbon II. Here, the $2s^2ns$ series is perturbed by the ^2S term of $2s2p^2$, which lies below the series. However, in this case, it is the $2s^23s$ which has the anomalously low *f* value,[17] and which is just the opposite of the behavior shown in Table IV. A comparison of the matrix elements from a direct calculation with those given by the dipole approximation shows that the dipole approximation gives the wrong sign. In addition to this, of course, a penetrating series, with the attendant core relaxation, makes the bordered matrix approximation rather questionable.

SUMMARY AND CONCLUSIONS

The preceding two sections have described a rather simple model of series perturbations, namely a single Rydberg series perturbed by a single foreign term. For a nonpenetrating series, the conclusions can be summarized as follows. If the energy matrix elements connecting the perturber with the series members are small compared to the unperturbed series spacings, then the perturber behaves classically, repelling the neighboring series states, and with the effect dying out fairly rapidly along the series. If the matrix elements are comparable to the unperturbed spacings, then the perturber interacts with the entire series as a single entity.

In this latter case, if the matrix elements are also moderately well represented by a dipole approximation, it appears reasonable to distinguish three different possibilities. (1) If the perturber is originally an autoionizing state lying above the series, it will be pushed up still further by the interaction and take up much of the series oscillator strength. (2) If the perturber is initially embedded in the series, the interaction will give rise to a "previously nonexistent" autoionizing state which takes up a large portion of the oscillator strength. This appears to be the case in Aluminum I and probably is responsible for the recently reported difficulties in calculating the $3s3p^2\,^2D$ state.[18] (3) If the perturber is initially below the series, the interaction pushes the perturbing state down and transfers oscillator strength from it to the series, and perhaps into the continuum.

While the main point of the present investigation has been a study of the standard model for perturbed series, it should be kept in mind that there are deficiencies in this treatment which can be quite serious. In the first place of course, a good deal of the residual correlation error has simply been neglected, and it is difficult to assess the cumulative effect of a large number of "correlation" configurations added into the wave functions. There does seem to be general, qualitative experimental support for some conclusions, such as the *f* value trends in the aluminum series and for a number of low-lying perturber states in other atoms.

Another important way in which this treatment is deficient is in the neglect of the continuum part of the spectrum, both with regard to its possible effect on the discrete spectrum as well as the behavior of the photoionization cross section. In the case of the ^2D series of aluminum, the fact that the perturber interacts so strongly with the discrete series suggests also a strong interaction with the continuum. Indeed, a rough estimate of the strength of the $3s3p^2$ interaction with $3s^2kd$ near threshold, using wave functions computed in a Hartree-Fock-Slater potential, indicates a width of approximately 1.0 eV for the autoionizing state.[19] This, no doubt, accounts for the underestimation of the higher-series member f values in Table III.

At one point in this research, it was thought that this predicted ^2D autoionizing state in aluminum accounted for the reported experimental observation of a doublet just beyond the ionization limit.[20] However, the identification of this doublet as belonging to atomic aluminum has recently been questioned.[21] Furthermore, with this kind of width it is doubtful if this state would appear as anything more striking than a hump on the photoionization cross section. It is of interest to note here that there does appear to be some evidence from solar uv spectra for an enhanced absorption just beyond the aluminum threshold.[22]

In conclusion, it seems clear that a more thoroughgoing study of the aluminum cross section near threshold is called for, probably along the lines of a recent study of photo-ionization in beryllium.[23]

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APPENDIX

In the case of the Al I configuration interaction

$$3s3p^2 + 3s^2nd\ ,$$

the matrix element reduces to a single radial integral,

$$R^1(3s3p|3pnd) = \int_0^\infty \int_0^\infty dr_1 dr_2 P_{3s}(1) P_{3p}(1) \times r_<r_>^{-2} P_{3p}(2) P_{nd}(2)\ , \qquad \text{(A1)}$$

where P_{nl} are the radial functions. Since now the nd function is a Rydberg orbital, the charge distribution for electron 2 should be radially much further out than that of electron 1. Thus one should be able to approximate (A1) by the product of one-electron integrals:

$$R^1(3s3p|3pnd) \simeq (3s|r|3p)(3p|r^{-2}|nd)\ . \qquad \text{(A2)}$$

The first factor is just the dipole integral for the transition from the ground state to $3s3p^2$.

