state by higher states. It was observed that the problem of cascading may complicate the analysis of data obtained using the beam-foil method and could result in erroneous conclusions.

Changing foil characteristics have also been observed in the course of these experiments. Aging of foils in the accelerator vacuum system and under ion bombardment produced apparent changes in ion-energy loss. Consistent results were obtained only by using fresh foils for mean-life measurements. It is also evident that the initial populations of atomic states depend on the thickness of the foil used.

The actual mechanism of the excitation process within the foil is not yet fully understood. Due to the fact that the mean-free paths of the incident ions are small compared to the foil thickness, many ion-foil atom collisons will occur. It may be that the actual final excitation process occurs at the emergent surface of the foil and if this is the case, surface contamination would affect the initial-state populations. Some understanding of the excitation mechanism may be reached through polarization studies of the emitted radiation. Preliminary experimental studies in this endeavor have not thus far revealed any polarization.

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# PHYSICAL REVIEW

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# **Regularities in Atomic Oscillator Strengths\***

# W. L. Wiese<sup>†</sup> and A. W. Weiss

## National Bureau of Standards, Washington, D. C. 20234 (Received 14 June 1968)

Many regularities and systematic trends among atomic oscillator strengths have been studied using the extensive material which has recently become available for the lighter elements. The quantum-mechanical background for the existence of these regularities is discussed, and in particular the relationship between oscillator strength and nuclear charge as predicted from conventional perturbation theory is reviewed in detail. A number of characteristic numerical examples are then presented. The regularities are of great parctical importance, since they may be exploited to obtain additional oscillator strengths by simple interpolation techniques as well as to evaluate the reliability of existing data by the degree of fit into established systematic trends.

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#### I. INTRODUCTION

Regularities in atomic spectra are commonly associated with characteristic patterns in the wavelength positions of spectral lines, i.e., the appearance of spectral series, and with systematic trends for a given line or energy level along an isoelectronic sequence. Both types of regularities have been widely studied by spectroscopists<sup>1</sup> and have been extensively exploited for the acquisition of many additional data.

Systematic trends in spectral line intensities, on the other hand, have been rarely noted up to now. Almost all of the few observed regularities have been found for the relatively simple spectra of the alkalis and alkaline earths. As early as 1925 Trumpy<sup>2</sup> observed that the oscillator strengths for the principal series of sodium, 3snp, decrease with increasing principle quantum number n in a regular fashion, which may be approximately represented by the expression "const.  $\times n^{-3}$ ". Similar systematic trends were later also observed<sup>3</sup> for other series of the alkali metals, alkaline-earth metals, and some other metals, but several anomalies were found, too. Theoretically, the "const.  $\times n^{-3}$ " behavior for oscillator strengths of the various spectral series of hydrogen was first derived from the correspondence principle and again immediately after the development of wave mechanics.<sup>4</sup> It was also shown then that for hydrogenlike ions of nuclear charge Z the transition probability Achanges as  $A_Z = Z^4 A_H$  ( $A_H$  is the hydrogen value for this transition), while there is no change in the *f*-value:  $f_Z = f_H$ . However, the first theoretical attempt to exploit regularities within isoelectronic sequences of nonhydrogenic systems for the determination of atomic f values was undertaken only a few years ago with the development of the nuclear charge expansion method, 5,6 which has been recently extended to include core polarization and has been also applied to the determination of photo-ionization cross sections at the head of spectral series,<sup>7</sup>

In view of the scarcity of reliable f-value data, it is hardly surprising that more trends have not been detected before. While even now the f-value data are very far from being complete and are often not too accurate, our knowledge has nevertheless reached the stage where it has become fruitful to search systematically for those systematic trends which are expected from general principles of atomic theory. This applies especially to the lighter elements, for which a comprehensive table of atomic f values is now available.<sup>8</sup> Thus these spectra have been extensively scanned for regularities.

In the following, some of the most significant results of the systematic searches will be discussed<sup>9</sup> and the quantum mechanical basis for the regularities will be presented. The three specific aims of this paper are (a) to show that many regularities exist and that they are quite obvious; (b) to provide the essential theoretical background for further searches of systematic trends; and (c) to point out the profits derived from the analysis of the regularities, such as finding additional f values simply by graphical interpolation.

#### **II. THEORETICAL PART**

#### A. Systematic Trends of Oscillator Strengths Along Isoelectronic Sequences

The theoretical behavior of oscillator strengths along an isoelectronic sequence can be studied most conveniently from the framework of conventional Rayleigh-Schrödinger perturbation theory, expanding in inverse powers of the nuclear charge Z. This Z-expansion method is well known, and has been used extensively to study a wide variety of atomic properties.<sup>10-12</sup> The theory will be reviewed here as it applies in particular to the dependence of f values and multiplet strengths on the nuclear charge.<sup>5, 6</sup>

The multiplet strength for a transition between states  $\Phi$  and  $\Phi'$  is given by

$$S = |\langle \Phi | \Delta \hat{r} | \Phi' \rangle|^2 , \qquad (1)$$

where the summation within the integrand is taken over all the electrons of the atom, and the squared matrix element is understood to be summed over any degeneracies in the two states. The oscillator strength for the same transition is given by

$$f = \frac{2}{3}(E - E')g^{-1}S.$$
 (2)

Here g is the statistical weight of the initial state, and E is the energy in atomic units.<sup>13</sup> The wave functions and energies will be taken to be solutions of the usual, nonrelativistic, spin-in-dependent Schrödinger equation.

$$\left[-\sum_{\mu} \left(\frac{1}{2}\Delta_{\mu} + Zr_{\mu}^{-1}\right) + \sum_{\mu > \nu} r_{\mu\nu}^{-1}\right] \Phi = E\Phi.$$
 (3)

It should be noted that the approximation of pure LS coupling, represented by Eq. (3), is likely to become questionable for very high stages of ionization. This point will be taken up later on.

Following Hylleraas, <sup>14</sup> the usual procedure to obtain Z as a variable is to divide equation (3) through by  $Z^2$  and scale all distances r by Z and energies by  $Z^{-2}$ , so that  $\rho = Zr$  and  $\epsilon = EZ^{-2}$ . <sup>15</sup> This puts (3) into the form

$$(\mathcal{K}_0 + Z^{-1}V)\Phi = \epsilon\Phi \tag{4}$$

with 
$$\mathcal{R}_{0} = -\sum_{\mu} (\frac{1}{2} \Delta_{\mu} + \rho_{\mu}^{-1})$$
, (5)

and 
$$V = \sum_{\mu} \rho_{\mu\nu}^{-1}$$
. (6)

The Laplacian in (5) is to be taken with respect to the scaled distance  $\rho$ . Equation (4) is now in the requisite form for perturbation theory, with  $Z^{-1}$  as the expansion parameter and the entire interelectronic repulsion energy V as the perturbation. Also, the zeroth-order Hamiltonian is a simple sum of hydrogen atom Hamiltonians, so that the zeroth-order equation is separable. The perturbation solutions now are

$$\Phi = \Phi_0 + Z^{-1} \Phi_1 + Z^{-2} \Phi_2 + \cdots , \qquad (7)$$

$$\epsilon = \epsilon_0 + Z^{-1} \epsilon_1 + Z^{-2} \epsilon_2 + \cdots, \qquad (8a)$$

or, 
$$E = \epsilon_0 Z^2 + \epsilon_1 Z + \epsilon_0 + \epsilon_3 Z^{-1}$$
. (8b)

Because of the separability of the zeroth-order approximation,  $\epsilon_0$  is a simple sum, over all the electrons, of hydrogen atom energies

$$\epsilon_0 = \frac{1}{2} \sum_{\mu} n_{\mu}^{-2} , \qquad (9)$$

where  $n_{\mu}$  is the appropriate one-electron principal quantum number.

