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Résumé. — La méthode habituelle de détermination des probabilités de transitions atomiques comporte le développement de fonctions d'ondes atomiques suivant des fonctions de base mono-configurationnelles en couplage *LS*. Il arrive fréquemment que l'on ne puisse avoir confiance dans les valeurs obtenues car il se produit des effets d'annulation provenant du mélange des fonctions de base par couplage intermédiaire et par interaction de configuration. Des exemples, dans les spectres de Ar I, Al I, et Si I, sont discutés. On fait la revue des circonstances générales dans lesquelles les probabilités de transition calculées peuvent être considérées comme les plus sûres.

Abstract. — The common method of computing atomic transition probabilities involves the expansion of atomic wavefunctions in terms of single-configuration, *LS*-coupled basis functions. Calculated values are frequently rendered very unreliable by cancellation effects resulting from intermediate-coupling and configuration-interaction mixing of basis functions. Examples are discussed in the spectra of Ar I, Al I, and Si I. The general circumstances under which computed transition probabilities may be expected to be most reliable are reviewed.

1. Qualitative discussion. — Theoretically computed atomic transition probabilities are of a notoriously low general level of accuracy. Although the reasons for this are fairly well known, we wish here to review the subject, with particular emphasis on configuration-mixing effects, and using certain transitions in the spectra of Ar I, Al I, and Si I as illustrations.

Weighted transition probabilities or oscillator strengths for electric dipole transitions are computed in terms of the line strength S according to the equations [1].

$$gA = (64 \pi^4 e^2 a_0^2/3 \, h) \, S\sigma^3$$
$$= 2.026 \times 10^{-6} \, S\sigma^3 \, s^{-1}$$
$$= 0.667 \, 0 \, gf\sigma^2 \, s^{-1} , \qquad (1)$$

where σ is the wavenumber of the spectrum line in cm^{-1}. The line strength for a transition between two states ψ and ψ' is in turn usually computed as the reduced dipole matrix element

$$S^{1/2} = \left(\psi \left\| \sum_i r_i \right\| \psi'\right) ,$$

where the sum is over all N electrons of the atom and r_i is the radial position of the ith electron in Bohr units. Evaluation of this matrix element is accomplished by expanding the functions ψ and ψ' in terms of basis functions, corresponding (in the method which we wish to discuss in this paper) to pure *LS*-coupling states of specific configurations ; then

$$S^{1/2} = \sum_{\alpha LS} \sum_{\alpha' L'S'} (\psi \mid \alpha LSJ)\left(\alpha LSJ \left\| \sum_i r_i \right\| \alpha' \, L' \, S' \, J'\right) \times$$
$$\times (\alpha' \, L' \, S' \, J' \mid \psi')$$

$$= \sum_{\alpha LS} \sum_{\alpha' L'S'} (\psi \mid \alpha LSJ) \, \left(nl \parallel r \parallel n' \, l'\right) (ww')^{1/2} \times$$
$$\times (\alpha LSJ \parallel C_N^{(1)} \parallel \alpha' \, L' \, S' \, J')(\alpha' \, L' \, S' \, J' \mid \psi') . \qquad (2)$$

The first reduced matrix element in this final expression is a radial integral

$$\mathbf{I}_{nl,n'l'} \equiv \left(nl \parallel r \parallel n'l'\right) = (-1)^l \, [(2 \, l+1)(2 \, l'+1)]^{1/2} \times$$
$$\times \begin{pmatrix} l & 1 & l' \\ 0 & 0 & 0 \end{pmatrix} \int_0^\infty r P_{nl} \, P_{n'l'} \, dr \qquad (3)$$

involving the radial one-electron functions $P_{nl}(r)$ and $P_{n'l'}(r)$ for the jumping electron in the two basis configurations

$$\ldots (nl)^w \ldots (n' \, l')^{w'-1} \quad \text{and} \quad (nl)^{w-1} \ldots (n' \, l')^{w'} \ldots . \qquad (4)$$

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The second matrix element in (2) is an angular integral whose value [1, 2] is precisely determined by the angular quantum numbers of the basis states, but which need not concern us here.

The difficulty in computing an accurate value of S is in considerable degree due to the fact that the various terms of the double sum in (2), though all real, are in general partly positive and partly negative. The cancellation effects which may result (and which may be viewed as a sort of destructive interference among the various pairs of basis wavefunctions) are compounded by the fact that this sum must be squared to give a transition probability.

A convenient measure of this significant-figure loss is the ratio of S properly computed from (2) to the value of « S » which would be obtained by arbitrarily using the absolute value of each term in (2) [3]. Such a cancellation factor (CF) must be viewed with a certain amount of care -- its value may be fictitiously small as a result of making the calculation in an LS basis, whereas its value might have been nearly unity if the calculation had been made in a basis more appropriate to the coupling conditions actually present. However, most arrays of interest either lie close to LS coupling conditions or do not lie too close to any pure coupling scheme, and results computed in a pure LS basis give a reasonably accurate picture. Calculations made for a large number of transition arrays indicate that cancellation factors of 0.1 are quite common, and that factors of 10^{-4} are not at all uncommon ; indeed, on a purely statistical basis one would expect factors of 10^{-2} or less for ten percent of all lines. A line in the spectrum of Pb I has even been found experimentally [4] to show a cancellation factor of something like 10^{-9} or 10^{-10}.

