OCTOBER 1, 1933 PHYSICAL REVIEW VOLUME 44

The Quantum Defect of Nonpenetrating Orbits, with Special Application to Al II

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(Received July 27, 1933)

The conventional formula for the displacement in energy due to polarization of the atom-core, the major cause of quantum defect in nonpenetrating orbits, is $-\frac{1}{2}\alpha e^2\overline{r^{-4}}$. Modifications of this formula are given which are necessary if the absorption frequencies of the outer electron are not negligible compared with those of the atom-core. These modifications are more important for alkaline earths than alkalis, since in the former the atom-core includes the inner valence electron. The modified formulas require the evaluation of certain mean or "centroid" frequencies, for which approximate methods are given. Our centroid methods are readily adaptable to other problems, such as, for example, derivation of Wigner's formula for the apportionment of the dispersion *f*-sum between $l-1$ and $l+1$. With the aid of the modified polarization formula, the numbers of dispersion electrons for the resonance lines $3s-3p$ of Al III, Si IV are calculated to be 0.83, 0.80, respectively, from the quantum defects of the *G* terms of Al II, Si III. These values are, we believe, as reliable as those by other, more standard methods. The absolute (but not the relative) term values given in the literature for the spectrum of Si III are shown to be all too low by 90 ± 15 cm^{-1} due to improper evaluation of the series limit. The calculated values of the quantum defect of the ^3F terms of Al II exclusive of the perturbation by $3p3d$, also the values of the interaction matrix elements $H(3p3d\,^3F;\,3snf\,^3F)$ as computed by wave functions, are found to agree within the limits of error with the values obtained in the preceding paper in connection with the multiplet anomaly. From the behavior of the $3snf\,^1F$ terms, it is estimated that the unknown term $3p3d\,^1F$ is about 10,000 cm^{-1} beyond the series limit. The centroid modifications of the quadrupole corrections are calculated. The negligible singlet-triplet separation in the *G* terms of Al II is due to a fortuitous cancellation of penetration and quadrupole effects. The conditions are derived under which Langer's perturbation formula is theoretically valid.

I. Introduction

In spectra involving one excited electron, the displacements of the energy levels from the hydrogenic values $-RZ^2/n^2$ are due primarily to two causes: (I) penetration of the inner regions of the atom by the excited electron, (II) polarization of the atom-core. By the atom-core is meant the ion obtained by stripping the atom of the excited electron. We do not consider the Heisenberg exchange effect as a separate cause, but exchange terms can enter in connection with both (I) and (II) after the wave functions are given the proper symmetry properties. In the present paper we shall consider spectral terms whose quantum defect is due primarily to (II), which is the main cause if the excited orbit has a large azimuthal quantum number and hence a large perihelion distance.

The effect of (II) is usually deduced by the following argument.[1] If the radius r of the excited electron's orbit is large compared to the dimensions of the atom-core, this electron exerts a sensibly homogeneous field $-e/r^2$ on the rest of the atom, and so induces a dipole moment $-\alpha e/r^2$ in the atom-core, where α is the latter's specific polarizability. This dipole will in turn react on the excited electron with an attractive force $F(r)=2\alpha e^2/r^5$, since a dipole of strength μ yields a field $2\mu/r^3$ at points along its axis. Thus the potential energy due to polarization of the atom-core is

$$\int F(r)dr=-\alpha e^2/2r^4.$$

If we regard this as a perturbative potential superposed on the ordinary Coulomb attraction, and if we neglect squares of α, the change in the quantized energy is approximately the mean value of this potential. Hence

$$W=-RZ^2/n^2-\tfrac{1}{2}\alpha e^2(\overline{1/r^4}). \qquad (1)$$

If the orbit is nonpenetrating, it is allowable to use the mean value of r^{-4} appropriate to Keplerian motion, *viz.*,[2]

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[1] Born and Heisenberg, Zeits. f. Physik **23**, 388 (1924).

[2] I. Waller, Zeits. f. Physik **38**, 635 (1926).

$$\overline{\frac{1}{r^4}}=\frac{(4\pi^2Ze^2m)^4}{2h^8(l^3-l)}\left[\frac{3}{n^3(l^2-\frac{1}{4})}-\frac{1}{n^5}\right].$$

Then the spectral terms will have the Rydberg-Ritz form, inasmuch as

$$-RZ^2/(n-\Delta-an^{-2})^2 = -RZ^2(n^{-2}+2\Delta n^{-3}+2an^{-5}+\cdots).$$

The preceding conventional derivation of (1) is based on an intuitive model in which the atom-core is endowed *ad hoc* with a polarizability α rather than deduced from the actual potential function

$$V=-\sum_i \frac{Ze^2}{r_i}+\sum_{i>j}\frac{e^2}{r_{ij}} \tag{2}$$

of the atom. The derivation of (1) from the intuitive model possesses simplicity, but clearly lacks rigor of detail. Instead it is possible to derive (1) from (2) by perturbation theory. This has been done independently by Joseph and Maria Goeppert Mayer[3] and by the writers.[4] The latter published only an abstract giving the conditions which underly the proof. In view of the subsequent appearance of the Mayer paper, we shall omit the explicit proof for the general atom. However, the proof for systems with two electrons is incidental to the general analysis of such systems given in the present paper, and the extension to more than two electrons is fairly obvious. The conditions under which (1) can be obtained from (2) are: (a) the atom-core must be in an S state; (b) the perihelion distance of the excited electron must be large compared to the diameter of the atom-core; (c) the Heisenberg exchange terms are to be neglected; (d) quadrupole and higher order terms are to be disregarded; and especially (e) the absorption frequencies of the atom-core must be large in magnitude compared to the frequencies associated with transitions of the valence electron.

Condition (b) is tantamount to disregarding the penetration, but if the penetration corrections are small, they may be considered as simply additive to the major polarization effect.

More important than any question of rigor is the fact that the proof of (1) by means of (2) has the great advantage that it shows us how (1) is to be modified when various of the conditions (a)—(e), notably (e), are not fulfilled. In an atom or ion with two electrons outside of closed shells, the portion of the atom-core which is most easily polarized by the excited valence electron is clearly the other, non-excited valence electron (e.g., the 3s electron in Al II). The remaining electrons involved in the atom-core are much more firmly bound, so that the interaction of the atom-core and the excited electron is effectively that characteristic of a system with two electrons. Thus in our application to Al II, we shall entirely disregard the polarization effect on the ten electrons $1s^2\ 2s^2\ 2p^6$. The inner valence electron is subject to a field only about twice as strong as for the outer one, so that the former's absorption frequencies are not exceedingly large compared with those of the latter. Thus (e) is a bad approximation in spectra isoelectronic with the alkaline earths. In the examples studied in the present paper we consequently encounter conditions radically different from those in the alkali atoms treated by J. and M. Mayer, where the atom-core is homologous with an inert gas rather than an alkali, and where, therefore, (e) is a valid approximation.

II. Matrix Elements of the Interelectronic Potential for Systems with Two Valence Electrons

As a first approximation, the wave functions for a system with two non-equivalent valence electrons may be taken to be

$$\Psi_{n_0l_0n_il_iLM}=2^{-\frac{1}{2}}\sum\nolimits_{m_i,\ m_o,\ (m_i+m_o=M)}\ a_{m_im_o}[\psi_{n_il_im_i}(1)\psi_{n_ol_om_o}(2)\pm\Psi_{n_ol_om_o}(1)\psi_{n_il_im_i}(2)], \tag{3}$$

where the minus or plus sign is to be used according as a triplet or singlet state is desired. The abbreviation $\psi(1)$ is used for $\psi(x_1y_1z_1)$, and $\psi_{n_il_im_i}$ is often contracted to ψ_i, etc. The letters n_i, l_i, m_i

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[3] J. E. and M. G. Mayer, Phys. Rev. **43**, 605 (1933).

[4] N. G. Whitelaw and J. H. Van Vleck, Phys. Rev. **41**, 389A (1932).

denote respectively the principal, azimuthal, and magnetic quantum numbers for the inner electron, while n_o, l_o, m_o have the corresponding significance for the outer one. All of our wave functions are exclusive of spin and so the m's are purely orbital spatial quantum numbers. The coefficients a are those of the well-known Clebsch-Gordan series[5] associated with the vectorial addition of l_1, l_2 to a resultant L. Oftentimes we are interested in states for which $L=l_1+l_2$; when this is the case no summation is necessary in (3) provided we take $M=L$, which involves no loss of generality in the absence of external fields. When the summation can thus be eliminated, the factor a reduces to unity. The subscripts i and o mean that the corresponding wave functions are solutions for a one body problem appropriate to inner and outer valence electrons, respectively. That is to say, $\psi_{n_il_im_i}$ is a solution of a three-dimensional wave equation with a potential function $f(r)$, while $\psi_{n_ol_om_o}$ is a solution of such an equation with a potential function $f(r)+e^2/r$. The physical basis for this procedure is of course that as a first approximation the inner electron affects the outer one as though it were concentrated at the nucleus. The potential $f(r)$, although central, will in general not be of Coulomb form, as some allowance for penetration of the inner shells is important in the construction of ψ_i, though usually trivial for ψ_o.

We must now proceed to solution of the accurate six-dimensional wave equation, using (3) as the unperturbed wave functions. The Hamiltonian operator for this equation is

$$\mathbf{H}=-(h^2/8\pi^2m)(\nabla_1^2+\nabla_2^2)+f(r_1)+f(r_2)+e^2/r_{12}. \tag{4}$$

Let

$$H(n_ol_on_il_i;\, n_o'l_o'n_i'l_i')=\int\Psi^*\mathbf{H}\Psi'dv_1dv_2. \tag{5}$$

In the evaluation of (5) it is convenient to use the familiar expansion

$$\frac{e^2}{r_{12}}=\frac{e^2}{r_b}+\frac{e^2r_a}{r_b^2}\cos(r_a,r_b)+\frac{e^2r_a^2}{2r_b^3}[3\cos^2(r_a,r_b)-1]+\cdots, \tag{6}$$

where r_b is the greater and r_a the lesser of the two quantities r_1, and r_2.