Our principal result, the Z dependence of the multiplet strength and f value, can now be derived by substituting (7) and (8b) into (1) and (2) and collecting terms of the same degree in Z

$$S = S_0 Z^{-2} + S_1 Z^{-3} + S_2 Z^{-4} + \cdots,$$
 (10)

$$f = f_0 + f_1 Z^{-1} + f_2 Z^{-2} + \cdots, \qquad (11a)$$

The leading terms here are given by

$$S_0 = |\langle \Phi_0 | \vec{\rho} | \Phi_0' \rangle|^2$$
(12a)

$$f_{0} = \frac{2}{3} (\epsilon_{0} - \epsilon_{0}') g^{-1} |\langle \Phi_{0} |\vec{p} | \Phi_{0}' \rangle|^{2}$$
(13)

$$f_{1} = \frac{2}{3} g^{-1}(\epsilon_{1} - \epsilon_{1}') |\langle \Phi_{0} |\vec{\rho} |\Phi_{0}' \rangle|^{2}$$
$$+ \frac{1}{3} g^{-1}(\epsilon_{0} - \epsilon_{0}') \langle \Phi_{0} |\vec{\rho} |\Phi_{0}' \rangle [\langle \Phi_{0}' |\vec{\rho} |\Phi_{1} \rangle + \langle \Phi_{1}' |\vec{\rho} |\Phi_{0} \rangle] . (14a)$$

The separability of the zeroth-order problem also implies that  $\Phi_0$  is simply an antisymmetrized product of hydrogen atom orbitals, so that  $S_0$  is simply given by

$$S_0 = \mathfrak{S}\sigma^2, \tag{15}$$

where  $\sigma$  is the hydrogenic transition integral and South the usual angular factor dependent on the angular momenta, number of equivalent electrons, etc. These last comments and Eq. (15) do *not* apply if there are any degeneracies in zeroth order, in which case some modifications are necessary. For the moment we will restrict ourselves to the nondegenerate problem.

In this case, Eqs. (10) and (11a) exhibit the explicit Z dependence for S and f. For very large Z, the multiplet strength goes to zero as  $Z^{-2}$ , or, equivalently,  $Z^2S$  approaches a hydrogenlike value as defined by (15). For the oscillator strength, one can distinguish between two different cases. If there is a change in the principal quantum number of the jumping electron,  $n \rightarrow n'$ , then the en-

ergy difference in the lead term,  $f_0$ , is just the hydrogen atom level spacing. The oscillator strength for large Z then asymptotically approaches the hydrogen f value, with the possible modification by the angular factor of Eq. (15). On the other hand, if there is no change in the principal quantum number,  $n \rightarrow n$ , the zeroth-order energy difference vanishes – Eqs. (9) and (13) – and the f value for large Z tends toward zero linearly with  $Z^{-1}$ . <sup>16</sup>, <sup>17</sup>

In this latter case, one can still say something about the way in which the f values go to zero. Equations (11a) and (14a) become

$$f = f_1' Z^{-1} + f_2' Z^{-2} + \cdots, \qquad (11b)$$

$$f_1' = \frac{2}{3}g^{-1}(\epsilon_1 - \epsilon_1')S_0$$
 (14b)

The first-order energy in Eq. (14b) is given by

$$\epsilon_1 = \langle \Phi_0 | V | \Phi_0 \rangle \tag{16a}$$

and is readily obtainable, since it only involves computing Slater integrals with hydrogenic orbitals. Thus for the case  $n \rightarrow n$  it is possible to predict fairly easily either the slope of the *f*-value curve for  $Z^{-1} \rightarrow 0$  or, alternatively, the limiting value of Zf.

Proceeding now to the case of zeroth-order degeneracy, this first occurs in the beryllium sequence with the well-known configuration interaction

$$2s^{2}S + 2p^{2}S$$
.

Since 2s and 2p are degenerate for hydrogen, both these configurations have the identical zerothorder energy. This degeneracy may be removed in first order by applying the standard procedures of degenerate perturbation theory. Any linear combination of the zeroth-order functions  $[\Phi^p]$ , will be an eigenfunction of  $\mathcal{K}_0$ , and the particular linear combination is determined by diagonalizing the first-order perturbation matrix,

$$V_{pq} = \langle \Phi_0^p | V | \Phi_0^q \rangle .$$
 (16b)

The eigenvalues of (16b) are the first order energies, and the eigenvectors provide the expansion coefficients, i.e.,  $\Phi_0$  becomes

$$\Phi_{0} = \sum \rho C_{p} \Phi_{0}^{p} . \tag{17}$$

The zeroth order multiplet strength is now given by

$$S_0 = |\sum pq C_p C'_q \langle \Phi_0^p | \vec{p} | \Phi'_0^q \rangle|^2$$
(12b)

and the oscillator strength is modified accordingly. All of the earlier discussion about asymptotic behavior applies as before, but with the difference that one uses (12b) instead of (12a) and (15), and the eigenvalues of (16b) are to be used instead of the  $\epsilon_1$  in (16a), i.e., the values of the asymptotes must now be determined by a numerical calculation instead of a table look-up.

In summary, since  $Z^{-1}$  appears from these considerations as the natural independent variable, regularities should be expected to show up most clearly in graphs of f (or  $Z^2S$ ) vs 1/Z. One has considerable assistance from theory here, since the zero end  $(Z^{-1} \rightarrow 0)$  of such curves can be determined theoretically, either by looking up already tabulated data or by doing a relatively minor calculation. If some fairly reliable data are available, then it also may be possible to read off values for other ions from the graph, especially since this really involves doing an interpolation rather than an extrapolation. Plotting against  $Z^{-1}$  has furthermore the advantage of compressing the entire isoelectronic sequence into the region between 0 and the neutral-atom value of  $Z^{-1}$ . Several words of caution are in order, however, concerning such graphical predictions.

The first difficulty concerns the readjustment of the atomic term scheme with increasing nuclear charge. It is well known that the energy levels for high stages of ionization are grouped according to the principal quantum numbers while for neutral atoms they often are not. Thus there should be a substantial amount of level crossing along many isoelectronic sequences, and in such regions fvalue anomalies are a distinct possibility. For example, for a highly ionized member of the carbon sequence, the lowest levels belong to the terms,  $2s^22p^2$ ,  $2s2p^3$ , and  $2p^4$ , followed by the n=3 terms, such as  $2s^22p3s$ ,  $2s^22p3p$ ,  $2s^22p3d$ ,  $2s2p^23s$ , etc. For neutral carbon, however, most terms of the first group lie quite high up, many of them unbound. As Z is increased, these levels will move down below those of the second group, and for those values of Z where they are close together it is possible to have quite strong perturbations of the *f*-values as well as the energy levels. It appears from the data, that this adjustment is normally already realized at moderately low stages of ionization.<sup>1</sup>

A second, and closely related problem has to do with the occurrence of cancellations within the transition integrand as the radial wave-function nodes shift inward with increasing Z. This would give rise to a minimum in the *f*-values for a given transition at some particular value of Z, and indeed a number of transitions in the sodium isoelectronic sequence have been found to exhibit such behavior. The phenomenon is quite similar to the Cooper minima<sup>18</sup> in photo-ionization cross sections which arise from cancellations for certain values of the free-electron energy. While these minima normally occur in the continuum, they have frequently been found to occur below threshold, i.e., among the discrete level transitions.

Finally, one should recall that the entire theoretical development here has been nonrelativistic, so that there are no allowances for departures from LS coupling. While for sufficiently large Z this will become important, it is difficult to assess just where and to what extent the LS coupling will break down. From the available experimental data and intermediate coupling calculations, <sup>19</sup> it appears that one can go to quite high stages of ionization without seriously disturbing the f values for LS-allowed transitions. At any rate, any multiplet strengths that one might interpolate for large Z should represent the correct starting point for an intermediate coupling calculation.

#### B. Regularities Based on One-Electron Model Considerations

A great many of the strong lines in atomic spectroscopy arise from transitions where the jumping electron is in a shell by itself, i.e., where a single electron is jumping around outside of a spectroscopically inert core. These cases may be readily treated by some kind of single-particle, central-potential model, with the well-known Coulomb approximation<sup>20</sup> being perhaps the best known and most generally useful of such models. It can be expected that for such cases regularities should exist which derive primarily from the oneelectron nature of the transitions.