Whether or not effects are accentuated by serious significant-figure loss, the uncertainties in computed transition probabilities are seen from (2) to arise from two sources. The first of these is an uncertainty in the computed value of the radial dipole integral I (which we assume to have a single value for transitions between all basis states belonging to a given pair of configurations). To the extent that configuration mixing can be neglected, the dipole integral can be factored out of the double summation in (2) ; it thus provides only a common scale factor for all lines of a transition array, and has no effect on *relative* line strengths. However, *absolute* line strengths are still uniformly affected by various types of uncertainty :

(*a*) It is well known [5] that results are particularly unreliable when there is a large degree of cancellation between positive and negative contributions to the radial integral in (3). A good example appears in the 3 p⁶-3 p⁵ 4 d and 3 p⁶-3 p⁵ 5 d transitions of the Ar I isoelectronic sequence, where 100 % cancellation is computed to occur in the vicinity of Ca III or Sc IV

[6], whereas lines of these arrays are actually found to be missing in Ti V [7].

(*b*) Even when there is not a great deal of mathematical cancellation, the radial integral is unreliable when the two functions P_{nl} and $P_{n'l'}$ are concentrated at much different values of r, since contributions to the integral then arise mainly from the outer tail of one function and the inner portion of the other, both of which are uncertain.

(*c*) Particularly poor also are cases (such as 3 p⁶-3 p⁵ 3 d in Ar I) which involve a wavefunction (in this case, 3 d) which is on the verge of collapsing to form the beginning of a transition or rare earth series, so that the computed radial function is unusually sensitive to the detailed form of the assumed central-field potential [6, 8].

The second basic source of uncertainty in (2) lies in the values of the wavefunction expansion coefficients (eigenvector components). For pure LS coupling in the single-configuration approximation, these coefficients are perfectly definite (being either unity or zero). But usually the departures from LS coupling are appreciable, and the coefficients then depend sizeably on the detailed nature of the computed coupling conditions. Uncertainties in configuration-mixing effects add further to the uncertainties of the coefficients.

When configuration mixing is important, then the various terms in (2) involve separate radial dipole integrals for the different pairs of configurations ; when the cancellation factor involved in the summation (2) is small, the relative values of these integrals may be very important, as will be seen in the examples to be discussed.

Contrary to the assumptions made above, calculations are frequently made which employ different radial wavefunctions for each term of a configuration. There are then several different radial dipole integrals even for a single pair of configurations ; the relative values of the different integrals are then critical if there is appreciable mixing of basis states and the cancellation factor is small. It is not logically consistent to use such variable dipole integrals if the eigenvector components are obtained by diagonalizing energy matrices which are set up on the assumption of a common set of radial wavefunctions for all basis states of a configuration. We consider it preferable to use the simpler, more-consistent approach except for very simple spectra showing a very close approximation to pure LS coupling conditions in all the configurations involved.

The examples which follow were calculated using a computer program described elsewhere [2], extended to include arbitrary types of configuration mixing. This program has been modified to automatically scale, by successively increasing factors, the various parameters involved in the calculation of energy levels and transition probabilities, and to plot the

results of each calculation on microfilm. The resulting computer-produced movies illustrate very vividly the sorts of destructive and constructive interference which occur in typical cases. Several of the figures in this paper consist of hand-tracings of selected frames from such movies.

2. Ar I isoelectronic sequence.

— As a first example of various aspects discussed qualitatively above, we consider the transitions 3 p^6-3 p^5 3 d in the Ar I isoelectronic sequence. These have been discussed previously [6] in the single-configuration approximation ; here we wish to discuss important configuration-interaction corrections.

TABLE I

Term energies in p^5 d configurations

^1P	: E_{av}	$- 0.200\ F^2$	$+ 1.267\ G^1$	$- 0.043\ G^3$
^1F	: E_{av}	$- 0.057\ F^2$	$- 0.067\ G^1$	$+ 0.325\ G^3$
^3D	: E_{av}	$+ 0.200\ F^2$	$- 0.067\ G^1$	$- 0.043\ G^3$
^1D	: E_{av}	$+ 0.200\ F^2$	$- 0.067\ G^1$	$- 0.043\ G^3$
^3F	: E_{av}	$- 0.057\ F^2$	$- 0.067\ G^1$	$- 0.043\ G^3$
^3P	: E_{av}	$- 0.200\ F^2$	$- 0.067\ G^1$	$- 0.043\ G^3$