If it is now supposed that the $3p$ and nd functions can be approximated by solutions of some screened Coulomb type of potential, then the second factor is just the dipole acceleration form of the transition integral for the transition from the ground state to $3s^2nd$,

$$R^1(3s3p|3pnd) \simeq (\Delta E_{nd})^2 (3s|r|3p)(3p|r|nd)\ . \qquad \text{(A3)}$$

Since the separation of the Rydberg states is small compared to their distance from the ground state, ΔE_{nd} is a slowly varying function of n. If it is taken as a constant, one now gets the dipole approximation (11), or conversely one gets a dipole approximation where λ is a slowly varying function of the series excitation energy. The latter case does not alter the conclusions drawn from (12).

As a check on the approximation, this formula was fit to the exact matrix element for the $5d$ of Al I and then all the other matrix elements computed. It was found that they all agreed with the correctly computed V_{0j} to within 10%.

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Variational-Bound Method for Autoionization States*

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A variational method which provides upper bounds to energies of atomic autoionization states (QHQ eigenvalues) without requiring knowledge of target eigenstates is sought. For two-electron atoms, it is found that such a method is provided by a superposition of configurations of a single set of arbitrarily chosen orbitals, with a (physically plausible) prescribed choice of secular-equation roots. This conclusion is applicable to calculations of Holøien, and explains the observed "stabilization of roots."

The states of interest herein are subject to autoionization within the nonrelativistic approximation, being associated with resonances in electron-atom scattering.[1] Many of the resonances are quite narrow and it is natural to attempt to calculate these quasidiscrete compound-atom[2] states by methods similar to those which are commonly used to calculate true discrete states. The Rayleigh-Ritz method when applied to discrete states has the desirable properties of providing energy bounds and being subject to indefinite extension so as to provide as good an approximation as desired. The variational theorem[3,4] guarantees that the lth lowest root of the secular equation is an upper bound to the energy of the lth lowest state which is not orthogonal to the trial function by symmetry. This theorem does not apply in a straightforward way to compound-atom autoionization states, which lie above an infinite number of states of the same symmetry; this limitation was formally overcome by O'Malley and Geltman,[2] as noted below. The variational theorem does apply to states such as the $^4S^e$ and $^4P^o$ states of Li below the lowest ^3S state of Li$^+$; these are true discrete states within the nonrelativistic approximation, even though they lie above the Li ionization threshold.[5]

Following O'Malley and Geltman,[2] we define autoionization states as eigenfunctions of QHQ, where $P = 1 - Q$ is the Feshbach projection operator which projects onto the energetically accessible target eigenstates. For two-electron atoms, and energies below the lowest inelastic threshold, we have

$$Q = Q_1 Q_2 = Q_2 Q_1 , \tag{1}$$

$$Q_i = 1 - P_i , \tag{2}$$

$$P_i = |u_0(\vec{r}_i)\rangle\langle u_0(\vec{r}_i)| . \tag{3}$$

For two-electron atoms an alternative, but equivalent, definition is that autoionization states are those states corresponding to stationary-energy functions in Q space, the space of quadratically integrable functions which have identically vanishing overlap with the wave function(s) of the lower-lying state(s) of the target. It seems plausible to assume that this alternative definition is also meaningful and appropriate for systems with more than two electrons. It is interesting to note that this definition also encompasses such states as the quartet states of Li referred to above, since the vanishing overlap is immediately assured by symmetry properties.

The eigenvalues of QHQ, as distinguished from those of H itself, are discrete in the energy range of interest; hence the Rayleigh-Ritz method is at least formally applicable and the variational theorem guarantees energy bounds. O'Malley and Geltman showed that one can deal variationally