In general, for complex atoms a one-electron jump specified by nl - n'l' gives rise to a large number of lines, the transition array, and the equivalent one-electron f value is then actually a mean f value averaged over the entire array. Regularities which derive from the one-electron models refer to this "transition array" f value. To connect this f value,  $f_T$ , with the line and multiplet values normally observed, one needs first the following relations:

The total strength of a transition array,  $S_T$ , is related to the multiplet strength,  $S_M$ , and the line strength  $S_L$ , by

$$S_T = \sum_M S_M = \sum_M \sum_L S_L .$$
 (18)

The relations between the corresponding f values are given by,

$$f_L = (S_L / S_T) (\lambda_T / \lambda_L) (g_T / g_L) f_T,$$
(19)

and

$$f_M = (S_M / S_T) (\lambda_T / \lambda_M) (g_T / g_M) f_T.$$
 (20)

The g's here are the statistical weights of the initial line, multiplet or array, as the case may be, and the  $\lambda_M$  and  $\lambda_T$  represent average wavelengths for the multiplet and array, respectively, obtained from weighted averages of the energy levels. In many cases, the wavelength ratios in Eqs. (19) and (20) are close to unity. The ratios  $S_M/S_T$  and  $S_L/S_T$  are readily available in the literature for the case of LS-coupling.<sup>20</sup> The foregoing considerations depend on the assumption that the transition integral,  $\sigma$ , is approximately constant throughout the array, a condition which has been found to be generally fulfilled.

The partial f sum rules readily suggest themselves as starting points to look for possible regularities. In particular, the Wigner-Kirkwood<sup>22</sup> sum rule for transitions of the type  $nl \rightarrow n'l + 1$  states that

$$\sum_{n'} f_{nl,n'l+1} = \frac{1}{3} (l+1)(2l+3)(2l+1)^{-1}.$$
 (21)

Here, the sum is to be taken over all states, n', including the continuum as well as all possible lower states (which may be filled shells). For the most common types of transitions, one finds

$$ns - n'p: \sum f = 1,$$
  

$$ns - n'd: \sum f = \frac{10}{9},$$
  

$$nd - n'f: \sum f = \frac{7}{5}.$$
(22)

If now a single transition overwhelmingly dominates the series, then the f value for this transition will be given approximately by the sum rule, Eq. (21). Such a situation may be expected to prevail when the l and l+1 wave functions overlap very strongly and are radially separated from the core, e.g.,  $(n+1)s \rightarrow (n+1)p$ , where the core electrons occupy the shells with principal quantum number n. An obvious case in point is the resonance line of the alkali atoms. Thus, for example, the 3s-3p transition in sodium with  $f \approx 0.98$  soaks up essentially all the oscillator strength, the same being true for the other alkalis. If the corresponding transition dominates the sum in Eq. (21)as one proceeds along columns of the periodic table (in the above example 4s-4p for K, 5s-5pRb, etc.), the sum rule then provides a method for estimating f values for homologous atoms.

It is now important to realize that the ratios  $S_L/S_T$  and  $S_M/S_T$  in Eqs. (19) and (20) are the same for homologous atoms, as long as the coupling scheme does not change. Since the wavelength ratios,  $\lambda_T/\lambda_L$  and  $\lambda_T/\lambda_M$ , should also be quite similar, we may conclude that, for homologous atoms, even the individual line and multiplet strengths will be approximately the same for the dominant transition array in analogous spectral series.

Another place where one may expect to find oneelectron model regularities is in the behavior of f values along a spectral series. It is well known that, for the hydrogen atom, oscillator strengths for any given series fall off as  $n^{-3}$ , i.e.,

$$f_{n \to n'} \simeq n'^{-3} , \qquad (23)$$

for large n'. Since the high-lying single-excitation levels of a complex atom should approach hydrogenlike behavior, one may expect f values for spectral series generally to decrease according to Eq. (23) for large enough n', i.e.,  $n'^3f$  should approach a constant. This prediction, of course, requires some modification if quantum defects are not small, namely, that n' should be replaced by  $n^*$ , the effective quantum number.

Finally, even more exact hydrogenlike behavior can be expected to prevail for transitions between levels with both large l and large n. In such excited states the wave function of the outer electron does not penetrate the core at all, and for all intents and purposes the electron sees the core only as a point charge. In these cases then, not only should the previously discussed regularities hold, but the absolute f values should correspond almost exactly to the purely hydrogenlike values.

Just as with isoelectronic sequence regularities, however, a word of caution is in order with respect to possible perturbations, e.g., those due to foreign terms. Series perturbations are well known in atomic spectroscopy, and it is always possible for the one-electron regularities discussed here to be seriously disrupted by such effects.

#### **III. ILLUSTRATIVE EXAMPLES**

## A. Z dependence of f values

We have confined our studies to the isoelectronic sequences of the lightest elements from helium to magnesium, since only for these sequences are sufficient amounts of reliable data for lower as well as higher ions available at this time.

Up to now about 100 cases with sufficient numerical data on nuclear charge dependence have been found. The material has been always critically selected and has been normally taken from the data evaluation and compilation now in progress at The National Bureau of Standards,<sup>8</sup> with some recent additions to the already published tables. In some instances the data are not too reliable, but normally they should be within 50% (often much less) of the true values. The studies were carried out with graphical methods, since Eqs. (10) and (11a) lend themselves readily to this most instructive type of presentation.

It appears that practically all the curves obtained by plotting f (or  $Z^2S$ ) versus 1/Z may be conveniently grouped into three classes according to their shapes. This classification appears to have also physical significance, since there is a clear correlation between each type of curve and the particular behavior of the transition integral (Table I). The most commonly encountered curve (class a of Table I) exhibits a dependence of f value on nuclear charge which is well approximated by a parabola, and for the higher ions, by a straight line. Thus a quadratic approximation to Eq. (11a) appears to represent the "basic" f-value dependence on Z. Such a curve is usually encountered when there is no interference of any kind in the transition integral, or when configuration interaction has a uniform effect along the entire sequence. The Z-expansion method<sup>5</sup>,  $^{6}$  provides a good theoretical representation for this type of transition. A second kind of curve (class b) shows a maximum near the neutral end of a sequence. This appears to occur when there is cancellation in the one-electron transition integral,  $\sigma$ , or when configuration interaction dominates for the neutral atom. In the latter case, configuration interaction produces an interference in the transition integral. It should be noted that configuration interaction can also act to enhance the f value, and if this were to happen for the neutral atom one would simply get a curve of type a, with perhaps a somewhat exaggerated rise at the neutral end. If enhancement were to occur somewhat further along the sequence, a curve of type b would be produced, but with the maximum being caused by configuration interaction. No clear and out-

Characteristics of $f$ value dependence on $1/Z$		Little or no configuration interaction	Strong configuration interaction	Cancellation in transition integral	
Class a.	parabola (approx. straight line for higher Z)	53	3 <sup>a</sup>	0	
b.	curve with maximum	0	14	$7^{b}$	
c.	curve with minimum	0	0	11	

TABLE I. Correlations between the functional dependence of f value on nuclear charge Z and the dominant physical mechanism acting on transition integral.

<sup>a</sup>Calculations with and without configuration mixing show that for two of the three cases the effects of configuration interaction are quite moderate, i.e., the values change by about 20-30%, and in the third case by about 70%.

<sup>b</sup>Maximum is caused in these cases by cancellation at the neutral end of isoelectronic sequence and by the asymptotic behavior  $f \rightarrow 0$  for  $1/Z \rightarrow 0$ .

standing examples of an enhancement effect have yet been found. Curves showing a minimum (class c), with the f values increasing again at the neutral end, have also been found. So far, these curves can be attributed simply to cancellation in the one-electron integral, apparently for those values of Z near which the integral changes sign. Finally, the combined effects of configuration interaction and other interference effects may occasionally give rise to curves with anomalous behavior, which, e.g., may show both a maximum as well as a minimum. However, we have observed only one anomalous curve as yet (for the boron transition  $2s^22p$   $^2P-2s^23s$   $^2S$ ).

Table I shows the statistics on the empirically found correlations between the various types of curves and the apparent cause for their shape. These correlations are so strong for the three classes of curves that this may be of significant aid in predicting the shapes of future curves if the effects which are important for particular transition integrals are known. Before presenting now some characteristics examples, it should be pointed out that, not unexpectedly, f values and energy levels show close correlations in their nuclear charge dependence with regard to perturbations. In particular, it is observed that when configuration interaction occurs, the perturbation effects for f values as well as energy levels are largest for the lowercmembers of an isoelectronic sequence while for the higher members the perturbations become rapidly smaller.