In Table I we give the Coulomb-interaction contributions to the energies of the terms of p^5 d. Because of the large coefficient of G^1, the ^1P level tends to lie at an energy appreciably above those of the other eleven levels — particularly in the ions K II, Ca III, ... where G^1 is larger than either F^2 or G^3 [6]. Since the configuration-interaction matrix elements between two p^5 d configurations are identical in form to the single-configuration expressions (with E_{av}, F^2, G^1, and G^3 replaced by zero, R^2, R^1, and R^3, respectively), the largest configuration-interaction effects tend to be shown by these same $^1P_1$ levels. Both
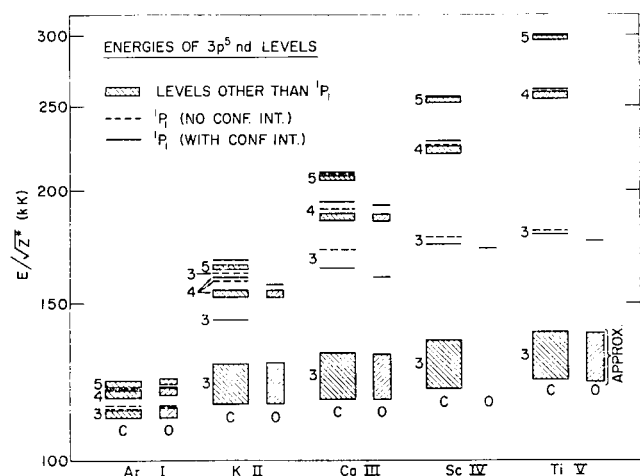
FIG. 1. — Computed (c) and observed (o) energies of the 3 p^5 3 d, 4 d, 5 d configurations in the Ar I sequence. Shaded block : the eleven levels of a configuration other than $^1P_1$. Dashed line : computed $^1P_1$ level neglecting configuration interaction. Solid line : $^1P_1$ level including configuration interaction.

of these properties of the $^1P_1$ levels are illustrated in figure 1 [9] ; note particularly that in K II the 3 d $^1P_1$ level is actually computed to lie above the 4 d $^1P_1$ level unless configuration mixing of the various nd configurations is taken into account [10].

Although the energy perturbations are most pronounced in K II, configuration-mixing effects on oscillator strengths are equally great in Ar I. These effects are shown in figure 2, where the three possible lines (one of negligible strength) 3 p^6 $^1S_0$-3 p^5 nd are shown for $n = 3, 4, 5,$ and 6. In section (a) of the figure
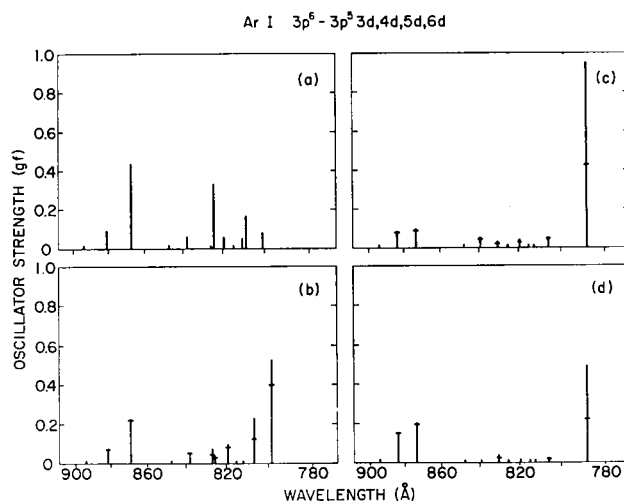
Ar I $3p^6 - 3p^5\,3d,4d,5d,6d$

FIG. 2. — Computer-plotted theoretical spectra, showing the three lines Ar I 3 p^6 $^1S_0$-3 p^5 nd $^3P_1$, $^3D_1$, $^1P_1$ for (left to right) $n = 3, 4, 5$ and 6. Sec. (a), zero configuration interaction ; (b) 50 % configuration interaction ; (c) full configuration interaction ; (d) same as (c) except with $(3\ p\ \|\ r\ \|\ 4\ d) = 0$. The tic marks on the spectrum lines indicate the configuration purity of the associated nd quantum states.

(zero configuration interaction), oscillator strengths decrease with increasing n in the manner to be expected from the monotonic decrease in value of the radial dipole integrals [11] shown in Table II. With interactions among all four configurations included (sections b and c), the phase relations for the $^1S_0$-3 d $^1P_1$ line are such (the eigenvector component for the 3 d $^1P_1$ basis state having opposite sign to the components for all higher nd $^1P_1$ basis states) that all nd ($n > 3$) contributions to the oscillator strength tend to cancel the 3 d contribution. For the highest $^1P_1$ state, on the other hand, phase relations (a common sign for eigenvector components of all $^1P_1$ basis states) are such that all contributions to oscillator strength add together. Thus the net result of configuration mixing is a shift in oscillator strength from the 3 d (and 4 d and 5 d) to the 6 d line — or more generally, if additional configurations are included, from low-d to high-d lines [12].