Definition of H_k, H_{k+}, H_{k-}. Let H_o denote (4) with r_{12} replaced by r_b and let $H_k(k>0)$ denote the terms of degree k in r_a in the expansion (6). It is well known that with any given Ψ and Ψ' the matrix element $H_k(;)$ vanish for all k above a certain critical value.[6] Furthermore the integral (5) vanishes unless the same choice of sign in (3) is used for the initial and final wave function, and unless also $L=L'$, $M=M'$, and $l_i+l_o-l_i'-l_o'$ is an even number. Since H is diagonal in L and independent of M, we do not always list M or L among the arguments of the H_k's; it is to be understood throughout that we are confining our attention to one particular value of L. Let

$$H_k(n_il_in_ol_o;\, n_i'l_i'n_o'l_o')=H_{k+}(n_il_in_ol_o;\, n_i'l_i'n_o'l_o')\pm H_{k-}(n_il_in_ol_o;\, n_i'l_i'n_o'l_o'), \tag{7}$$

where the choice of sign is the same as that in (3), and where hence the plus and minus sign are appropriate respectively to singlet and triplet terms. It is seen that $H_+(\ )$ and $H_-(\ )$ denote respectively the parts of (5) which do and which do not change sign when the signs in (3) are reversed for both Ψ and Ψ'. The H_{k-} may be regarded as the exchange terms, for they are responsible for the singlet-triplet separation.

The determination of the characteristic values W of the wave equation associated with (5) is equivalent to solution of an infinite secular equation. If we retain only diagonal elements, the solution for states having $l_i=0$ is

$$W_o=H_{o+}(n_ol_on_il_i;\, n_ol_on_il_i)\pm H_{l_o-}(n_ol_on_il_i;\, n_ol_on_il_i) \tag{8}$$

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[5] Cf., for instance, E. Wigner, *Gruppentheorie*, p. 205.

[6] Cf. J. C. Slater, Phys. Rev. **34**, 1293 (1929).

with[7]

$$H_{o+}=W(n_ol_o)+W(n_il_i)+\int\int[e^2/r_b-e^2/r_1]|\psi_o(1)|^2|\psi_i(2)|^2dv_1dv_2, \tag{9}$$

$$H_{l_o-}=\int\int[e^2r_a^{l_o}/r_b^{l_o+1}]\psi_o^*(1)\psi_i^*(2)\psi_i(1)\psi_o(2)dv_1dv_2. \tag{10}$$

Here $W(n_ol_o)$ and $W(n_il_i)$ are the characteristic values of the three dimensional wave equations satisfied by ψ_o and ψ_i, respectively. Since penetration of the interior closed shells is unimportant for the outer electron, $W(n_ol_o)$ will have the hydrogenic form $-RZ^2/n^2$. In the specification of spectral terms for systems with two electrons it is customary to choose the origin for the energy in such a way that the term value vanishes when one electron is removed to infinity and the other is left in its normal state. Hence we take $W(n_il_i)=0$ when the inner electron is unexcited. The integrand in (9) vanishes except when the outer electron is nearer the nucleus than the inner one. The nondiagonal elements of (5) affect the energy only when squares and higher powers of these terms are considered by using the well-known perturbation formula[8]

$$W=W_o+\sum_{n_i'l_i'n_o'l_o'}\frac{|(H_1+H_2+\cdots)(n_ol_on_il_i;\, n_o'l_o'n_i'l_i')|^2}{h\nu(n_ol_on_il_i;\, n_o'l_o'n_i'l_i')}, \tag{11}$$

which is valid provided

$$|(H_1+H_2+\cdots)(\ ;\ )|\ll|h\nu(\ ;\ )|. \tag{12}$$

The squared terms in (11) are actually more important than the integrals in (9) and (10) if the azimuthal quantum number is so large that polarization is more important than penetration.

Definition of $H_{k\pm}'$. Let $H_{k\pm}'$ $(k>0)$ be the value of $H_{k\pm}$ which is obtained if one replaces r_a, r_b by r_i, r_o, respectively. Here r_i, r_o denote the radii associated with the coordinate arguments of ψ_i, ψ_o respectively. The relation

$$H_{k+}(n_ol_on_il_i;\, n_o'l_o'n_i'l_i')=H_{k\pm}'(n_ol_on_il_i;\, n_o'l_o'n_i'l_i') \tag{13}$$

is never accurately fulfilled, as Ψ does not entirely vanish in the region for which $r_i>r_o$, but nevertheless (13) is usually a fairly good approximation. The explicit value of H_{1+}' is

$$H_{1+}'(n_il_in_ol_o;\, n_i'l_i'n_o'l_o')=e^2r_o^{-2}(n_ol_o;\, n_o'l_o')r_i(n_il_i;\, n_i'l_i')\cos(r_1,r_2)(Ll_il_o;\, Ll_i'l_o'), \tag{14}$$

where[9]

$$r_a^s(n_al_a;\, n_a'l_a')=\int R_ar^sR_a'dr, \quad (a=i \text{ or } o) \tag{15}$$

$$\cos(r_1,r_2)(Ll_il_o;\, Ll_i'l_o')=\int\Phi^*\cos(r_1,r_2)\Phi'd\omega_1d\omega_2, \tag{16}$$

with the notation R_i, R_o for the radial factors of ψ_i, ψ_o, respectively, and Φ for the "angular" part of Ψ, obtained by deletion of all radial factors. The radial factors are independent of m_i, m_o and so can be taken outside the summation in (3). It is to be further understood that the exchange or "cross" terms are to be omitted in evaluating the integral in (16) since we are at present interested only in the portion H_+ of H. The expressions (15) are not to be confused with ordinary matrix elements, as the angular factor essential to the complete wave functions is omitted. The initial and final functions

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[7] W. Heisenberg, Zeits. f. Physik **39**, 499 (1926).

[8] Rigorously, H_0 contains nondiagonal terms which should be included in the squared part of (11), but these terms are a second-order penetration effect and may be neglected in our work.

[9] We always take the radial part of the generalized volume element as dr rather than r^2dr. This is legitimate, since the "weight factor" r may be eliminated by changing the definition of R by a factor r, so that R satisfies a self-adjoint differential equation.

R_a, R_a' belong to different sets of orthogonal functions in the variable r except when $l_a=l_a'$. Despite this fact there are relations of the form

$$\sum\nolimits_{n_o'} |r^s(n_ol_o;\, n_o'l_o')|^2 = r^{2s}(n_ol_o;\, n_ol_o), \tag{17}$$

as one of us has shown elsewhere.[10] The element on the right side of (17) is an ordinary matrix element, as here the initial and final l indices are the same. It is to be particularly noted that we do not sum over l_o' in (17), and that (17) holds for any value of l_o'. Incidentally, (17) would still hold for any function of the single variable r rather than a simple power function; also inner rather than outer radial functions and coordinates could be used. Our use of (17) will be confined mainly to the case $s=-2$.

Now

$$\cos(r_1,\, r_2)(Ll_il_o;\, Ll_i'l_o') = 0 \quad \text{unless} \quad |l_i-l_i'| = |l_o-l_o'| = 1, \tag{18}$$

as is easily verified from the properties of spherical harmonics. The nonvanishing elements of $\cos(r_1, r_2)$ are rather complicated unless we assume that the inner electron is in an s state, which we shall do henceforth. If we apply one of the invariance theorems known as the "principle of spectroscopic stability" to the passage from LM to individual space (i.e., m_i, m_o) quantization,[11] and if we use the diagonality in M we have the relation

$$|\cos(r_1,\, r_2)(Ll_il_o;\, Ll_i'l_o')|^2 = \sum\nolimits_{m_i',\, m_o'} |\cos(r_1,\, r_2)(l_il_om_im_o;\, l_i'l_o'm_i'm_o')|^2. \tag{19}$$

Here the indices on the left side of the equation relate to an L, M system of representation; those on the right to an m_i, m_o one. Eq. (19) as it stands, is only valid if the inner electron is initially in an s state making $L=l_o$, $l_i=m_i=0$, $l_i'=1$. Otherwise a summation over L on the left and over m_i, m_o (with $m_i+m_o=M$) would be necessary, and then (19) would be of much less value. The value of $\cos(r_1, r_2)$ is proportional to that of $(x_1x_2+y_1y_2+z_1z_2)$, and in a system of individual space quantization the averages for the inner and outer electrons may be computed independently. Hence in connection with the right side of (19) we may utilize the principle of spectroscopic stability in the following form:

$$(x_1x_2+y_1y_2+z_1z_2)^2 = 3\overline{z_1^2}\,\overline{z_2^2} \quad \text{since} \quad \overline{x_1y_1}=0, \quad \text{etc.} \tag{20}$$

The bars denote a spatial average and signify quantum-mechanically a summation over the magnetic quantum number. Eq. (19) thus becomes

$$|\cos(r_1,\, r_2)(l_o0l_o;\, l_o1l_o\pm1)|^2 = 3\frac{|\cos\theta_i(00;\,10)|^2}{2l_o+1}\sum\nolimits_{m_o}|\cos\theta_o(l_om_o;\, l_o\pm1m_o)|^2 = \frac{l_o+\frac{1}{2}\pm\frac{1}{2}}{6l_o+2}, \tag{21}$$

with $\cos\theta=z/r$. The indices on the left side of the first equality sign specify L, l_i, l_o; those on the right give l_i, m_i or l_o, m_o. In the final form of (21) use has been made of the explicit form of the matrix elements of $\cos\theta$ for the one electron problem.[12]

Since the unperturbed energies of the inner and outer electrons are additive

$$h\nu(n_il_in_ol_o;\, n_i'l_i'n_o'l_o') = h\nu_i + h\nu_o = W(n_il_i) - W(n_i'l_i') + W(n_ol_o) - W(n_o'l_o'). \tag{22}$$

If one can assume that the frequencies associated with transitions of the outer electron are small in absolute magnitude compared to those associated with transitions of the inner electron, then

$$|\nu_o(n_ol_o;\, n_o'l_o')| \ll |\nu_i(n_il_i;\, n_i'l_i')|, \qquad \nu(n_il_in_ol_o;\, n_i'l_i'n_o'l_o') \sim \nu_i(n_il_i;\, n_i'l_i'). \tag{23}$$

If we can disregard the part H_{1-} of H_1, and all of H_2, H_3, $\cdots$ and if one can legitimately make the approximations (13) and (23), then (11) becomes in virtue of (14), (17), (21) and (23)

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[10] J. H. Van Vleck, Proc. Nat. Acad. Sci. **15**, 757 (1929).

[11] Cf., for instance, J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities*, p. 139.

[12] Cf. p. 151 of reference 11.

$$W=W_o-\tfrac{1}{2}\alpha e^2\left[\frac{l}{2l+1}+\frac{l+1}{2l+1}\right]\frac{1}{r^4}(n_ol_o;n_ol_o)\quad\text{with}\quad\alpha=-2\sum\nolimits_{n_i'}\frac{|r(n_i0;n_i'1)|^2}{3h\nu(n_i0;n_i'1)}.\tag{24}$$

The expression α defined in (24) is the polarizability of the inner electron.[13] If we disregard penetration (i.e., neglect the integrals in (9) and (10) by setting $W_o=-RZ^2/n^2$), Eq. (24) is the same as (1).[14] The physical significance of the various approximations is as set forth in Section I.