In the following, some characteristic examples for the various types of curves are discussed. First three curves are presented where the dependence of f value on nuclear charge is very nearly given by a parabola:

(a) Some of the most accurate data are available for the 2s-2p transitions of the lithium sequence. For these lines, configuration interaction effects are negligible. The overall dependence of f value on 1/Z, shown in Fig. 1, is thus well represented by a parabola and for the higher ions by a straight line, which goes to zero for 1/Z - 0 as required by Eq. (11b). For this graph, one experimental and three theoretical sources were chosen from the substantial amount of available material. The three theoretical methods are variational calculations for the ions Li I through O VI,<sup>16</sup> self-consistent-field (SCF) calculations for F VII and Ne VIII,<sup>16</sup> and nuclear-charge expansion calculations.<sup>5</sup> The experimental data have been obtained from lifetime measurements with the beam-foil excitation method.<sup>23</sup> For C IV the estimated theoretical

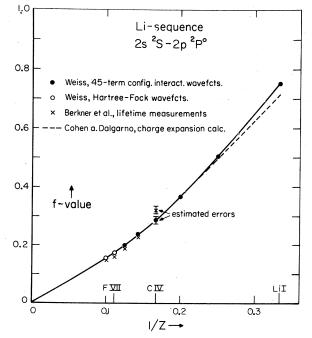


FIG. 1. Oscillator strengths versus 1/Z for the principal resonance line of the lithium isoelectronic sequence. The solid line represents simply the best fit through the data.

and experimental errors are indicated by error flags. The experimental error given is simply the standard deviation of the mean value; thus the slight discrepancy is probably of no particular significance. The otherwise very close agreement between experiment and theory may be considered as an indirect experimental proof of Eq. (11b) since the experimental values are obtained with no knowledge or assumptions about any possible nuclear-charge dependence of the f value. The solid line drawn through the data points is simply the best estimated fit and may be used to obtain f values for very highly charged ions by just reading these off the curve.

(b) As a second example for a curve of type I the transition  $2s2p^{3}P^{\circ}-2p^{2}P$  of the Be sequence is presented. This transition, in contrast to the previous one, may be expected to show some configuration interaction effects, especially since there are equivalent electrons present in the upper level. But closer inspection shows that no configuration interaction is possible in the n = 2 shell since the only other even-parity configuration  $2s^2$  does not have a  $^{3}P$  state. Configuration interaction reduces therefore to the normally much smaller interactions with states of higher n, and one should thus expect a nuclear-charge dependence similar to those cases with negligible configuration interaction. As Fig. 2 shows, this seems to be indeed borne out by the various available theoretical as well as experimental data. The theoretical sources used are SCF calculations with and without configuration mixing, done by one of us, nuclear-charge expansion calculations.<sup>5</sup> and calculations based on hydrogenlike wave functions.<sup>24</sup> The two experimental data are both from lifetime measurements.<sup>25,26</sup> It is important to note that the value for Be I, obtained theoretically from a full configuration-interaction treatment, smoothly joins the theoretical values for B II, C II, etc., which were done without consideration of configuration interaction. This fact clearly indicates the insensitivity of this transition against configuration-mixing effects.

(c) As was mentioned in the beginning of this section, the class-I dependence of f value on nuclear

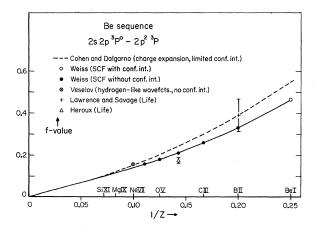


FIG. 2. Oscillator strengths versus 1/Z for the  $2s2p^{3}P^{\circ}-2p^{2}{}^{3}P$  transitions of the beryllium isoelectronic sequence.

charge may be also obtained if a considerable configuration-interaction effect influences the transitions over the whole isoelectronic sequence to approximately the same degree. This apparently happens in the case of the boron sequence transitions  $2s^22p^2P^\circ - 2s^2p^{22}P$ , where calculations based on SCF wave functions but without considering configuration-interaction effects<sup>27,28</sup> differ along the whole isoelectronic sequence by an almost constant amount from those for which the full configurationmixing treatment is included (Fig. 3).<sup>27</sup> These latter calculations in turn agree closely with the nuclear-charge expansions<sup>5</sup> in which only limited configuration interaction is included, namely, the mixing of the  $2p^3$  state with the  $2s^22p$  state. Apparently most of the change of *f* value originates from this particular admixture. The experimental datum point for N III comes from a lifetime measurement performed with the beam-foil excitation technique<sup>26</sup> and is in excellent agreement with the theoretical results based on configuration mixing. This example demonstrates two points: conventional SCF calculations cannot be considered reliable in situations where configuration interaction is expected even when they give smooth and reasonable Z-dependence plots, and secondly, an approximately linear relationship between f value and 1/Zmay also be obtained for cases with significant configuration interaction.

Next, two plots will be presented where configuration interaction strongly influences the f-value data. These are curves categorized as class b in Table I:

(d) Accurate theoretical as well as experimental material is available for the  $2s^22p \, {}^2P^{\circ}-2s2p^2 \, {}^2D$  transitions of the boron sequence (Fig. 4). These transitions again do not involve a change in principal quantum number so that the *f* value goes to zero for 1/Z. The experimental data are all obtained from lifetime measurements performed either with the beam-

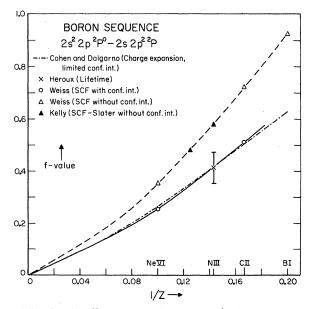


FIG. 3. Oscillator strengths versus 1/Z for the  $2s^22p^2P^\circ - 2s2p^2P^\circ$  transitions of the boron sequence.

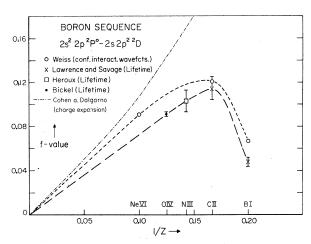


FIG. 4. Oscillator strengths versus 1/Z for the  $2s^22p^2P^{\circ}-2s2p^2p^2$  transitions of the boron isoelectronic sequence. The broken curves represent the best fits for the theoretical and experimental data.

foil excitation technique<sup>26,29</sup> or the phase-shift technique.<sup>25</sup> The error flags given are the experimental errors estimated by the authors and do not include any systematic errors due, for example, to cascading. Extensive superposition-of-configuration calculations, carried out by one of us,<sup>27</sup> are quite close to the experimental results, while the nuclearcharge-expansion calculations of Cohen and Dalgarno,<sup>5</sup> which include configuration interaction only to a very limited degree, provide fairly good results only for ions of higher charge. The dominant configuration interaction here is the mixing of  $2s^23d$ with  $2s2p^2$ . Since these levels separate rapidly with increasing Z, the effect should be expected to die out fairly soon along the sequence, and this is exactly what is observed.

(e) The  $3s3p P^{\circ}-3s3d D$  transitions of the Mg sequence may serve as a second example for curves of Class b. In this case we have plotted  $Z^2S$  versus 1/Z (Fig. 5) for reasons to be given later. As was shown earlier (Eq. 10), for  $Z^2S$  a finite value is obtained at infinite Z even though this transition involves no change in principal quantum number. The numerical value of  $Z^2S$  for infinite Z has been taken from the nuclear-charge-expansion calculations of Crossley and Dalgarno.<sup>6</sup> All other adopted data for this transition originate from theoretical sources, too, and involve the SCF approach, with configuration mixing included in various degrees of refinement.<sup>30-33</sup> Two authors<sup>30,33</sup> have also calculated values in the basic SCF approximation without considering configuration mixing, in order to have a measure by what amount the results are changed by configuration interaction effects. These data are included in Fig. 5 and show even more drastically than Fig. 3 that a smooth Z dependence obtained with data from just one or several similar methods indicates only that the methods are consistently applied, but does not reflect at all on the accuracy of the data. Therefore, great caution has to be exercised in the judgment of the reliability of data coming from just one or several similar sources.