The computed strengths of the highest-d lines included in the calculation are of course fictitious : the excess oscillator strength would be passed on to still higher-d lines (and probably into the contin-

TABLE II

HX reduced dipole elements $(3 \text{ p} \parallel r \parallel n\text{d})$ *and cancellation factors for* 3 p^6-3 p^5 *nd transitions*

	3 p-3 d	3 p-4 d	3 p-5 d	3 p-6 d
Ar I	0.878(− 0.999)	0.736(− 0.997)	0.561(− 0.995)	0.429(− 0.991
K II	2.063(− 0.996)	0.429(− 0.600)	0.207(− 0.457)	0.129(− 0.396;
Ca III	1.848(− 0.993)	0.081(− 0.117)	0.002(− 0.005)	− 0.012(0.035)
Sc IV	1.631(− 0.991)	− 0.090(0.127)	− 0.092(0.202)	− 0.074(0.224)
Ti V	1.457(− 0.989)	− 0.188(0.264)	− 0.140(0.311)	− 0.103(0.320)
Cr VII	1.201(− 0.986)	− 0.281(0.412)	− 0.175(0.418)	− 0.121(0.408)
Fe IX	1.023(− 0.983)	− 0.314(0.491)	− 0.180(0.466)	− 0.121(0.442)
Ni XI	0.892(− 0.980)	− 0.322(0.540)	− 0.174(0.491)	− 0.115(0.457)

uum) if these states were included in the calculation. However, the strengths of the 3 d lines are realistic, as shown by the good agreement with experiment in Table III. It is important to note that if one uses eigenvectors obtained by a single-configuration least squares fitting of the experimental 3 d energy levels, then the computed strengths of the $^1S_0$-$^3D_1$ and $^1S_0$-$^1P_1$ lines are about equal, as observed, but are too large by a factor of about 3 ; one could interpret

TABLE III

Oscillator strengths gf $(\times$ 1 000)
for Ar I 3 p^6 $^1S_0$-3 p^5 3 d, 4 s

	$^3P_1$	$^3D_1$	$^1P_1$	$^3P_1$	$^1P_1$
Least square ab initio (HX)	1	274	260	57	226
3 d only	3	96	438	—	—
3 d-4 d	3	91	144	—	—
3 d-5 d	3	88	113	—	—
3 d-6 d	3	86	101	—	—
4 s only	—	—	—	63	220
4 s-6 s	—	—	—	63	208
Experiment [a] {	—	87	101	59	228
	—	± 6	± 14	± 3	± 21

[a] LAWRENCE (G. M.), *Phys. Rev.*, 1968, **175**, 40 ; WIESE (W. L.), BRIDGES (J. M.), KORNBLITH (R. L.), and KELLEHER (D. E.), *J. Opt. Soc. Am.*, 1969, **59**, 1206.

this as meaning simply that the value used for $(3 \text{ p} \parallel r_1 \text{ 3 d})$ was very poor (too large by a factor $\sqrt{3}$). However, the fact of the matter is that the 3 d levels can be fit accurately either in the single-configuration or in the multi-configuration approximation (the fit of the 3 d $^1P_1$ level being accomplished through G^1 in the first case and the R^1 in the second), and in either case the inferred coupling conditions are such as to give about equal strengths for the two lines ; however, only in the second case does a transfer of oscillator strength to higher nd configurations occur, so that the absolute strengths of the 3 d lines are as low as observed. Note also that if a multi-configuration least-squares energy level fit is attempted, the mathematical equations to be solved are very ill-conditioned, and there is no accurate way of ascertaining to what degree the fitting of the $^1P_1$ levels is to be accomplished through the parameters G^1 and to what degree via the R^1 ; theoretical parameter values are indispensable as a guide.

By comparison, configuration-interaction effects among the (low) 3 p^5 ns configurations are small, and it makes little difference whether one employs a single- or multi-configuration, theoretical or least-squares calculation (see Table III).

Table IV gives computed wavelengths, oscillator strengths, and transition probabilities for the 3 d resonance lines of Ar I to Ni XI, computed including interactions among 3 d to 6 d. The table supersedes

TABLE IV

Wavelengths (Å), *oscillator strengths, and transition probabilities* (s^{-1}) *of the resonance lines* 3 p^6 $^1S_0$-3 p^5 3 d *in the* Ar I *isoelectronic series, computed including configuration interactions among* 3 d-6 d.