Isolation of the contributions due to $l_o'=l_o+1$ *and* $l_o'=l_o-1$. The first and second terms of the bracketed factor of (24) are the contributions due to interactions with states having $l_o'=l_o-1$ and $l_o'=l_o+1$, respectively. This separation of unity into two parts would be banal if our primary object were only the derivation of (1), as then one could immediately replace $\cos^2(r_1, r_2)$ by its mean value 1/3 without the necessity of using the explicit matrix elements embodied in (24). This value 1/3, however, is consummated only after complete matrix multiplication, wherein one sums over l_o', as well as n_i, n_o, m_i, m_o. When (1) is not valid, it often proves very convenient to have isolated the contributions corresponding to $l_o'=l_o+1$ and $l_o'=l_o-1$, respectively. For instance, Eq. (24) tells us that when (23) is valid, 3/7 of the polarization effect for *sfF* terms is due to interaction with *pd F* terms and 4/7 to that with *pg F*. Similarly, 4/9 of the effect for an *sg G* is due to *pf G* and 5/9 to *ph G*. These particular apportionment ratios will often be used in our later work.

III. PROCEDURES FOR CALCULATING CENTROID FREQUENCIES

We have already mentioned in Section I that the approximation (23) is inadequate for systems with two valence electrons. In such systems, however, it is usually true that virtually all the absorption intensity associated with the inner electron arises from the first line of the principal series. If this is so, it is possible without much error to assume, as we shall henceforth throughout the article that

$$r_i(n0;n'1)=0\qquad\text{unless}\quad n_i'=n_i+1.\tag{25}$$

If we assume (25), but not (23) we have in place of (24)

$$W=W_o-\tfrac{1}{2}\alpha e^2\,\overline{\frac{1}{r^4}}\,\frac{\nu_i}{2l_o+1}\left[\frac{l_o}{\nu_{-4}(n_ol_o\rightarrow l_o-1)}+\frac{l_o+1}{\nu_{-4}(n_ol_o\rightarrow l_o+1)}\right],\tag{26}$$

where $-\nu_i$ is an abbreviation for the frequency of the first line of the principal series of the inner electron, and where the $\nu_{-4}(n_ol_o\rightarrow l_o\pm 1)$ are "centroid frequencies" defined by

$$\frac{1}{\nu_{2s}(n_ol_o\rightarrow l_o')}=[r^{2s}(n_ol_o;n_ol_o)]^{-1}\sum\nolimits_{n_o'}\left\{|r^s(n_ol_o;n_o'l_o')|^2\frac{1}{\nu_i+\nu_o(n_ol_o;n_o'l_o')}\right\}.\tag{27}$$

Whenever we use an arrow in the argument of a frequency, it means that it is some sort of a centroid or average frequency. It turns out that the centroids for $l_o'-l_o=+1$, -1 are quite different. If we could equate the centroids to ν_i, Eq. (26) would, of course, reduce to (24) or (1).

The centroids can be determined accurately by explicit calculation of the matrix elements of r^s and direct evaluation of the sum in (27). The most difficult part of the sum is the integration over the continuous spectrum. The matrix elements appropriate to the continuous part have been given in Eq. (10) of the preceding paper for the case $n_o=l_o+1$, $s=-2$, and when these elements are known the integration of the continuum may be performed graphically. Centroids obtained in this fashion we shall term "exact." The general extension of the exact procedure to $n_o>l_o+1$ appears rather

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[13] See Eq. (28), p. 195 of reference 11.

[14] Since diagonal matrix elements have the physical significance of being time averages, we oftentimes, as in Eq. (1), omit the indices of the diagonal elements and employ instead the bar commonly used for averages.

laborious, and so it is convenient to devise approximate ways of determining the centroids. Two methods suggest themselves.

Method 1. By an expansion in $\nu_o(n_ol_o;\, n_o'l_o') - \nu_{2s}^{(1)}(n_ol_o \rightarrow l_o')$ and use of (17) and (22), we have the following development

$$\sum\nolimits_{n_o'} \frac{|r^s(n_ol_o;\, n_o'l_o')|^2}{\nu_i + \nu_o(n_ol_o;\, n_o'l_o')} = \frac{r^{2s}(n_ol_o;\, n_ol_o)}{\nu_i + \nu_{2s}^{(1)}(n_ol_o \rightarrow l_o')} - \left\{ \frac{\sum_{n_o'} |r^s(n_ol_o;\, n_o'l_o')|^2 [\nu_o(n_ol_o;\, n_o'l_o') - \nu_{2s}^{(1)}(n_ol_o \rightarrow l_o')]}{[\nu_i + \nu_{2s}^{(1)}(n_ol_o \rightarrow l_o')]^2} \right\} + \cdots. \tag{28}$$

Method 1 consists in adjusting $\nu_{2s}^{(1)}(n_ol_o \rightarrow l_o')$ so as to make the second term in this development vanish. Thus $\nu_{2s}^{(1)}(n_ol_o \rightarrow l_o')$, which is not to be confused with $\nu_{2s}(n_ol_o \rightarrow l_o')$, is defined by the relation

$$\nu_{2s}^{(1)}(n_ol_o \rightarrow l_o') = \{\sum\nolimits_{n_o'} \nu_o(n_ol_o;\, n_ol_o') |r^s(n_ol_o;\, n_o'l_o')|^2\} / r^{2s}(n_ol_o;\, n_ol_o). \tag{29}$$

Method 1 consists in using $\nu_i + \nu_{2s}^{(1)}(n_ol_o \rightarrow l_o')$ as an approximate value of $\nu_{2s}(n_ol_o \rightarrow l_o')$. It is clear that these two expressions would be identical if one could neglect the unwritten higher order terms in the development (28). Hence method 1 will be a good approximation if the summand in (27) has a sharp maximum at some particular term, so that the convergence of the development is good.

The value of (29) is calculated by the following method. We utilize the Bohr frequency condition $h\nu_o = W_o' - W_o$. The term proportional to W_o can be evaluated by (17) since W_o is a constant factor which can be taken outside the summation. The terms proportional to W_o' are calculated by using a relation

$$\sum\nolimits_{n_o'n_o''} r^s(n_ol_o;\, n_o''l_o') H_{l_o'}(n_o'';\, n_o') r^s(n_o'l_o';\, n_ol_o) = (r^s H_{l_o'} r^s)(n_ol_o;\, n_ol_o), \tag{30}$$

which is analogous to (17) except that there is a triple rather than double product. Here

$$\mathbf{H}_l = -\frac{h^2}{8\pi^2 m}\left[\frac{\partial^2}{\partial r^2} - \frac{l(l+1)}{r^2}\right] - \frac{Ze^2}{r}, \qquad H_{l_o}(n_o;\, n_o') = \int R_{n_o'l_o} \mathbf{H}_{l_o} R_{n_o'l_o} dr = \delta(n_o;\, n_o') W_{n_ol_o}, \tag{31}$$

with δ the usual Kronecker symbol. The right side of (30) is the same as

$$\left[r^{2s}\mathbf{H}_{l_o'} - \frac{h^2}{8\pi^2 m}\left(s(s-1)r^{2s-2} + 2sr^{2s-1}\frac{\partial}{\partial r}\right)\right](n_ol_o;\, n_ol_o) = \overline{r^{2s}} W_{n_ol_o} + \frac{h^2}{8\pi^2 m}[s^2 + l_o'(l_o'+1) - l_o(l_o+1)]\overline{r^{2s-2}}. \tag{32}$$

Here in the second form the term in $\partial/\partial r$ has been eliminated by a partial integration, and $\mathbf{H}_{l_o'}$ has been expressed in terms of $\mathbf{H}_{l_o}$. Thus finally, we have

$$\nu_{2s}^{(1)}(n_ol_o \rightarrow l_o') = [s^2 + l_o'(l_o'+1) - l_o(l_o+1)][hr^{2s-2}(n_ol_o;\, n_ol_o)/8\pi^2 m r^{2s}(n_ol_o;\, n_ol_o)]. \tag{33}$$

The mean value of r^{-6} needed in connection with (33) when $s = -2$ can be computed by direct quadrature for simple cases. A general formula for this mean value has, however, been obtained by another method, and will be published elsewhere by one of us.

Method 2. The second method utilizes the fact that in the special case $s = -2$ a closed expression can be found for the right side of (27) if we set $\nu_i = 0$. This is, of course, the opposite of the usual approximation $\nu_o = 0$ made to obtain (1). Let $1/\nu_{2s}(n_ol_o \rightarrow l_o')_{i=0}$ be the value of the right side of (27) with $\nu_i = 0$. Then an approximate value of $\nu_{-4}(n_ol_o \rightarrow l_o')$ is $\nu_i + \nu_{-4}(n_ol_o \rightarrow l_o')_{i=0}$.

To evaluate $\nu_{-4}(n_ol_o\rightarrow l_o')_{i=0}$, we utilize the relation

$$\int[R_{n_o'l_o'}(\mathbf{H}_{l_o}-W_{n_ol_o})R_{n_ol_o}-R_{n_ol_o}(\mathbf{H}_{l_o'}-W_{n_o'l_o'})R_{n_o'l_o'}]dr=0, \tag{34}$$

which is an obvious consequence of the radial wave equation. If we use (15), the definition of **H** in (31), and Green's theorem, Eq. (34) becomes

$$(W_{n_o'l_o'}-W_{n_ol_o})1(n_o'l_o';\,n_ol_o)=(h^2/8\pi^2m)(l_o'^2+l_o'-l_o^2-l_o)r^{-2}(n_o'l_o';\,n_ol_o), \tag{35}$$

with $1(n_o'l_o';\,n_ol_o)=\int R_{n_o'l_o'}R_{n_ol_o}dr$. By means of (35) the frequency denominator can be eliminated from (27) when $\nu_i=0$, $s=-2$, and then (27) becomes

$$\frac{1}{\nu_{-4}(n_ol_o\rightarrow l_o')_{i=0}}=\frac{8\pi^2m\sum r^{-2}(n_ol_o;\,n_o'l_o')1(n_o'l_o';\,n_ol_o)}{r^{-4}(n_ol_o;\,n_ol_o)h^2(l_o'^2+l_o'-l_o^2-l_o)}=\frac{8\pi^2m\overline{r^{-2}}}{h^2(l_o'^2+l_o'-l_o^2-l_o)\overline{r^{-4}}}. \tag{36}$$

The results of the various methods are compared in Table I for some typical cases.