(f) Next, we turn to an example for a Z depen-

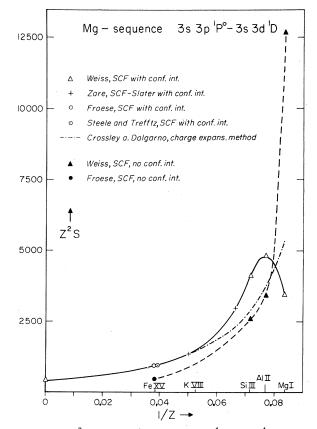


FIG. 5.  $Z^2S$  versus 1/Z for the 3s3p  $^1P^{\circ}-3s3d$   $^1D$  transition of the magnesium isoelectronic sequence. The solid line gives the best fit through the data.

dence of class c. Z-dependence curves exhibiting minima are probably caused simply by a very pronounced cancellation effect in the transition integral for a particular ion within an isoelectronic sequence. It appears that drastic cancellation effects are normally encountered only for transitions involving principal quantum numbers at least one larger than the ground state. Material for such moderately or highly excited transitions has been, with few exceptions, available only on the Li and Na sequences. Examples are the 3s-4p transitions of the Na sequence given in Fig. 6. The data for this graph are taken from central field approximation calculations for Na I;34 from calculations using a scaled Thomas-Fermi potential for Mg II, Cl VII, and<sup>35</sup> CaX; from SCF calculations for Al III and Si IV;36,37 and finally from the Coulomb approximation  $^{\rm 20}$  for S VI. It is observed that the minimum for Mg II is smoothly approached from both directions. The calculations based on the scaled Thomas-Fermi potential as well as the Coulomb approximation indicate that indeed just for this ion the positive and negative contributions to the transition integral very nearly cancel. By studying the *f*-value behavior in the spectral series 3s-np for the ions Na I, Mg II, Si III, etc., one finds furthermore that Mg II shows a most pronounced anomalous series behavior, while the neighboring ions show much less evident anomalies in their corresponding series. This comes out clearly in Table II where the *f*-value

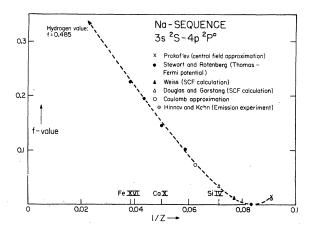


FIG. 6. Oscillator strengths versus 1/Z for the  $3s^2S-4p^2P^\circ$  transition of the sodium isoelectronic sequence.

ratios  $f_{3S-np}/f_{3S-(n+1)p}$  for the first few members of these series are tabulated for Na I, Mg II, Al III, and Si IV.

At this point, it is of interest to point out that, analyses of the kind presented here have occasionally even revealed inconsistencies in the normally much more accurate atomic energy level data and have led to their improvements. Examples are the  $3s3p P^{\circ}-3s3d D$  transitions of the Mg sequence, for which a smooth  $Z^2S$  versus 1/Z plot was presented in Fig. 5. If these same data, including those given by Froese for Fe XV,<sup>33</sup> are converted from S into f values by applying the available energy level values,<sup>38</sup>,<sup>39</sup> one obtains the rather ragged f-value dependence of Fig. 7. Since f and S are essentially related through the energy level difference E - E' [Eq. (2)], one has to look into the Z dependence of  $\tilde{E}$  and  $\tilde{E}'$  as the source for the ragged f-value behavior. While a Z-dependence plot of the lower state  $E(3s3p P^{\circ})$  produces a smooth curve, the analogous plot for the upper level E' $(3s3d \, {}^{1}D)$ , given in Fig. 7, shows that this level appears to be wrongly classified for PIV, K VIII, and Ca IX. For Si III, a similarly erroneous classification existed until recently when a new classification<sup>39</sup> placed the  $3d^{1}D$  level about 20% higher than the older value.38 New approximate energy levels for the higher ions may be then obtained for this case from the requirement that the Z-dependence of the *f*-values should smoothly connect the lower ions via Fe XV to the asymptotic value at infinite Z. The energy level dependence which does just that is indicated with the broken line in Fig. 7.

TABLE II. Ratios  $f_{3s-np}/f_{3s-(n+1)p}$  for some members of the 3s-np series of the Na sequence.<sup>a</sup>

f-value ratios	Na I	Mg II	A1 III	Si IV
$f_{3s-3p}/f_{3s-4p}$	69	4100	79	24.4
$f_{3s-3p}/f_{3s-4p}$ $f_{3s-4p}/f_{3s-5p}$	6.43	0.23	1.63	2.6

<sup>a</sup>The data are all taken from Ref. 8.

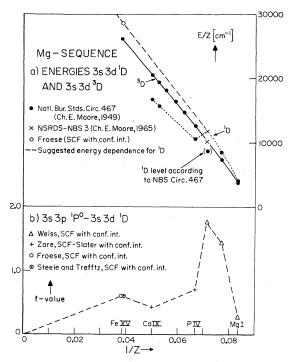


FIG. 7. (a). E/Z versus 1/Z for the 3s3d <sup>1</sup>D and 3s3d <sup>3</sup>D levels of the magnesium isoelectronic sequence. The energies E are taken with respect to the ground state. (b). Oscillator strengths versus 1/Z for the 3d3p<sup>1</sup> $P^{\circ}$  -3d3d<sup>1</sup>D transitions of the magnesium isoelectronic sequence.

## B. Regularities Based on One-Electron Model Considerations

## (a) Homologous Atoms

It was shown in the theoretical part that for homologous atoms the f values for analogous individual lines in the dominant transition arrays of spectral series should be approximately equal. Since this result hinges primarily on the fulfillment of the partial f-sum rule, an extensive test of how well the available data support the sum rule appears to be in order. This rule has been often applied by astrophysicists to obtain approximate f-value data, even for complex atomic systems, but it seems to have been tested only for such simple systems as H, He, and the alkalis.

We have thus computed – whenever there were sufficient individual data available – the average f values  $f_T$  for dominant transition arrays of the ns-n'p, np-n'd, and nd-n'f series in the lighter elements, and have compiled them in Table III. The dominant transition arrays are usually those where n' equals n, but for all 2p-nd series the first transition goes necessarily to n=3, and for the 3p-3d transition of Li the energy difference is so small that – in the spirit of the sum rule – 3p-4d is the dominant transition of the 3p-nd series. Because of the energy degeneracy one has also to set n'=n+1 for all hydrogen transitions. All the listed  $f_T$  values are those selected from the critical NBS data tables<sup>8</sup> and are considered to be

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TABLE III. Average f values  $f_T$  for some common transition arrays<sup>a</sup>

#### I. s-p transition arrays:

(a) One equivalent electron in lower level

Sum-r

$\mathbf{red}$	iction $f$ (	ns–np)≈1
Ι	(2 <b>s-</b> 3 <b>p</b> )	- 0.435
I	(3 <b>s-4</b> p) -	→ 0.485
Ι	(4 <b>s-5p</b> )	→ 0.544
I	(5 <b>s-</b> 6 <b>p</b> )	<b>→</b> 0.608
Ι	(2 <b>s-</b> 2 <b>p</b> )	<b>→</b> 0.48
I,	(3 <i>s</i> -3 <i>p</i> )	<b>→</b> 0.81
I	(4 <b>s-</b> 4 <b>p</b> )	<b>→</b> 1.09
Ι	(2 <b>s-</b> 2 <b>p</b> )	<b>→</b> 0.75
Ι	(3 <b>s-3</b> p)	→ 1.07
Ι	(3 <i>s-3p</i> )	→ 0.92
I	(3 <b>s-</b> 3 <b>p</b> )	<b>→</b> 0.87
II	(3 <b>s-</b> 3 <b>p</b> )	<b>→</b> 0.90
I	(3 <b>s-</b> 3 <b>p</b> )	<b>→</b> 0.97
п	(3 <b>s-</b> 3 <b>p</b> )	<b>→</b> 0.97
Ι	(3 <b>s-</b> 3 <b>p</b> )	<b>→</b> 0.85
Ι	(3 <b>s-</b> 3 <b>p</b> )	→ 0 <b>.9</b> 8
Ι	(4s - 4p)	→ 1.41
I	(4 <b>s-</b> 4 <b>p</b> )	→ 1.15
I	(4s-4p)	→ 1.05
Ι	(4 <b>s-</b> 4 <b>p</b> )	<b>→</b> 0.96
	I I I I I I I I I I I I I I I I I I I	$\begin{array}{cccccccccccccccccccccccccccccccccccc$