Transition :	$^1S_0$-$^1P_1$				$^1S_0$-$^3D_1$				$^1S_0$-$^3P_1$			
	(a)				(a)				(a)			
	λ_{exp}	λ_{calc}	gf	gA	λ_{exp}	λ_{calc}	gf	gA	λ_{exp}	λ_{calc}	gf	gA
Ar I	866.80	875.79	0.10	8.83+8	876.06	886.46	0.086	7.37-8	894.31	897.03	0.002 6	2.13
K II	—	483.08	1.51	4.31-10	550.30	551.98	0.002	4.64+7	607.92	609.20	0.000 2	3.87
Ca III	357.97	346.01	4.74	2.64 11	439.69	437.62	0.002	5.65-7	490.55	489.32	0.000 2	4.93
Sc IV	289.85	285.03	5.61	4.61 11	—	369.60	0.002	9.01 7	—	413.87	0.000 2	7.25
Ti V	252.96	247.82	5.32	5.78+11	323.37	322.01	0.002	1.50+8	363.15	360.48	0.000 2	1.13
Cr VII	202.78	200.98	4.45	7.35+11	259.18	259.04	0.004	3.83 8	—	289.87	0.000 3	2.35 7
Fe IX	171.06	170.43	3.76	8.65 11	217.10	217.27	0.006	8.99 8	—	243.27	0.000 4	4.35
Ni XI	148.37	148.30	3.27	9.90 11	—	187.16	0.010	1.95 9	—	209.90	0.000 5	7.14 7

[a] Ref. [9].

an earlier one [6] in which configuration interaction was neglected : comparison of the two shows the expected decrease in magnitude of the effects as ionization stage increases beyond K II.

All of the results discussed above for the Ar I sequence were computed *ab initio*, using *HX* [11] radial wavefunctions, with the electrostatic and spin-orbit radial integrals scaled down by factors of 0.85 and 0.95, respectively [6]. The results are not greatly different from *HF* values in the case of K II and higher members of the sequence, where the 3 d wavefunction is tightly bound, close to the core electrons. In Ar I, however, the 3 d function is teetering on the verge of collapsing into the core, and is consequently quite sensitive to the assumed central-field potential. The *HF* potential is sufficiently different from the *HX* one that the *HF* values of the integrals R^k are considerably smaller than the *HX* values ; interactions among the 3 d-6 d configurations are thus too small to produce nearly equal strengths for the 3 d ^3D and ^1P lines, though this equality would perhaps be achieved if many higher configurations were included. The points we wish to make here are simply that p^5 d $^1P_1$ (and, analogously, p^5 p $^1S_0$, d^9 d, $^1S_0$, etc.) states tend to show strong Rydberg-series type interactions with accompanying interference effects in transition probabilities, and that oscillator strengths are particularly difficult to compute accurately for the relatively unstable d and f electrons near the beginnings of the transition and rare-earth series, respectively.

3. Al I- group elements.

— It is well known that configuration interactions of the type sp^{m+2}-$s^2 p^m$ d are usually quite strong. A particularly interesting example (with $m = 0$) occurs in Al I : the series of observed ^2D terms is sufficiently regular that it is difficult to say which of the ^2D terms should be assigned to 3 s 3 p^2, and so the observed terms are usually simply labeled as the Rydberg series 3 s^2 nd ^2D ($n \geqslant 3$) as though 3 s 3 p^2 ^2D did not even exist [13-15]. It has been variously suggested that the 3 s 3 p^2 ^2D term should be identified with the lowest [13] observed ^2D, with the second or third such term [16-19] (because theory locates it at about this point, and because there are fine-structure, quantum-defect, and oscillator-strength anomalies at this point), and with an observed absorption feature a short distance above the series limit [20, 21]. Recently it has been shown theoretically by Weiss [22] and semi-empirically by Eriksson [23] that the unperturbed position of the sp^2 ^2D term indeed lies low in the s^2 d Rydberg series (accounting for the above-mentioned anomalies in this region), but that configuration interactions are so strong as to push the sp^2 ^2D term to its observed position above the series limit. Weiss showed also that configuration-mixing effects accounted for the abnormally-low observed oscillator strength for the 3 s^2 3 p $^2P^0$-3 s^2 4 d ^2D transition [24].

For higher elements of the Al I group   Ga I,

In I, and Tl I the observed anomalies are rather different : in particular, the abnormally weak lines lie higher up the series — at 9 d or 10 d in In I, for example [25]. These differences arise from the fact that the unperturbed position of the sp^2 ^2D term lies much higher for the three heavy elements than for Al, as is shown both by Hartree-Fock calculations and by semi-empirical fitting of the observed unperturbed sp^2 terms. In ions, on the other hand, the sp^2 ^2D term lies much lower — usually below the lowest member of the Rydberg series.