TABLE I.

Initial state	$\nu_{-4}(n_ol_o\rightarrow l_o+1)/4R$ Exact	Method 1	Method 2	$\nu_{-4}(n_ol_o\rightarrow l_o-1)/4R$ Method 1	Method 2
3*d*	−0.4175	−2.3475	−0.3450	−0.1245	+0.0260
4*f*	−0.2160	−0.3725	−0.189	−0.0807	−0.0726
5*g*	−0.1660	−0.1975	−0.151	−0.1010	−0.0995

Here R denotes the usual Rydberg constant. The minus signs mean that we are dealing with negative or absorption frequencies, i.e., that the final or summed states usually have higher energy than the given initial state. All the numerical entries in Table I relate only to Al II, as they are inclusive of the contribution ν_i of the inner electron to the total frequency, and use has been made of the explicit value $-\nu_i=0.491R$ appropriate to Al II, i.e., the value of $\nu(3s;\,3p)$ of Al III. In Table II we give the corresponding values of our other centroids which we have defined in such a way that they are exclusive of any contribution of the inner electron and which therefore, apply to any one electron system for which the given state nl can be treated by means of hydrogenic wave functions. The states $n'l'\pm1$ need not be hydrogenic, as they do not appear in the right sides of (33) or (36); this is fortunate, since $l-1$ usually has much more quantum defect than l.

TABLE II.

Initial state	$\nu_{-4}^{(1)}(nl\rightarrow l')/RZ^2$ $l'-l=+1$	$l'-l=-1$	$\nu_{-4}(nl\rightarrow l')_{i=0}/RZ^2$ +1	−1	$\nu_2^{(1)}(nl\rightarrow l')/RZ^2$ +1	−1	"First Line"$/RZ^2$ +1	−1
1*s*	– – –	– – –	– – –	– – –	−1.500	– – –	−0.750	– – –
2*p*	– – –	– – –	−1.00	+0.5000	−0.1666	+0.0333	−0.1389	+0.750
3*d*	−2.225	−0.000	−0.2225	+0.1483	−0.0555	+0.0238	−0.0486	+0.1389
4*f*	−0.250	+0.0418	−0.0665	+0.0499	−0.0250	+0.0143	−0.0225	+0.0486
5*g*	−0.075	+0.0214	−0.0285	+0.0228	−0.0133	+0.0085	−0.0122	+0.0225

Our immediate interest is only in ν_{-4}; the values of ν_2 are for later use. Values marked – – – – – indicate that the corresponding centroids do not exist, due to divergence of the integrals for mean values of negative powers of r for sufficiently small l. The values in the columns labelled "first line" are the frequencies of the lowest members of the series emanating from the given initial state, i.e., $\nu(1s;\,2p)$, $\nu(2p;\,3d)$, etc. for the columns under $l'-l=+1$, and $\nu(2p;\,1s)$, etc., for the columns under $l'-l=-1$. It is seen that with $l>2$ centroids $\nu_{-4}(n_ol_o\rightarrow l_o-1)_{i=0}$ and $\nu_{-4}^{(1)}(n_ol_o\rightarrow l_o-1)$ are nearly equal to each other and to the "first line." This means that practically all the contribution to the summation involved in the definition of the centroid comes from the first line. For this reason it has not seemed worth while to use the exact method of calculating the centroids ν_{-4} in the case $l'-l=-1$. The situation is quite different for $l'-l=+1$ as both $\nu_{-4}(nl\rightarrow l+1)_{i=0}$ and $\nu_{-4}^{(1)}(nl\rightarrow l+1)$ are usually in the continuous region, and the discrepancy between the methods is considerable, showing that there is a large "dispersion" or "spread" among the important frequencies. The absence of a sharp maximum for the case $3d\rightarrow f$, is also clear from the graph of the squares of the elements of $1/r^2$ in the continuous region given in Fig. 2 of the preceding paper. Method 1 always furnishes an upper limit in absolute magnitude when all of the frequency denominators in the sum have the same sign, as is always true in our applications. This upper limit is too high to be of any great value when the spread in important frequencies is large, as in the case $l'-l=1$, $s=-2$. Method 2 furnishes a lower limit in absolute magnitude if none of the important terms involve positive values of ν_o; this condition is met if $l'-l=+1$. The reason that method 2 is then low is that terms for which ν_o is small are weighted very heavily in (27) when $\nu_i=0$.[15]

It is believed that our methods of computing centroid frequencies may be useful for other problems besides the particular one which we are considering. Method 2, unlike 1, is peculiar to $s=-2$.

Very often one is interested in calculating centroids defined by (29) rather than (27), as in many problems the frequency originally appears in the numerator rather than the denominator. In this case no series expansion is necessary, and the centroid may be evaluated accurately, since (33) is an exact expression for (29). The case $s=1$, is particularly common, as the centroid $\nu_2(n_ol_o\rightarrow l_o+1)$ is the mean absorption frequency for the transitions $nl\rightarrow n'l\pm1$. The procedure involved in (29–33) can easily be used to obtain formulas given by Wigner and by Kramers, Jonker and Koopmans[16] for the number of dispersion electrons f_-, $f_+=1-f_-$, associated respectively with the totality of transitions $l'-l=-1$ and $l'-l=+1$ emanating from a given state. The f's are connected with the centroids defined in (29) by the relation

$$-(h^2/8\pi^2m)f_\pm=\sum_{n'}\nu(nl;n'l\pm1)\,|z(nl;n'l\pm1)|^2=[(l+\tfrac{1}{2}\pm\tfrac{1}{2})/3(2l+1)]\nu_2^{(1)}(nl\rightarrow l\pm1)r^2(nl;nl). \quad (37)$$

The bracketed factor in the final form of (37) arises from the integration over the angular coordinates and expresses the apportionment of $\cos^2\theta$ between $l'=l-1$ and $l'=l+1$ as discussed at the end of Section II. Instead of giving the f's it is illuminating to compute some of the corresponding centroids $\nu_2^{(1)}$. This has been done in the preceding table. It is seen that when $l'-l=+1$, the centroid $\nu_2^{(1)}$ nearly coincides with the first line of the series, while the higher members are important when $l'-l=-1$. There is thus an interesting contrast between the behavior of positive and negative powers of r, since the table shows that the exact opposite is true for the negative case $s=-2$, where the first line is predominant for $l'-l=-1$ rather than $l'-l=+1$.

IV. The ^3G Terms of Al II; Number of Dispersion Electrons for $3s-3p$ of Al III and Si IV

The G terms of Al II furnish a case where all the approximations underlying (26), though not the more customary formula (1) or (24), are very nearly fulfilled. Penetration effects, including exchange, and the quadrupole correction to be discussed in Section VI, account for only five percent of the quantum defect. Allowance for this displacement due to penetration and quadrupole

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[15] This difficulty can sometimes easily be avoided by evaluating explicitly the terms in the summation (27) for which ν_0 is particularly small, and which usually correspond to low ordinal numbers for the primed state. The effect of the remaining terms in the sum may then be calculated approximately by adaptation of method 2. If three terms are thus segregated for exact treatment, the values 0.345, 0.189, 0.151 in the table are raised to 0.400, 0.215, 0.164 respectively, or almost the exact values. Unfortunately this method of improving method 2 is easily feasible only for the case $n=l+1$, and so we do not mention it further. In the general case $n>l+1$, the contribution of the first few terms is relatively much less important than when $n=l+1$, and an appreciable improvement is secured only if an unduly large number of terms is segregated.

[16] E. Wigner, Phys. Zeits. **32**, 450 (1932); H. A. Kramers, C. C. Jonker and T. Koopmans, Zeits. f. Physik **80**, 178 (1933).

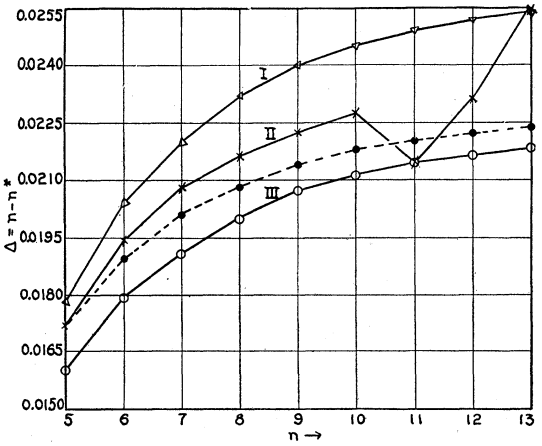

FIG. 1. $3sng\ ^3G$ series of Al II. Curve I gives the theoretical upper limit, Curve II the observed values, and III the theoretical lower limit for the quantum defect as a function of the principal quantum number n. The dashed curve is obtained if one uses (1) rather than (26) in the theoretical calculations and adjusts α to give perfect agreement with experiment at $n=5$. Eq. (26) is much more rigorous than (1) but unfortunately only the limits can be readily calculated for the centroids involved in (26) except when $n=5$.

terms has, nevertheless, been made in all calculations reported in the present section, including Fig. 1, and makes the values of α five percent lower than they would have been otherwise.

The magnitude of α for Al III may be calculated from (26) and the empirical value of $W-W_o$ for the term $3s5g\ ^3G$ of Al II. We thus obtain $\alpha=2.03\times10^{-24}$ in c.g.s. units. Unfortunately $3s5g\ ^3G$ falls in an inconvenient spectral region and so has not been observed directly and in this calculation we have taken the empirical value of this term to be 17,678 cm^{-1}, an estimate which is obtained by Sawyer and Paschen[17] by a Ritz extrapolation from the known positions of $6g\cdots13g$ and which is doubtless sufficiently precise for our purposes. The exact value of the centroid $\nu_{-4}(5g\rightarrow h)$ has been used, while $\nu_{-4}(5g\rightarrow f)$ has been obtained by method 1, which, as stated in the preceding section, is a sufficiently good approximation when $l_o'-l_o=-1$. For convenience, we use spectroscopic notation for the arguments of the centroids where possible, writing $\nu(nl\rightarrow l')$, for instance, as $\nu(5g\rightarrow h)$ when $n=l'=5$, $l=4$.

Analogous calculations can also be made from the $5g$ term of Si III. Here we find $\nu_{-4}(5g\rightarrow f)=0.461R$ and $\nu_{-4}(5g\rightarrow h)=1.005R$. We use 39,831 cm^{-1} for the spectroscopic value of the $5g$ term of Si III rather than 39,741 as usually given, since at the end of the present section we shall present what we consider convincing evidence that the series limit has been incorrectly estimated by A. Fowler[18] and that in consequence the term values given in Bacher and Goudsmit for Si III should all be raised 90±20 cm^{-1}. Eq. (26) then gives $\alpha=1.07\times10^{-24}$. Had (24) been used in place of (26), the values of α would have been 1.88×10^{-24} and 1.06×10^{-24} for Al III and Si IV, respectively. It is purely accidental that the values of α are so nearly the same with (24) and (26), as the two centroids in (26) are smaller and larger than ν_i, but happen to counterbalance to make the bracketed factor in (26) nearly $(2l+1)/\nu_i$.