(b) Two equivalent electrons in lower level

Sum-rule prediction  $f(ns-np) \approx 2$ 

Be	I	$(2s^2 - 2s2p)$	 1.36
Mg	Í	$(3s^2 - 3s3p)$	 1.85
Ca	I	(4s <sup>2</sup> -4s4p)	 1.80

#### II. p-d transition arrays:

Sum-rule	pre	ediction $f(np-n'd) \approx 1.1$
н	I	$(2p-3d) \rightarrow 0.696$
H	Ι	$(3p-4d) \rightarrow 0.618$
He	I	$(2p-3d) \rightarrow 0.711$
		$(2p-3d) \rightarrow 0.67$
		$(3p-4d) \rightarrow 0.53$
В	Ι	$(3p-3d) \rightarrow 0.90$
С	Ι	$(3p-3d) \rightarrow 0.94$
N	I	$(3p-3d) \rightarrow 0.95$
N	п	$(3p-3d) \rightarrow 0.75$
Na	I	$(3p-3d) \rightarrow 0.83$
Al	Ι	$(4p-4d) \rightarrow 0.71$
К	I	$(4p-4d) \rightarrow 0.96$
III. d	l-f	transition arrays:
Sum-rule	e pr	rediction $f(nd-n'f) \approx 1.4$

н	I	(3d-4f)	<b>→</b> 1.02	
He	Ι	(3d-4f)	→ 1.02	
Li	I	(3d-4f)	→ 1.01	
Na	Ι	(3d-4f)	→ 1.00	

<sup>a</sup> All data are from the critical data compilation in Ref. 8. Since the listed numbers are from numerous different sources, and are often averaged, it was not feasible to quote all the individual authors, and we have to refer to Ref. 8 for details. fairly accurate, with uncertainties in the majority of cases estimated not to exceed 25%. The data which involve primarily experimental sources are set in italics. Judging from these examples we may conclude that the application of the partial f-sum rule may normally provide f values good within 50% for lines of dominant transition arrays. Excepted from this estimate are still the very complex atomic systems.

It is seen from Table III that the values from the *f*-sum rule tend to be in the majority of cases higher than those for the dominant transition arrays and may be regarded as upper limits. This has been taken into account in a number of applications. For example, Allen<sup>40</sup> has adjusted his *f* sum rule values by multiplying them with a factor of 0.7 before applying them to the leading transition arrays.

Next we shall investigate how closely the *f* values for analogous transitions in homologous atoms agree with each other as predicted in Sec. II. B. Table IV contains the available examples for multiplets of second and third row atoms of the periodic table (and Ca) for which the estimated uncertainties are smaller than 50%.<sup>41</sup> All data from experimental sources, or averaged values containing experimental data, are underlined. Also given are estimates of the uncertainties according to Ref. 8. By inspecting Table IV it is seen that for 39 of the 52 transitions listed, that is for 75%of the lines, the f values agree within the estimated error limits. Taking the s-p transitions separately. Ne and Ar excepted (see below), one finds even 100% agreement. Several disagreements observed for p-d transition can be definitely traced to cancellation in the transition integrals, e.g., for  $4p P - 4d P^{\circ}$  of Si I,  $4P^{3}P - 4d^{3}D^{\circ}$  of S I and, to a lesser extent,  $4p \,{}^5P-4d^5D^\circ$  of S I; in other cases, insufficient data do not allow definite conclusions at this time. The disagreements between some Ne and Ar f values appear to be mostly due to changes in the coupling scheme, which lead a redistribution of the individual line strengths, but leave the total s-p strength nearly unaffected. Thus for groups of lines starting from a given level a strong disagreement in one direction is usually balanced by a similarly strong deviation in the other direction. However, the average f value for Ar 4s-4pappears to be about 25% higher than that for Ne 3s-3p, as seen from Table III. Also in all other s-p comparisons one observes that the thirdperiod elements have slightly larger f values than the second-period elements.

To sum up, for many lines of the dominant transsition arrays in homologous atoms the f-value agreements are quite impressive and may therefore be used to predict additional fairly reliable f values, probably within 50%, by simply drawing analogies with existing data.

Since these comparisons have proved to be so successful for the dominant transition arrays, it is tempting to extend them to other transitions in homologous atoms. Such comparisons are presented in Table V. For the great majority of lines again good agreement is observed, which is quite unexpected. Nevertheless, extrapolations to other homologous atoms for these and similar

Transition		f value	Error	f value	Error
		Boron	(n = 2)	Aluminu	n (n = 3)
(n+1)s - (n+1)p	$^{2}S - ^{2}P^{\circ}$	1.07	25%	1.41	25%
(n+1)p-(n+1)d	$^{2}P-^{2}P^{\circ}$	0.90	25%	0.71	25%
		Carbor	(n = 2)	Silicon (	n = 3)
np(n+1)s - np(n+1)p	${}^{3}P^{\circ} - {}^{3}D$	0.50	50%	0.61	50%
	${}^{3}P^{\circ} - {}^{3}P$	0.31	50%	0.39	50%
	${}^{3}P^{\circ} - {}^{3}S$	0.10	50%	0.13	50%
	$^{1}P^{\circ} - ^{1}D$	0.42	50%	0.67	50%
	${}^{1}P^{\circ} - {}^{1}S$	0.11	50%	0.12	50%
ip(n+1)p - np(n+1)d	${}^{1}P - {}^{1}D^{\circ}$	0.63	25%	0.48	50%
	${}^{3}D - {}^{3}F^{\circ}$	0.70	25%	0.32	50%
	${}^{1}P$ - ${}^{1}P^{\circ}$	0.26	25%	0.00021	>50%
		Nitrog	en $(n=2)$	Phosph	orus $(n=3)$
$np^2(n+1)s - np^2(n+1)p$	${}^4P - {}^4D^\circ$	0.36	25%	0.57	50%
	${}^4P$ – ${}^4P^{\circ}$	0.23	25%	0.36	50%
	${}^{4}P - {}^{4}S^{\circ}$	0.088	25%	0.13	50%
	$^{2}P-^{2}P^{\circ}$	0.318	25%	0.39	50%
$np^2(n+1)p - np^2(n+1)d$	$^{2}S^{\circ}-^{2}P$	0.945	10%	0.30	50%
		Oxygei	n (n = 2)	Sulfur	(n = 3)
$np^{3}(n+1)s - np^{3}(n+1)p$	${}^{5}S^{\circ} - {}^{5}P$	0.922	10%	<u>1.1</u>	50%
	${}^{3}S^{\circ}-{}^{3}P$	0.898	10%	<u>1.1</u>	50%
$np^3(n+1)p - np^3(n+1)d$	${}^{5}P - {}^{5}D^{\circ}$	0.90	25%	0.22	50%
	${}^{3}P - {}^{3}D^{\circ}$	0.75	25%	0.059	> 50%
		Fluori	ne $(n=2)$	Chlori	ne $(n=3)$
$np^4(n+1)s - np^4(n+1)p$	${}^4P$ – ${}^4P^{\circ}$	0.29	50%	0.30	50%
•	${}^{4}P - {}^{4}D^{\circ}$	0.53	50%	0.57	50%
	${}^4P - {}^4S^{\circ}$	0.11	50%	0.12	50%
	$^{2}P-^{2}D^{\circ}$	0.53	50%	0.58	50%
	$^{2}P-^{2}S^{\circ}$	0.11	50%	0.11	50%
	$^{2}P-^{2}P^{\circ}$	0.34	50%	0.36	50%
		Neon	(n = 2)	Argo	n $(n=3)$
$np^{5}(n+1)s - np^{5}(n+1)p$	$1s_2 - 2p_1^{b}$	0.123	10%	0.134	25%
	$1s_2 - 2p_2$	0.164	10%	0.173	25%
	$1s_2 - 2p_3$	0.265	25%	0.436	25%
	$1s_2 - 2p_4$	0.158	10%	0.161	25%
	$1s_2 - 2p_6$	0.228	10%	0.125	25%
	$1s_2 - 2p_8$	0.047	10%	0.039	25%

TABLE IV. Comparison of f values for homologous atoms in leading transition arrays.<sup>a</sup>