It is thus instructive to examine the qualitative changes which are computed to occur as the unperturbed energy of the sp^2 ^2D term in varied from a position below the lowest s^2 d ^2D to a position above the series limit, keeping all other quantities fixed. Figure 3 shows such computed changes in oscillator strengths, all fixed quantities (radial dipole integrals
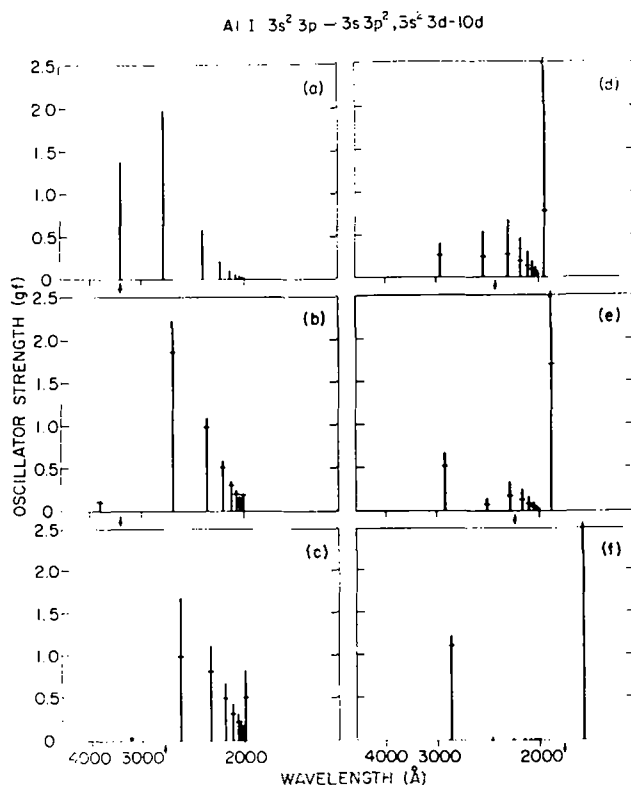

Al I $3s^2 3p - 3s 3p^2, 3s^2 3d-10d$

FIG. 3. — Computed spectra for Al I 3 s^2 3 p $^2P_{3/2}$-3 s 3 p^2. 3 s^2 3 d-10 d $^2D_{5/2}$. Sec. (a), no configuration interaction ; secs. (b)-(f), full configuration interaction, but variable unperturbed position of the sp^2 ^2D term, as indicated by the arrow below each frame. In secs. (a)-(c) the sp^2 line is the longest-wavelength one ; in secs. (d)-(f), the sp^2 line is the shortest-wavelength one, with computed gf · 2.9, 4.0, and 5.0, and computed purity   27 °/₀, 45 %, and 79 %, respectively.

and energy parameters) being *HX* values for Al I, except with the spin-orbit and configuration-interaction parameters scaled by factors of 0.95 and 0.85, as was done for Ar I ; in each section of the figure, an arrow indicates the unperturbed position of the sp^2 ^2D term. Sections (b) and (c) of the figure, with the sp^2 ^2D term below the lowest s^2 d ^2D, show strong cancella-

tion in the s^2 p $^2P^0$-sp^2 ^2D transition and enhancement of all s^2 p-s^2 d lines, and are similar to the situations in most ions [26]. Section (d), with the unperturbed sp^2 ^2D near the second s^2 d term, is analogous to the first few ions of the Tl I series, except that interactions in these ions are smaller and the sp^2 ^2D remains near its unperturbed position. Section (e), with the unperturbed sp^2 ^2D term at about the (unperturbed) position of the third member of the s^2 d series but with the perturbed position above the series limit, and with an abnormally low oscillator strength for the second ^2D, corresponds to the actual conditions in Al I. Section (f), with the unperturbed sp^2 ^2D and the oscillator-strength minimum both lying much higher, are analogous to conditions in Ga I, In I, and Tl I. (*HX* and *HF* calculations have been made for all four elements. *HX* and *HF* energies and radial integrals are approximately equal, and values for the three heavy elements are semi-quantitatively the same as for Al I, except for the higher sp^2 ^2D. Detailed results for oscillator strengths and ^2D term splittings are in fairly good agreement with experiment, but are too extensive to include here.)

In the Al I case (Fig 3e), the computed cancellation factors for the 3 d and 4 d lines (which are much weaker than when configuration interaction is neglected) are 0.20 and 0.04, respectively. Values of the *CF* for the 5 d to 10 d lines range from 0.13 to 0.22 ; in spite of this, the computed oscillator strengths are *larger* with than without configuration interaction. For the three heavier elements, values of the *CF* beyond the second or third series members are of the order 0.1 to 0.01, with strong destructive interference, making *ab initio* computed oscillator strengths for these lines very unreliable.

Similarly to the high-d lines in the Ar I case, the oscillator strengths computed for the sp^2 ^2D lines [Fig. 3, Secs. (d)-(f)] are much too high. observed values being of the order 0.1 or less [27-29]. As before, the discrepancy is probably due to neglect of configuration interaction with continuum states, most of the oscillator strength from the low s^2 d lines actually going into the continuum rather than into the semi-discrete sp^2 ^2D lines.