Since we have assumed (cf. Eq. (25)) that all the polarization of Al III or of Si IV arises from the resonance line $3s-3p$, the value of α is connected with the number of dispersion electrons f_{3s3p} for this line by the relation

$$f_{3s3p}=4\pi^2m\alpha\nu_i^2/e^2. \qquad (38)$$

This furnishes a new method of estimating the number of dispersion electrons. The results are given in Table III under the columns labelled Eq. (38). The value in parenthesis is that which would have been obtained had the series limit for Si III not been revised. For purposes of comparison we have also included values calculated by quadrature from the wave functions by the relation

TABLE III. *Number of dispersion electrons for $3s-3p$.*

	Eq. (38)	Confl. hyper. wave functions	McDougall's functions
Al III	0.83	0.94	
Si IV	0.80±0.05 (0.55)	0.75	0.89

$$f_{3s3p}=(8\pi^2m\nu_i/h)\left[\int rR_{3s}R_{3p}dr\right]^2. \qquad (39)$$

To obtain proper wave functions one may use the well-known confluent hypergeometric development,[19] as the field over the outer portion of

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[17] R. A. Sawyer and F. Paschen, Ann. d. Physik **84**, 1 (1927).

[18] A. Fowler, Phil. Trans. Roy. Soc. **A225**, 1 (1925).

[19] Whittaker and Watson, *Modern Analysis*, Chap. XVI.

the orbit is approximately Coulomb, while the inner portion contributes but little to (39). This development yields the following wave functions for Al III

$$R_{3s}=1.69e^{-1.44x}x^{2.08}(1-.780x^{-1}+\cdots)a_0^{-\frac{1}{2}} \qquad (40)$$

$$R_{3p}=1.305(x^3e^{-1.38x}-14.5x^2e^{-5x})a_0^{-\frac{1}{2}}, \qquad (41)$$

with $x=r/a_o$, $a_o=h^2/4\pi^2e^2m$. In the case of the $3p$ state the hypergeometric series converges only slowly and so we have approximated the series by the sum of two exponentials, somewhat in the Slater fashion.[20] The Hartree wave method could, of course, also have been used. For Al III, no Hartree calculations have been published, but for Si IV functions are found by the Hartree procedure in an article by McDougall.[21] Numerical values of the functions are not tabulated in this paper, but they may be estimated from the graphs.

Since the total number of dispersion electrons must sum to unity,[22] the value of f_{3s3p} must be nearly unity if the resonance line is by far the most important absorption line of the atom-core, as assumed in (25) and (38). Some of the polarization arises from the higher members so that, strictly speaking, Eq. (38) furnishes only an upper limit to f_{3s3p}. Actually, the values of f_{3s3p} are so nearly unity that the error due to the effect of the higher series members is not important. This is true because α and f involve the frequency in the denominator and numerator respectively, so that the higher series members are weighted much less in α than in f (cf. (24) and (39), or the factor ν_i^2 in (38)). To illustrate this point, let us as an extreme case assume that all of the f-sum not due to f_{3s3p} is due to f_{3s4p}, making $f_{3s4p}=0.20$ in Si IV. Since ν_{3s4p} is about three times $\nu_i=\nu_{3s3p}$, then $3s-4p$ contributes only about 2 percent of α even though it contributes 20 percent of the f-sum. In reality, much of the residual 20 percent probably arises from $3s-5p$, $3s-6p$, rather than solely from $3s-4p$, as f decreases slowly after the first line; if so the contribution of the higher members to α may be even less than the preceding estimate.

Besides our polarization method and the method of wave functions, still another way of calculating the number of dispersion electrons is from absorption intensities. Unfortunately no proper intensity measurements are available for Al III or Si IV. It is hard to estimate the comparative accuracy of the different methods, but we feel that the polarization method is fully as accurate as the others when the series limit has been carefully determined, as in Al II. In view of the effect of higher members discussed in the preceding paragraph, the polarization values of f_{3s3p} should perhaps be reduced to 0.81 and 0.78 for Al III and Si IV, respectively; but the other methods, in our opinion, usually involve more error than 2 percent.[23] In connection with the wave method, it must be remembered that the right side of (39) is very sensitive to the location of the nodes of the wave functions, and the confluent development is a good approximation only for extremely large r, while on the other hand the

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[20] J. C. Slater, Phys. Rev. **42**, 33 (1932).

[21] McDougall, Proc. Roy. Soc. **A138**, 550 (1933).

[22] Strictly speaking, one can apply the f-sum rule to an individual electron, as we are doing, only if we include the transitions from $3s$ to all the p states, including the state $2p$ which already has its full quota of electrons. The transition $3s-2p$ under such circumstances has no physical significance but is needed for mathematical completeness (cf. Kramers and Kronig, Zeits. f. Physik **48**, 174 (1928)). This transition has such a sign for its frequency factor that it makes a negative contribution to f. Thus when we regard this transition as a physical impossibility the f-sum should be greater than unity. However, the $2p$ state is so firmly bound that this transition has an exceedingly small amplitude and so makes only a quite small contribution to the f-sum when it is included. (Cf. Y. Sugiura, Phil. Mag. **4**, 495 (1927).) Consequently no serious error is committed in saying that the f-sum is unity without including the transition to $2p$.

[23] The value of α by the polarization method will tend to be high if there are any other causes of quantum defect which we have overlooked. Possibly, for instance, there may be some polarization of the K and L shells, which we have neglected. One might, for instance, try to correct for the K and L polarization by assuming that its effect is given by (1) if we use the values of α for Al IV and Si V respectively determined from the quantum defects of the g terms of Al III and Si IV. The result for Si is meaningless, as the $5g$ term of Si IV has $\Delta<0$, perhaps due to improper evaluation of the series limit. With this procedure one would, however, conclude that our estimate f_{3s3p} for Al III should again be reduced by 0.02. This reduction may easily be excessive as the polarization of the K and L shells by the $5g$ electron will be considerably weakened by the presence of the $3s$ electron. This electron is repelled by the $5g$ one, and tends to drag the K and L shells along with it because of its proximity, so that these shells are sucked towards the $5g$ electron much less than otherwise.

McDougall functions do not give exactly the right characteristic values for the energy and so are inaccurate for very large r.

Higher members of the G series of Al II. After α has been determined from the observed $3s5g$ term by use of exact centroids, one may reverse the procedure and employ (26) to compute the departures of the higher series members $3s6g$, $3s7g$, $\cdots$ from hydrogenic character. Upper and lower limits for $|W-W_o|$ are obtained according as one uses method 2 or method 1 to evaluate the centroid $\nu_{-4}(ng\rightarrow h)$; it matters little which method is used for $\nu_{-4}(ng\rightarrow f)$.

The experimental values are between the upper and lower limits, as one would expect. This is shown graphically in Fig. 1. Instead of plotting $W-W_o$ against the ordinal number, we plot the quantum defect Δ defined by $W=-RZ^2/(n-\Delta)^2$, as this scheme of graphing is more sensitive in illustrating departures from the too simple Rydberg formula $\Delta=$constant. The irregularity in the observed values for $n=11$, 12 is probably experimental error and not a perturbation, as experimental precision is difficult for large n. For comparison we also show as the dashed curve in Fig. 1 the theoretical result which would have obtained had Eq. (1) or (24) between used rather than (26), with α adjusted so as to give perfect agreement for $3s5g$. The dashed curve does not give a rapid enough increase of Δ with n to agree with experiment. On the other hand both the upper and lower limits based on (26) give a more rapid increase than the dashed curve. The physical significance of this is that both experimentally and theoretically the variation of the centroids with n is much as to make the bracketed factor of (26) increase in magnitude with n.

Series limit of Si III. The conventional series limit for Al II is doubtless correct to 1 cm^{-1} or better, as it is based on a long series. In Si III, however, only the first two members $3s5g$, $3s6g$ are known for the G series. The series limit was determined by A. Fowler by assuming that these two terms conform to the Rydberg formula $\Delta=$constant. Fig. 1 shows that this supposition is clearly incorrect, since in the analogous case of Al II there is both theoretically and experimentally a marked increase of Δ with n. We have therefore redetermined the series limit so as to make the ratio Δ_{5g}/Δ_{6g} have the theoretical value which is obtained by employing method 1 to evaluate the centroid $\nu(ng\rightarrow f)$, and method 2 for $\nu(ng\rightarrow h)$. This procedure corresponds to the upper limit in Fig. 1, but it is probable that the percentage error due to use of these approximate methods is nearly the same for $n=5$ and $n=6$ and so largely cancels in the ratio. We thus find that Fowler's series limit should be raised 90 cm^{-1}; this estimate is perhaps accurate to 20 cm^{-1}. Had (1) been used rather than (26), the increase would have been 50 instead of 90. An independent check on our revised series limit is furnished by the fact that we have seen that it makes (38) yield a reasonable value for f_{3s3p}, whereas without the revision the value was unreasonably low.

V. THE ^3F TERMS OF AL II

These are the terms whose multiplet structure has been studied in the preceding paper.[24] They are amenable to fewer of the approximations basic to the usual polarization formula (1) than are the ^3G terms, and so, quite irrespective of the multiplet anomaly, are interesting because they illustrate how Eq. (1) must be modified in complicated cases. In Al II, the matrix elements $H(3snf;3p3d)$ are so big as to be comparable with $h\nu$ $(3snf;3p3d)$ contrary to the usual assumption (12) of perturbation theory. The situation is particularly marked in the vicinity of $n=6$. Hence the ordinary perturbation formula (11) cannot be used insofar as $H(3snf;\ 3p3d)$ is concerned. Instead the influence of $3p3d\ ^3F$ upon $3snf\ ^3F$ must be handled by means of a secular determinant which does not require the amount of perturbation to be small, and which has been exhibited in the preceding paper. On the other hand, in that paper, the interaction of $3snf\,^3F$ with $3pn'd\,^3F$ $(n'>3)$ and with $3pn'g\,^3F$ was not regarded as a perturbation, and the displacement of $3snf\,^3F$ due to such interaction was considered to be included in the unperturbed portion of the energy, represented by the diagonal elements $H(nn)+\sigma_{nn}{}^{(J)}$ in the notation there used. Our problem is now to calculate the magnitude of this displacement and hence the proper "unperturbed levels" for use in the secular problem of the preceding paper. This calculation can be effected by the usual perturbation formula (11), since

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[24] N. G. Whitelaw, Phys. Rev. **44**, 544 (1933).