Transition			f value	E	rror	f value	Erro
	$1s_3 - 2p_2^{b}$		0.273	-	10%	0.342	25%
	$1s_3 - 2p_4$		0.394	:	10%	0.561	25%
	$1s_3 - 2p_7$		0.246		10%	0.095	25%
	$1s_3 - 2p_{10}$		0.073	:	10%	0.057	25%
	$1s_4 - 2p_2$		0.034	:	10%	0.016	25%
	$1s_4 - 2p_3$		0.157	2	25%	0.120	25%
	$1s_4 - 2p_4$		0.018	:	10%	0.0002	25%
	$1s_4 - 2p_5$		0.114	2	25%	0.122	25%
	$1s_4 - 2p_6$		0.050		10%	0.075	25%
	$1s_4 - 2p_7$		0.170		10%	0.274	25%
	$1s_4 - 2p_8$		0.245		10%	0.415	25%
	$1s_4 - 2p_{10}$		0.077	:	10%	0.084	25%
	$1s_5 - 2p_2$		0.040	:	10%	0.030	25%
	$1s_5 - 2p_3$		0.056	2	25%	0.030	25%
	$1s_5 - 2p_4$		0.014		10%	0.003	25%
	$1s_5 - 2p_6$		0.122	-	10%	0.242	25%
	$1s_5 - 2p_7$		0.027	-	10%	0.031	25%
	$1s_5 - 2p_9$		0.373		10%	0.509	25%
	$1s_5 - 2p_{10}$		0.085		10%	0.160	25%
		Ber	yllium $(n=2)$	Magnes	sium $(n=3)$	Calciu	(n = 4)
s(n+1)s - ns(n+1)p	${}^{3}S - {}^{3}P^{\circ}$	1.13	25%	1.41	25%	1.38	50%
	${}^{1}S - {}^{1}P^{\circ}$	1.15	25%	1.24	25%	1.00	50%

TABLE IV. (Continued)

<sup>a</sup>All data are from the critical data compilation in Ref. 8. Since the listed numbers are from numerous different sources, and are often averaged, it was not feasible to quote all the individual authors, and we have to refer to Ref. 8 for details. <sup>b</sup>Paschen notation.

transitions should be done with great caution, since the f values are often much smaller than those for the dominant lines, and cancellation seems to occur more often. It may be of interest to note that for transitions which exhibit strong configuration effects no meaningful comparisons are available as yet.

## (b) Hydrogenlike Transitions

An inspection of Table III shows very close agreement with the hydrogen values for 3d-4ftransitions and slightly worse agreement for anal-ogous p-d transitions. This gradual approach to hydrogenic values for transitions between higher excited states with larger values of l is of course to be expected, since electrons in high-lying spherical orbits have little interaction with the core. In such cases, the "Bohr" radius is so great that it is a good approximation to represent

the core simply as a point charge, as in hydrogen. Nevertheless, the closely hydrogenlike behavior of the relatively low-lying 3d-4f transitions for atomic systems smaller than Mg is rather unexpected. One may thus extrapolate that for these atoms and their isoelectronic ions, all 3d-4f and higher transitions involving more circular orbits, such as, e.g., 4f-5g, may be simply represented by the corresponding hydrogen f values. This is of considerable practical importance, since transitions such as 3d-4f are quite prominent in atomic spectra. For the next group of atoms through K, where the core electrons occupy the shells through n = 3, one may similarly expect hydrogenlike f values for transitions such as 4*f*-5*g*, etc.

#### (c) Systematic Trends for f Values In Spectral Series

The series structure of spectra is most evident

Transiti	on	f value	Uncertainty	f value	Uncertainty
		Boron $(n=2)$		Aluminum $(n=3)$	
np-(n+1)s	$^{2}P^{\circ}-^{2}S$	0.11	50%	0.12	25%
(n+1)p-(n+3)s	${}^{2}P^{\circ}-{}^{2}S$	0.018	25%	0.020	50%
		Carbon $(n=2)$		Silicon $(n=3)$	
$np^2-np(n+1)s$	<sup>3</sup> P- <sup>3</sup> P°	0.17	50%	0.155	25%
np(n+1)s-np(n+2)p	${}^{1}P^{\circ} - {}^{1}D$	0.011	50%	0.019	50%
		Nitrog	(n=2)	Phospho	orus $(n=3)$
$np^3-np^2(n+1)s$	${}^{4}S^{\circ}-{}^{4}P$	0.35	50%	0.31	25%
	${}^{2}D^{\circ} - {}^{2}P$	$\frac{0.00}{0.11}$	50%	$\frac{0.01}{0.13}$	25%
$np^3-np^2(n+1)s'$	$^{2}D^{\circ}-^{2}D$	$\frac{0.11}{0.11}$	50%	$\frac{0.13}{0.145}$	25%
up = up (u + 1)s	$D^2 D^2$ $P^{\circ} - D^2 D$	$\frac{0.11}{0.026}$	50%	And the second sec	
	-P' <b>-</b> -D			0.071	25%
		Oxyge	en (n=2)	Sulfu	$\mathbf{r}$ $(n=3)$
$np^4-np^3(n+1)s$	${}^{3}P-{}^{3}S^{\circ}$	0.031	50%	0.11	25%
$np^{3}(n+1)s-np^{3}(n+2)p$	${}^{5}S^{\circ}-{}^{5}P$	0.0023	25%	0.0074	50%
	${}^{3}S^{\circ}-{}^{3}P$	0.0056	25%	0.0048	50%
$np^{3}(n+1)p-np^{3}(n+2)d$	<sup>5</sup> <i>P</i> − <sup>5</sup> <i>D</i> °	0.07	10%	0.09	50%
$np^4(n+1)p-np^4(n+3)s$	<sup>5</sup> P- <sup>5</sup> S°	0.015	10%	0.018	50%
	<sup>3</sup> <i>P</i> - <sup>3</sup> <i>S</i> °	0.016	25%	0.018	50%
×		Neon	(n=2)	Argo	n (n=3)
$np^{5}(n+1)s-np^{5}(n+2)p$	$1s_4 - 3p_3^{b}$	0.0051	25%	0.0051	25%
	$1s_5 - 3p_9$	0.0251	25%	0.0036	25%
	$1s_2 - 3p_1$	0.0045	25%	0.0037	25%
	, <b>-</b>	Berylli	um $(n=2)$	Magnes	ium $(n=3)$
$isnp-np^2$	<sup>3</sup> P° - <sup>3</sup> P	0.466	25%	0.607	25%
nsnp-ns(n+1)s	${}^{3}P^{\circ} - {}^{3}S$	0.034	50%	$\frac{0.007}{0.139}$	10%
1011p-110 (11 1. 1/0	$^{1}P^{\circ}-^{1}S$	0.13	50%	$\frac{0.139}{0.18}$	10% 50%
$a_{n+1}$	P = 3 $^{3}P^{\circ} = {}^{3}D$	0.16	50%		
nsnp-ns(n+1)d	$^{1}P^{\circ} - ^{1}D$			$\frac{0.13}{0.11}$	25%
	$P^{\circ} - D^{\circ}$	0.19	50%	$\frac{0.11}{0.000}$	50%
nsnp-ns(n+2)d		0.084	50%	0.088	50%
nsnp-ns(n+3)d	${}^{1}P^{\circ} - {}^{1}D$	0.041	50%	0.10	50%
			f value	Uncertainty	
		Calciu		i = 4)	
$nsnp-np^2$	$^{3}P^{\circ}-^{3}P$		0.52	25%	
nsnp-ns(n+1)s	${}^{3}P^{\circ}-{}^{3}S$		0.12	25%	
-	${}^{1}P^{\circ} - {}^{1}S$				
nsnp-ns(n+1)d	${}^{3}P^{\circ}-{}^{3}D$		0.12	25%	
•	${}^{1}P^{\circ} - {}^{1}D$		0.27	50%	
nsnp-ns(n+2)d	$\overline{{}^{1}P^{\circ}} - \overline{{}^{1}D}$		0.044	50%	
nsnp-ns(n+3)d	$1 P^{\circ} - 1 D$			•••	

TABLE V. Comparison of f Values for miscellaneous multiplets of homologous atoms.<sup>a</sup>

<sup>a</sup>All data are from the critical data compilation in Ref. 8. Since the listed numbers are from numerous different sources, and are often averaged, it was not feasible to quote all the individual authors, and we have to refer to Ref. 8 for details.