4. Si I 3 s^2 3 p 4 f-3 s 3 p^3, 3 s^2 3 p*n*d. — Recently,

several experimental and theoretical papers have appeared which are concerned with oscillator strengths of visible and near infrared lines of Si I, of interest for the determination of the abundance of silicon in the sun [30-34]. The disagreement between experiment and calculation was mostly quite large (factors of 3 to 5), and is mainly the result of the same type of cancellation effects appearing in the examples already discussed.

One set of lines investigated experimentally by Schulz-Gulde [30] consists of transitions between 3 p 4 f levels and the lowest odd ^3D term. The latter term is referred to in the literature as both 3 s 3 p^3 $^3D^0$

and 3 s^2 3 p 3 d $^3D^0$. As will be seen later. the second designation is probably better [35], but in any case we again have strong configuration mixing of the type sp^{m+2}-s^2 p^m d considered in Al I, this time with *m* = 1. However, there is no tendency for the sp^3 $^3D^0$ term to be perturbed above the series limit, in the manner of the sp^2 ^2D in Al I, partly because the $^3D^0$ lies lower (between the first two members of the *n*d series) and partly because the interactions are somewhat smaller. Indeed, it is reasonably accurate to include in calculations only the three configurations 3 d, sp^3, and 4 d which were considered by Warner [32] and by Armstrong and Liebermann [34].

The principal calculations described below were made using the same least-squares eigenvectors [35] employed by Warner [32], but with radial dipole integrals computed from configuration-average *HF* wavefunctions (Table V) rather than from scaled Thomas-Fermi-Dirac functions for individual terms. The difficulty in computing accurate oscillator strengths arises partly from the nature of the 4 f eigenvectors, which are more closely *jK* (*jl*) than *LS* coupled, but mainly from the fact that the 3 d eigenvectors, though close to *LS* coupling, show strong mixing with sp^3 and 4 d states.

The computed odd energy levels are shown in figure 4, both excluding and including the configuration-interaction terms. Note that the 3 d $^1D^0$ level

TABLE V

Reduced dipole elements $(l \parallel r \parallel l')$ *for* Si I

Array	HF(CF)	Warner (ave)	A-L (ave)
3 p 3 d-3 p 4 f	— 15.14(1.00)	— 19.2[a]	- — 19.6[a]
sp^3-3 p 4 f	0.00	0.0	0.0
3 p 4 d-3 p 4 f	28.40(— 0.94)	27.6[a]	28.4[a]
Ratio (4 d/3 d)	— 1.88	— 1.44	— 1.45
3 p 4 s-3 p 4 p	7.41(— 1.00)	6.71	
3 p 4 s-3 p 5 p	0.70(— 0.19)	0.78	0.85
3 p 5 s-3 p 4 p	- 6.67(0.80)	— 6.17	
3 p 5 s-3 p 5 p	14.65(- 0.98)	13.8	

[a] Weighted average for *n*d $^3D^0$ only. (It has been assumed that the value 12.7 in Armstrong and Liebermann's Table II should read 127, and the signs have been assumed to be the same as for our and Warner's values.)

is essentially unperturbed, because the sp^3 $^1D^0$ level lies far away ; the 3 d $^3D^0$ term, on the other hand, is pushed by the close-lying sp^3 $^3D^0$ from a position above the 3 d $^1D^0$ to a position well below the $^1D^0$.

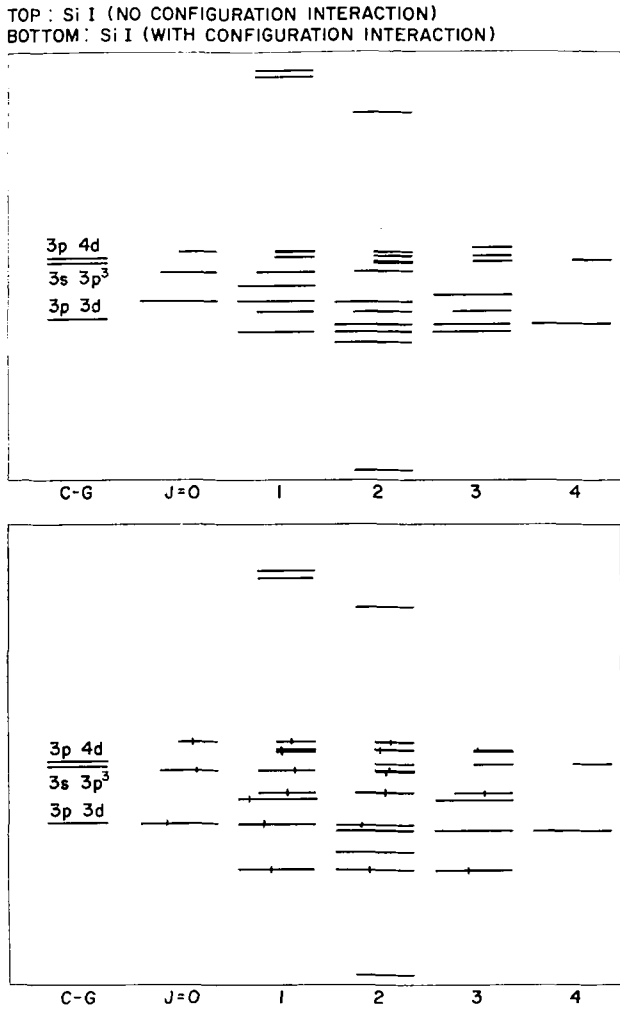Computed oscillator strengths for the set of lines

$$3\text{ d }^{1,3}D^0\text{-}4\text{ f}$$

TOP : Si I (NO CONFIGURATION INTERACTION)
BOTTOM : Si I (WITH CONFIGURATION INTERACTION)