$3pn'd\,{}^3F$ $(n'>3)$, and $3pn'g\,{}^3F$ are remote enough from $3snf\,{}^3F$ (at least for $n<10$) to warrant the assumption (12).

To calculate the displacement in energy exclusive of the influence of $3p3d$ we must modify (26) by replacing

$$l_o/\nu_{-4}(n_ol_o\rightarrow l_o-1)$$

by

$$l_o(1-y_n)/\nu_{-4}(n_ol_o\rightarrow l_o-1)_{>3}.$$

Here

$$y_n=|r^{-2}(nf;\,3d)|^2/r^{-4}(4f;\,4f), \qquad (42)$$

and $\nu_{-4}(n_ol_o\rightarrow l_o-1)_{>3}$ is the centroid which is obtained by deletion of the term $(nf;\,3d)$ in (27).[25] Eq. (26) then yields a displacement 308 cm^{-1} for $3s4f\,{}^3F$. In this calculation the "exact value 0.863 R has been used for the centroid $\nu_{-4}(4f\rightarrow g)$, while $\nu_{-4}(4f\rightarrow d)_{>3}$ has been given the approximate value $1.82R$, determined by method 1, with proper deletions. To the above displacement due to polarization we must add that due to penetration, which is much larger than it was for the G terms. By means of (8), (9), (10) and (40), one finds that the displacement due to penetration is 129 cm^{-1}. There is also a rather large quadrupole correction, which will be given in the next section, and which amounts to about 65 cm^{-1}. Thus, exclusive of the perturbation by $3p3d$, the total displacement should be about 502 cm^{-1}. The agreement is gratifying with the value 469 cm^{-1} found in the preceding paper, which is presumably fairly accurate since the multiplet anomaly was found to be very sensitive to the value assumed for the location of $3s4f\,{}^3F$ before perturbation by $3p3d$. Had (1) been used rather than (26), the calculated value would be 725 rather than 502 cm^{-1} and all agreement would be destroyed; in other words, the F and G series will not yield consistent results in their polarization behavior unless allowance is made for the fact that the centroids are not identical with ν_i.

Higher series members. Analogous methods may also be used to calculate the displacements of the higher series members $3s5f$, $3s6f$,—exclusive of the perturbation by $3p3d$. As in the preceding section, the centroids are not evaluated accurately for $n>l+1$. The centroid $\nu_{-4}(n_ol_o\rightarrow l_o-1)$ can be calculated, to be sure, with sufficient accuracy by method 1, but methods 1 and 2 provide upper and lower limits to $\nu_{-4}(n_ol_o\rightarrow l_o+1)$. Some of the numerical values of the centroids, and of y_n defined by (42) are shown in Table IV. For purposes of comparison, we tabulate $\nu(nf\rightarrow d)$ both with and without the needed deletion.

TABLE IV.

	$4f$	$5f$	$6f$	$7f$	$8f$	$9f$
y_n	0.982	0.824	0.744	0.702	0.678	0.660
$\nu_{-4}{}^{(1)}(nf\rightarrow d)+\nu_i$	$0.323R$	$0.277R$	$0.254R$	$0.241R$	$0.233R$	$0.227R$
$\nu_{-4}{}^{(1)}(nf\rightarrow d)_{>3}+\nu_i$	1.84	0.612	0.537	0.508	0.495	0.484
$\nu_{-4}{}^{(1)}(4f\rightarrow g)+\nu_i$	1.49	1.768	1.905	1.985	2.034	2.065
$\nu_{-4}(4f\rightarrow g)_{i=0}+\nu_i$	0.756	0.788	0.806	0.816	0.823	0.828

To the quantum defect calculated from the modified form of (26), we must add the corrections for penetration and for "quadrupolarizability." The penetration effect was assumed to conform to the Ritz formula so that the value 129 cm^{-1} calculated for $3s4f\,{}^3F$ can immediately be extrapolated to higher series members. As in the dipole case, only upper and lower limits can be calculated for the quadrupole corrections by analogous methods to be explained in the next section. The results are shown graphically in Fig. 2.

Our calculations are of a lower order of accuracy for the ${}^3F$ than for the ${}^3G$ terms, and this is reflected by the wide divergence between the

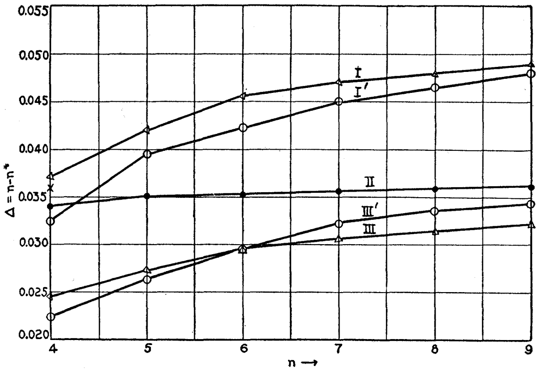

FIG. 2. $3snf\,{}^3F$ series of Al II. As in Fig. 1, curves I, II, and III represent respectively the theoretical upper limit, observed values, and theoretical lower limit for the quantum defect. Curves I′, III′ are similar to I, III except that I′, III′ are exclusive of the quadrupole correction. In all cases only the portion of the quantum defect not due to perturbation by $3p3d$ is considered. The "observed" values are furnished by the Ritz formula obtained in the preceding paper from the multiplet anomaly.

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[25] In calculating $\nu_{-4}(n_ol_o\rightarrow l_o-1)_{>3}$ by means of (27) it is to be understood that $(1-y_n)r^{-4}$ is to be substituted for r^{-4} in (27), as y_n is the fractional amount of (17) consumed by the transition $(nf;\,3d)$ when $s=-2$.

various curves in Fig. 2. The decreased accuracy is due to a variety of causes. First the divergence between the different methods of locating centroids is wider; second, the quadrupole correction which is more difficult to determine accurately than dipole contributions, is much larger than in the case of the G terms. Then finally, the sexta and higher order poles are probably not entirely negligible although they undoubtedly are insignificant in the G case. One can easily see that the octapole correction, which we have not included reduces materially, because of exchange effects, the perturbation by $3pn'g\ {}^3F$, just as we shall show in the next section that quadrupole effects reduce the intensity of the perturbation by $3pn'd\ {}^3F$, and that furthermore this correction is more important for large values of n. This perhaps explains why the upper limits in Fig. 2 are too steep and not as close to the observed points as the lower limits, for the octapole correction would thus lower and flatten the curves. In any case we may safely conclude that the empirical and presumably fairly accurate Ritz formula for the positions of $3snf\ {}^3F$ before perturbation by $3p3d$, which was obtained in the previous paper by means of the multiplet anomaly, agrees with the present theoretical calculations within the latter's limits of error.

VI. The Effect of Electron Exchange and of Quadrupole Terms

In order to derive our basic formula (26), we had to assume that in (11) we could replace $H=H_+\pm H_-$ by H_+ and could take $H_2=H_3=\cdots=0$, i.e., that we could neglect electron exchange and could disregard "quadrupole" and higher order terms. We did, to be sure, include an electron exchange term (10) in (8), but (8) is only a "zeroth approximation" which neglects polarization. In the present section we shall consider the modifications resulting from removal of these restrictions.

From the nature of the expansion (6) and the properties of spherical harmonics one can easily show that

$$H_{1+}(n_il_in_ol_o;\ n_i'l_i'n_o'l_o')=0 \quad \text{unless } |l_i-l_i'|=|l_o-l_o'|=1; \tag{43}$$

$$H_{1-}(n_il_in_ol_o;\ n_i'l_i'n_o'l_o')=0 \quad \text{unless } |l_i-l_o'|=|l_o-l_i'|=1; \tag{44}$$

$$H_{2+}(n_il_in_ol_o;\ n_i'l_i'n_o'l_o')=0 \quad \text{unless } |l_i-l_i'|=0,\ 2, \quad |l_o-l_o'|=0,\ 2; \tag{45}$$

$$H_{2-}(n_il_in_ol_o;\ n_i'l_i'n_o'l_o')=0 \quad \text{unless } |l_i-l_o'|=0,\ 2, \quad |l_o-l_i'|=0,\ 2. \tag{46}$$

Eq. (44) shows that electron exchange does not enter in the dipole perturbation of states having $l_i=0$, $l_o>2$, such as, for example the states $3snf\ {}^3F$ and $3sng\ {}^3G$ whose polarization we have examined in detail. Also neither type of quadrupole term (45–46) gives any interaction between $3sng\,G$ states and the states $3pn'f\,G$ and $3pn'h\,G$ which are involved in the dipole perturbation of $3sng\,G$, or between $3snf\,F$ and $3pn'g\,F$. (We omit superscript from F or G when we mean both singlet and triplet.) On the other hand, nonvanishing quadrupole exchange terms do exist between $msnf\,F$ and $3pn'd\,F$, so that in reality we must use the full expression

$$H(3snf;\ 3pn'd)=H_{1+}(3snf;\ 3pn'd)\pm H_{2-}(3snf;\ 3pn'd) \tag{47}$$

rather than just the first term. The upper and lower sign is to be used in (47) according as we are dealing with ${}^1F$ or ${}^3F$.