<sup>b</sup>Paschen notation.

in simple atomic systems with one or two valence electrons, where the number of transitions is small. Thus, the available experimental material is essentially confined to a few series of helium, the alkalis, the alkaline earths, and a few other metals. Most theoretical investigations have been confined to these elements or their isoelectronic ions, too.

As an example for a regular monotonic decrease of f values, the resonance series of Na, 3s-np is presented in Fig. 8 in a plot of  $n^{*3}f$  versus effective principal quantum number  $n^*$ . The selected data are, for the principal resonance line, n=3, the average of six experimental and theoretical sources<sup>8</sup>; for n=4 to n=6 they are from the central field calculations by Prokof'ev.<sup>34</sup> and for n=7 to n=13 they are an average of the results of semi-empirical calculations by Anderson and Zilitis<sup>42</sup> and anomalous dispersion measurements of Fillipov and Prokof'ev.<sup>43</sup> (The latter are relative values put on an absolute scale by the best fit to Anderson and Zilitis's numbers.) The

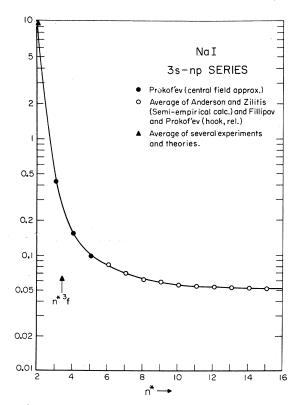


FIG. 8. Oscillator strengths multiplied by  $n^{*3}$  versus effective principal quantum number  $n^*$  for the resonance series 3s-np of Na I.

smooth overlap of the data originating from the different sources is quite remarkable. Except perhaps for the rather sudden decrease in f value from the 3s-3p to the 3s-4p transition which may indicate some cancellation effect, the series behavior is very much akin to that for the hydrogen series and approaches gradually the expected asymptotic "const.  $\times n^{*3}$ " dependence.

As a second example the 2s-np series of Li I has been selected which shows pronounced cancellation in the transition integral for n = 3. This is reflected both in a set of experimental data obtained from anomalous dispersion measurements by Fillipov<sup>44</sup> and in a set of theoretical data, obtained from the semi-empirical calculations of Anderson and Zilitis.<sup>42</sup> Both sets of data are shown in Fig. 9. A Z-dependence plot of the 2s-3p transition shows that the cancellation is most marked for Li I and becomes rapidly smaller for the higher ions.<sup>45</sup> It should be noted here that anomalies in the series behavior may occur quite often because of the earlier mentioned Cooper minima.<sup>18</sup> These are caused by the following: If the wave functions of the lower state involved have a node - for example, 2s; or 3s, 3p; or 4s, 4p, 4d - then the transition integral for a spectral series starting from these states, like 2s - np, will change sign somewhere along the series at some n, and the f value, being essentially the square of the transition integral, will go through a minimum. The minimum may occur anywhere along a series including the con-

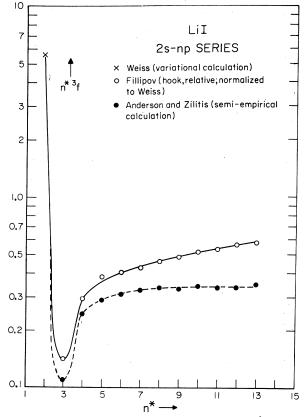


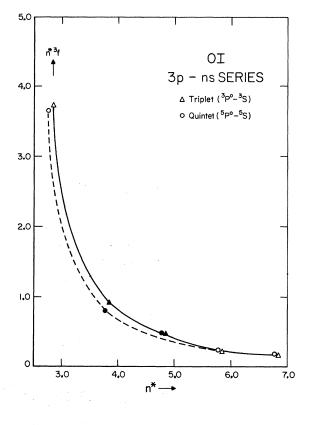
FIG. 9. Oscillator strengths multiplied by  $n^{*3}$  versus effective principal quantum number  $n^*$  for the resonance series 2s-np of Li I.

tinuum. Apparently, we observe here that this minimum occurs at a rather low value for n, namely, n=3. A similar case appears to be that of the 3s-np series Mg II, where the cancellation occurs at n=4, as may be seen from Table II.

Another interesting example is the 3p-ns series of O I (Fig. 10), insofar as it is one of the very few instances where some f-value material is available for a series of a fairly complex atomic system even though these data are by no means sufficient. For all transitions between n = 4 and n = 8 results from SCF calculations<sup>28</sup> are available. In addition, data have been obtained from the Coulomb approximation for n = 3 to n = 6, and the transitions 3p-5s and 3p-6s are also covered by several experiments all performed with stabilized arcs.<sup>46–48</sup> The measured values agree so closely with the before-mentioned material, that we have averaged all these results as discussed in Ref. 8.

## IV. SUMMARY

It has been shown that for atomic oscillator strengths many regularities exist, which provide a valuable means for evaluating the reliability of f values as well as an exceedingly simple way to determine additional f values. The regularities tie many individually determined data together so that now a reliable framework of f values can be established, and other data may be judged by the de-



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<sup>†</sup>Part of this work was performed while on leave at the Max Planck Institut für Extraterrestrische Physik, München, Germany.

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FIG. 10. Oscillator strengths multiplied by  $n^{*3}$  versus effective principal quantum number  $n^*$  for the 3p-nsseries of O I. The solid circles and triangles indicate that experimental values are involved in the data.

gree of fit into apparent systematic trends. Such consistency checks are especially important for theoretically determined data, for which normally no error analysis can be carried out. Thus the study of regularities should prove to be a valuable research tool for significantly improving our knowledge of atomic transition probabilities.

Among the various regularities, the systematic trends of *f* values in isoelectronic sequences appear to be of the greatest significance because they readily permit the determination of f values in highly charged ions, which are of much recent interest in plasma physics as well as space physics and astrophysics.

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#### PHYSICAL REVIEW

## VOLUME 175, NUMBER 1

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# Spins and Nuclear Moments of Sb<sup>115</sup>, Sb<sup>117</sup>, Sb<sup>118</sup>, Sb<sup>119</sup>, and Sb<sup>120</sup><sup>†</sup>

# A. D. Jackson, Jr., <sup>\*</sup> E. H. Rogers, Jr., <sup>‡</sup> and G. J. Garrett <sup>§</sup> Palmer Physical Laboratory, Princeton University, Princeton, New Jersey (Received 19 July 1968)

We have measured the spins and hyperfine structures of several antimony isotopes by atomicbeam magnetic-resonance methods. The isotopes were produced by proton bombardment of isotopically-enriched tin in the Princeton cyclotron. The experiments gave the following results:

	Isotope	I.	a (MHz)	b (MHz)
Sb <sup>115</sup> Sb <sup>117</sup> Sb <sup>118</sup> Sb <sup>119</sup>	(38 h)	5/2 5/2 1 5/2	-307.68(19) -237.91(15) $\pm 547(13)$ -307.16(6)	-3.7(5) -5.5(5)  -3.8(4)
Sb <sup>120</sup>	(16min) $\mu_I \ (\mu_N)$ (diamagnetically corrected)	1	±520(47) Q(b)	
	+3.46(1) +2.67(1) $\pm 2.46(7)$		-0.20(4) -0.30(5)	
	+3.45(1) ±2.34(22)		-0.21(4)	

The experiment on Sb<sup>119</sup> gives  $g_J$  (Sb) = -1.970 60(6). The magnetic moments of these and other antimony isotopes are discussed in terms of configuration-mixing calculations using matrix elements of the Hamada-Johnston potential.

## 1. INTRODUCTION

Theoretical investigations of nuclear structure have been particularly rewarding in regions of the periodic table where properties are known for a large number of related nuclei. In such cases it is often possible to explain the data with a relatively small number of parameters which are taken from theory or from best fits to experimental data. In view of the overdetermination of these parameters, the quality of the agreement between experiment and theory can be a useful measure of the validity of the nuclear model under consideration. The numerous isotopes of the element antimony provided an opportunity for work along these lines. There are two stable antimony isotopes and 32