Dipole-quadrupole cross terms. Since (11) involves the squares of matrix elements, and since $H=H_1+H_2+\cdots$, it is clear that when there are simultaneously nonvanishing dipole and quadrupole elements connecting the same pair of states, the quadrupole effect will first influence the energy through terms of the order H_1H_2, which we shall call "dipole-quadrupole" cross terms. Otherwise this effect will first manifest itself in terms of the order H_2^2, which we shall call "pure quadrupole terms," and which are usually smaller than the cross terms, since ordinarily $|H_2|<<|H_1|$. The cross terms are an exchange phenomenon, since (43–46) show that H_{1+}, H_{2+} can never connect the same pair of states, nor can H_{1-}, H_{2-}. From the preceding paragraph it is seen that the only case where the dipole-quadrupole cross effect enters in our calculations on F and G states is in the perturbation of

3snf F by *3pn′d F*. By far the most important perturbation of this type is that due by the first member *3p3d*. One can easily convince oneself that $H_{1+}(3snf; 3p3d)$ has the same sign as $H_{2-}(3snf; 3p3d)$. Hence the matrix elements connecting *3snf* and *3p3d* should be smaller for ^3F than for ^1F terms, as in the latter case the upper rather than lower sign is to be used in (47). In the next section we shall show that actually these elements are considerably smaller for the triplets than for the singlets. The cross effect also has an appreciable effect in reducing the interaction (*3snf*; *3pn′d*) for $n' > 3$. In constructing the upper limit I in Fig. 2 we have utilized only the pure quadrupole correction exclusive of the cross term, and so have not allowed for this reducing action. In drawing the lower limit III we have assumed that the cross effect reduces $H(3snf\ ^3F; 3pn'd\ ^3F)$ $(n' > 3)$ in the same ratio as that between the empirical matrix element $H(3snf\ ^3F; 3p3d\ ^3F)$ determined from the preceding paper and the theoretical value of $H_{1+}(3snf\ ^3F; 3p3d\ ^3F)$. The relative importance of the higher members $n' > 3$ in the type of perturbation (*3snf*; *3pn′d*) increases with *n*, as the table in Section V shows that y_n defined by (42) decreases with *n*. Hence it is not surprising that the curve I in Fig. 2 which neglects the cross effect and so overestimates $H(3snf\ ^3F; 3pn'd\ ^3F)(n' > 3)$ slopes upwards too much and so gives increasing divergence from the observed Δ for large *n*.

Pure quadrupole terms. The pure quadrupole effect has been computed by J. and M. Mayer[3] under the assumption that the influence of the outer electron on the frequency denominators is negligible. They thus obtained an expression for the quadrupole energy which is the analogue of Eq. (1) for the dipole energy. They neglected electron exchange and hence had no cross terms, so that their expressions for the dipole and quadrupole displacements were additive. Actually, it seems to us that it is necessary to investigate electron exchange if one desires a quantitatively accurate quadrupole correction. In the alkali case considered in the Mayer paper the quadrupole effects were so small that probably no serious error was incurred by the omission of exchange, but with two electron systems, these effects are by no means negligible (cf. Fig. 2) and so it seems desirable to compute the quadrupole correction as accurately as possible without undue labor. We shall now give a formula for the pure quadrupole correction ΔW_q which includes modulation of the frequency denominators by the outer electron, and which represents the same sort of improvement over the Mayer formula that (26) did over (1):

$$\Delta W_q = \frac{3e^4}{10}\,\overline{r_i^4}\,\overline{\frac{1}{r_o^6}}\,\frac{1}{(4l_o^2-1)(2l_o+3)}\left[\frac{(2l_o-1)(l_o+1)(l_o+2)}{h\nu_{-6}(nl_o\to l_o+2)}+\frac{2(l_o^2+l_o)(2l_o+1)}{3h\nu_{-6}(nl_o\to l_o)}+\frac{(2l_o+3)(l_o^2-l_o)}{h\nu_{-6}(nl_o\to l_o-2)}\right]. \quad (48)$$

Here the centroids are defined as in (27), except that ν_i now has the significance $\nu(3s; 3d)$ rather than $\nu(3s; 3p)$ of Al III, etc. Auxiliary calculations show that practically all the quadrupole absorption intensity of the form $\Delta l_i = 2$ for the atom-core is located in the first member. These calculations consisted in showing that $\nu_2^{(1)}(3s\to d)$, as defined by (29), differs but little from $\nu(3s; 3d)$, or, alternatively, that $|r_i^2(3s; 3d)|^2$ is almost as great as $r_i^4(3s; 3s)$. We have assumed, as elsewhere, that the inner electron is initially in an *s* state; because of this, it can be shown that the quadrupole matrix elements involving $l_i' - l_i = 0$ vanish, even though this is not required by (45, 46). Thus (48) is constructed entirely from interaction of the form $l_i' - l_i = 2$, but the three parts of (48) represent the three possibilities $l_o' - l_o = 2$, 0, -2 for the outer electron. We omit the details of the derivation of (48). The method is similar to that used in the proof of (28), but the spatial averaging is considerably more complicated than in the dipole case (21).

In the part $l\to l-2$ of (48), one readily calculates that the centroid is nearly the same as the "first line." Hence in the application of (48) to *3snf F* and *3sng G* states, most of the quadrupole interaction involved in $l\to l-2$ comes from the perturbation by *3d2p F* and $3d^2\,G$ respectively. Now it is impossible for an electron to make a transition to a *2p* state, since the *L* shell in Al has the full Pauli quota of electrons. Hence no perturbation of the type (*3snf*; *3d2p*) is possible when the wave functions are made antisymmetric in all the electrons of the atom, as such a perturbation would necessitate a configuration $2p^7$. Furthermore the configuration $3d^2$ admits only a

^1G and not a ^3G state according to the Pauli principle and so cannot possibly perturb any ^3G state. Analytically this is expressed in the fact that $(H_{2+} \pm H_{2-})(3sng; 3d^2)$ vanishes with the lower choice of sign. Hence in applying (48) to ^1F, ^3F or ^3G states we must *omit* entirely the term of structure $l \rightarrow l-2$. If we applied (48) to a ^1G state we should, on the other hand, double this term. Such an effect tends to make the ^1G terms deeper than the ^3G. Actually the singlet-triplet separation of the G terms of Al II is so minute (<0.2 cm^{-1} for $n>5$)[26] that the lines $^1F-{}^1G$ have usually been mistaken for intersystem combinations $^1F-{}^3G$. The small separation is undoubtedly due to a cancellation of this quadrupole effect by the usual exchange separation which is given by twice the expression (10) and which tends to depress the triplets below the singlets. It would be very difficult to make the theoretical calculations with sufficient accuracy to show that the cancellation is as exact as observed experimentally. Rough calculations yield a value $175/n^3$ cm^{-1} for (10) and $-375/n^3$ for the last term of (48). The latter estimate of the quadrupole effect is, however, surely too large in magnitude, as (48) is based on the approximation (13) which is not here allowable and which exaggerates this effect. Namely, it is not at all accurate to consider one electron as always inferior to the other, since in the final configuration $3d^2$ both electrons are on a par, though in the initial state $3sng$ the separation into an inner and outer electron is quite complete. The resulting error may easily be enough to account for a discrepancy by a factor 2; it cannot be determined accurately until more is known about $3d^2$ wave functions. The same objection, incidentally, does not apply to our use of the other terms $l \rightarrow l$, $l+2$ of (48), as here the inner-outer distinction is pronounced in both the initial and final states.

Method 1, applied now to ν_{-6} rather than ν_{-4}, has been used to evaluate the centroid $\nu_{-6}(nl_o \rightarrow l_o+2)$ in (48) for the quadrupole correction in the "lower limit" curve III of Fig. 2. The value of this centroid furnished by method 1 is doubtless unduly large. An adaptation of method 2 furnishes a better procedure, which we have used in the "upper limit" I in Fig. 2, as well as in our calculations of the quadrupole corrections for G terms and in our attempted exact calculation for $3s4f\ ^3F$, indicated by the cross in Fig. 2. The adaptation consists in writing the product involved in the matrix multiplication as $r^{-4} \times r^{-2}$ rather than the actual $r^{-3} \times r^{-3}$. Then (35) may be used; otherwise the requisite sum cannot be directly evaluated in closed form. The substitution of $r^{-4} \times r^{-2}$ for $r^{-3} \times r^{-3}$ probably does not introduce serious error, as the "tapering off" of $r^{-3}(nl; n'l+2)$ with increasing n' is intermediate between that involved in $r^{-2}(nl; n'l+2)$ and $r^{-4}(nl; n'l+2)$. To illustrate this point one may make calculations by method 1 both with and without the substitution; namely with $r^{-4} \times r^{-2}$ rather than $r^{-3} \times r^{-3}$ there is only the difference in (33) that s^2 is replaced by s^2-1 in the first factor. Method 2 cannot be adapted to the case $l_o \rightarrow l_o$, as (35) becomes a trivial identity $0=0$ when $l_o = l_o'$. In this case, method 1 gives an excessively large centroid and so in all our calculations, including both upper and lower limits, we have used as the value of $\nu_{-6}(nl \rightarrow l)$ the expression $\nu_i(3s; 3d) + k\nu_{-6}^{(1)}(nl \rightarrow l)$ where k is so determined as to make $\nu_i(3s; 3p) + k\nu_{-4}^{(1)}(nl \rightarrow l+1)$ equal the "exact value of $\nu_{-4}(nl \rightarrow nl+1)$." As the quadrupole corrections are not the major cause of quantum defect, it has not seemed worth while to make exact calculations of ν_{-6} by the rather laborious explicit calculation of the matrix elements involved as individual terms in the sum (27).

One point is of particular interest. The usual development in higher and higher poles, i.e., consideration first of dipoles, then quadrupoles, etc., would converge very poorly indeed were it not for increases in some of the centroids and for the blocking off of certain interactions by the exclusion principle. Also one must abandon the approximation (13), which greatly exaggerates the effect of the higher poles. For instance, if one used the Mayer formulas which do not include any of these alleviating modifications, the quadrupole perturbation of $3snf\ ^3F$ would be 43 percent of the dipole perturbation exclusive of the influence of $3p3d\ ^3F$. The poor convergence is due to the fact that $\overline{r_i^4} > \overline{(r_i^2)}^2$, $\overline{r_o^{-6}} > (\overline{r_o^{-4}})^{\frac{3}{2}}$, so that $\overline{r_i^4/r_o^6}$ is not necessarily small compared to $\overline{r_i^2/r_o^4}$, even though $\bar{r}_i << \bar{r}_o$. Even with the helpful modifications, the convergence in the F case is only moderate.

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[26] Cf. S. Goudsmit and R. F. Bacher, Phys. Rev. **43**, 894 (1933).

VII. The ${}^1F$ and ${}^1D$ Series of Al II; Langer's Perturbation Formula

The lower members of the ${}^1F$ series are less severely perturbed than ${}^3F$ terms, simply because $3p3d\,{}^1F$ is more remote than $3p3d\,{}^3F$. Hence the perturbing effect of the former on $3snf\,{}^1F$ may be treated by the usual series formula (11) and the displacements of the $3snf\,{}^1F$ terms from hydrogenic values should be given by the formula

$$W-W_0=\Delta W+\frac{|(H_{1+}+H_{2-})(3snf;\,3p3d)|^2}{h\nu(3snf'F;\,3p3d'F)}+2H_{3-}(3snf;\,3snf) \tag{49}$$

where ΔW denotes the displacement of $3snf\,{}^3F$, exclusive of the perturbation by $3p3d{}^3F$. The last term in(49) arises in connection with the zeroth approximation (8–9–10), and it represents the difference in the penetration effect for singlets and triplets, which is usually considered to be the main cause of the singlet-triplet separation, as, for example, in Heisenberg's[7] calculations on helium. In our case, however, the diversity in the perturbation by $3p3d$ is a more important factor. The perturbations by other configurations are either so small or so similar that in (49) we have not considered them to be different for the singlets and triplets.[27]

The position of $3p3d\,{}^1F$ is unknown spectroscopically, but it may be located approximately by the following considerations. Let

$$[(H_{1+}+H_{2-})(3snf;\,3p3d)]^2=k_n{}^2[(H_{1+}-H_{2-})(3snf;\,3p3d)]^2. \tag{50}$$

The factor in brackets on the right side of (50), as well as the magnitude of ΔW in (49), is known from the secular problem of the preceding paper. (This factor is $H(1j)$ in the notation there employed.) It is true that the secular problem extended only to $n=9$, but the Ritz formula given for ΔW may be extended without difficulty to $n>9$, while the values of the right bracketed factor in (51) for $n>9$ may be determined from the observed positions of $3snf\,{}^3F$ ($n>9$) by the use of the perturbation formula (11) rather than by the secular method, since with $n>9$ the difficulty of excessive perturbations does not occur acutely. The last term of (49) can be computed from (10) and (40). Hence if, in addition, we substitute (50) and observed values of ΔW in (49) we obtain a relation in which k_n and $W(3p3d\,{}^1F)$, involved through ν, are the only unknowns and from which the former can be determined with any assumed value of the latter. There is one such relation for each value of n. Now k_n should vary only slowly with n, tending to increase with n for small n, and approach asymptotically a constant value at large n. This is because $r^{-3}(3pnf)/r^{-2}(3dnf)$ increases with n, approaching a finite nonvanishing limit at $n=\infty$. The value of k_n is fairly sensitive to the value assumed for $W(3p3d\,{}^1F)$ which is consequently roughly determined by the requirement that a reasonable sequence of values be obtained for $k_4, k_5, \cdots$. It is thus estimated that $3p3d\,{}^1F$ is between -5000 and $-15{,}000$ cm. The minus sign indicates that the term is beyond the usual series limit corresponding to the configuration 3*s* of Al III. Another way of reaching essentially the same result on the location of $3p3d\,{}^1F$ is to make use of the fact that $|(H_{1+}+H_{2-})(3p3d;\,3snf)|^2$ should vary asymptotically as n^{-3} when n is large. This asymptotic characteristic of matrix elements of the form $f(r)$ has been proved by Hartree[28] and is simply a statement of the continuity of their squares when normalized with respect to the energy W, as $dW=2RZ^2dn/n^3$. The graph of $|H|^2\times n^3$ as a function of n is shown in Fig. 3 for $3snf\,{}^3F$, and for $3snf\,{}^1F$ with two assumed locations for $3p3d\,{}^1F$. It is seen that the points are rather irregular, espe-

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[27] We thus neglect the dipole-quadrupole effect in the perturbation by the states $3pn'd(n'>3)$ but our calculations of the position of $3p3d\,{}^1F$ are not refined enough to make this an important source of error. Also it is at least partially counterbalanced by an error opposite sign due to our disregard of the different location of $3pn'd\,{}^1F$ and $3pn'd\,{}^3F(n'>3)$. The greater remoteness of the former weakens the singlet perturbation, whereas the cross effect intensifies it.

[28] D. R. Hartree, Proc. Cambridge Phil. Soc. **24**, 436 (1928). He considers explicitly only the matrix elements of r, but his methods apply equally well to any power of r. There is no discontinuity at $W=0$ when the squares of the discrete and continuous elements are each weighted according to the energy interval which they represent.

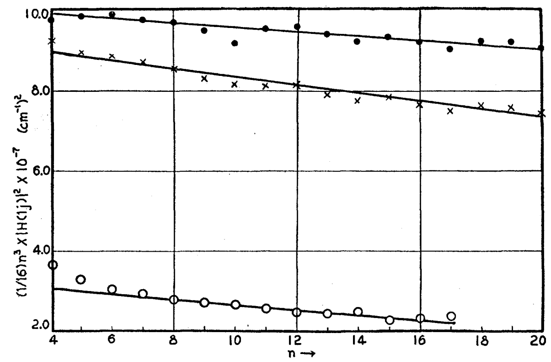

FIG. 3. This figure is to illustrate the near constancy of the product of n^3 into the squares of the perturbing matrix elements, and the larger magnitude of these elements for the singlets than the triplets. The points ● and × apply to the singlet elements $H(3p3d\,^1F;\,3snf\,^1F)$ and are deduced under the assumption that $3p3d\,^1F$ is located at 10,000 and 8000 cm^{-1}, respectively, beyond the series limit. The points O are for the triplet elements $H(3p3d\,^3F;\,3snf\,^3F)$. The solid curves are simply attempts to smooth out the irregularities.

cially for large values on n. This is partly doubtless because of experimental error, as precision on quantum defect is difficult when n is large, and is partly because of the approximate nature of the calculations. When n is very large, in the case of the F series of Al II, the perturbations are not negligible compared with the separation between consecutive term members. Under such conditions, the use of perturbation series developments is not a particularly good approximation, as higher powers of H than considered in (11) ought to be retained. This might cause some systematic error, but probably should not cause irregularities.

According to (26), the mean $\frac{1}{2}[H(3snf\,^3F;\,3p3d\,^3F)+H(3snf\,^1F;\,3p3d\,^1F)]$ of the singlet and triplet interaction, which we shall abbreviate to $=\frac{1}{2}[H(^3F)+H(^1F)]$ should have the significance $H_{1+}(3snf;\,3p3d)$ which simplifies to[29]

$$H_{1+}'(3snf;\,3p3d)=(3\alpha\nu_ie^2/14)^{\frac{1}{2}}r_o^{-2}(3d;\,nf) \tag{51}$$

provided we make the approximation (13), i.e., provided we overlook the fact that the outer electron is sometimes nearer the nucleus than the inner one. A comparison of the two expressions for various values of n is given in Table V. The values in the last row are those empirically derived from observed displacements, as in Fig. 3, under the assumption that $3p3d\,^1F$ is located at -8000 cm^{-1}. If the position $-10,000$ cm, for instance, were taken instead, these values would be raised slightly. The agreement can be improved if one takes account of the fact that (13) is not accurately fulfilled. Calculations by means of the approximate wave functions (40) indicate that $H_{1+}(3s4f;\,3p3d)$ should be about nine percent lower than $H_{1+}'(3s4f;\,3p3d)$. We have throughout assumed hydrogenic wave functions for the $3d$ and $4f$ states. Actually there is an appreciable penetration in the $3d$ state, and this tends to make $r^{-2}(3dnf)$ smaller than the hydrogenic value, about ten percent less according to

TABLE V.

$n=$	4	5	6	7	8	9
$(3\alpha\nu_ie^2/14)^{\frac{1}{2}}r^{-2}(3dnf)$	4780	3323	2470	1940	1573	1313
$\frac{1}{2}[H(^3F)+H(^1F)]_n$	3820	2830	2030	1600	1287	1080

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[29] One proves (51) by substituting (21) in (14) and using the definition of α given in (24) with the simplification (25). An alternative method is to write out (26) explicitly as a sum by substitution of (27) in (26) and then compare the terms in (11) and (26) representing perturbation by the same state.

provisional calculations made with a confluent development for $3d$. With $H_{1+}(3snf;\, 3p3d)$ nineteen percent less than the tabulated hydrogenic value of (51), the agreement between the theoretical and empirical values of $\frac{1}{2}[H(^3F)+H(^1F)]$ is very good.

The difference $\frac{1}{2}[H(^1F)-H(^3F)]_n$ should have the significance $H_{2-}(3snf;\, 3p3d)$ or

$$H_{2-}'=3e^2r_i^2(3s3d)r_o^{-3}(3pnf)/(175)^{\frac{1}{2}}$$

if one makes the approximation (13).[30] A comparison of theoretical and experimental values is here difficult because H_{2-} is an exchange term which is extremely sensitive to the location of the nodes of the inner wave functions, and the difference between H_{2-} and H_{2-}', unlike that between H_{1+} and H_{1+}', is enormous. For instance, if we assume that $3p3d\ ^1F$ is located at -8000 cm the empirical value of $\frac{1}{2}[H(^1F)-H(^3F)]_4$ is 870 cm^{-1}, while with the wave functions (39), the values of $H_{2-}'(3snf;\, 3p3d)$ and $H_{2-}(3snf;\, 3p3d)$ are respectively 2910, 470 cm^{-1}. Not much significance, however, should be attached to the theoretical in distinction to empirical calculations of $\frac{1}{2}[H(^1F)-H(^3F)]_n$, as any deviations of the $3d$ wave functions from hydrogenic character affect the results enormously.

The ^1D series was treated by Pincherle in Al II and by Bacher in Mg I,[31] so we need only mention how its behavior correlates with the general perturbation scheme. The important point is that here the exchange effect enters even in the dipole approximation H_1, or in another language, there are dipole-dipole cross terms. This is particularly manifest in the fact that the configuration $3p^2$ give rise only to a ^1D and not to a ^3D term, and so is capable of exerting a dipole perturbation on only the singlet terms of $3snd$.

Langer's formula. Langer[32] has suggested the formula

$$RZ^2/[n-\Delta+\sigma/(W_n-W_i)]^2=RZ^2/(n-\Delta)^2-2\sigma RZ^2/n^3(W_n-W_i)+\cdots \tag{52}$$

for the representation of "perturbed" terms disturbed by a state of energy W_i. We here give the more special of two formulas mentioned by Langer, which is the one tested by Shenstone and Russell.[33] Langer also gives an obviously more general formula in which σ is replaced by an undetermined function σ_n of σ, but such a formula is too ambiguous to be especially useful. Langer does not give the proof of (52). From our preceding analysis of the ^1F terms, however, which serves by way of illustration, it is clear that the conditions under which (52) should hold theoretically are (a) that the perturbing term be far enough away that one can use (11) and (b) that the ordinal number be high enough so that one can assume that the squares of the matrix elements of interaction are proportional to n^{-3}. The common occurrence of deviations from (52) in the immediate vicinity of the perturbing member or for small n has been noted by Shenstone and Russell, although they find that otherwise (52) fits remarkably well. Just such exceptions are obviously to be expected.

In summary, the polarization effects are much more complicated in two electron spectra than can be represented by the simple formula (1). It is thus not surprising that Schrödinger[34] found that with (1) different series lead to discordant results on α, especially since the centroids in (26) vary considerably from series to series.

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[30] This formula for H_{2-}' can be established by the second method given in note 29, with, of course, the understanding that (48) is used rather than (26).

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