FIG. 4. — Computer-plotted energy levels of Si I 3 s² 3 p 3 d (longest lines), 3 s 3 p³ (intermediate-length lines), and 3 s² 3 p 4 d (shortest lines) for least-squares parameter values : lower figure, including configuration interaction ; upper figure, same as lower except with all configuration-interaction parameters set to zero. The center-of-gravity of each configuration is shown at the left. Tic marks on the levels indicate the configuration purity of the states (high purity for tic marks at the left) when the purity is less than 90 %. The lowest level is sp³ $^5S_2^0$, the next four levels are the 3 d $^1D_2^0$, $^3D_{123}^0$ of interest here, and the highest J = 2 level is sp³ $^1D_2^0$.

are shown in figure 5, with the configuration-interaction parameters multiplied successively by 0, 2/3, and 1. Note that the interactions not only perturb the positions of the 3 d $^3D^0$ lines, but also greatly reduce the line strengths. This loss of strength is a result of destructive interference between the 3 d and 4 d contributions to the 3 d $^3D^0$ states, as is indicated by the fact that most of the lines have cancellation factors greater than 0.5 when either the configuration interaction or the 4 d — 4 f dipole integral is set to zero (Fig. 5a and 5d, respectively), but that all lines have CF's less than 0.06 when all quantities are given their « correct » values (Fig. 5c). By contrast, all but one of the eight 3 d $^1D^0$ lines

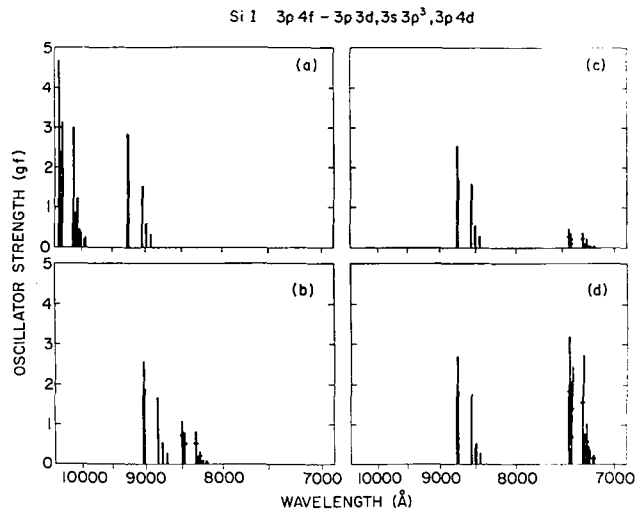always have CF's greater than 0.8, and all show very little change in strength.

FIG. 5. — Computed spectra for transitions between 3 p 4 f and the lowest odd $^{1,3}D$ terms of Si I, using least-squares energy parameter values and HF radial dipole integrals. In sections (a)-(c), the configuration-interaction parameters have been scaled by factors of 0, 2/3, and 1, respectively ; the lines with relatively fixed wavelength and oscillator strength involve the $^1D_1^0$ level, the others involve the $^3D^0$ levels. Tic marks indicate the configuration purity (when less than 90 %) of the $^{1,3}D^0$ states. Section (d) is the same as (c) except that the 4 f-4 d radial dipole integral has been set to zero, and shows that the small oscillator strengths in (c) are the result of destructive interference between the 3 d and 4 d contributions to the low $^3D^0$ states.

The computed 3d $^3D^0$-4 f oscillator strengths (corresponding to Fig. 5c) are given in column «LS-HF» of Table VI ; the agreement with experiment is fairly good considering the small cancellation factors involved in the calculation and the experimental uncertainties of about a factor two [30]. It is interesting to note that the three weakest computed lines (with wavelengths in parentheses in Table VI) have never been observed experimentally [35]. The third line (λ = 7 239.1) has a computed CF of 0.05 like most of the other lines, and is weak primarily because of operation of LS selection rules — the 3 d level being fairly pure $^3D^0$, and the 4 f level fairly pure K = 9/2 which necessarily is pure $^{1,3}G$. The other two lines show CF < 10^{-4} ; of this, a factor of about 0.05 is again due to 3 d-4 d mixing in the 3 D⁰ state, and the remaining factor of < 0.002 is accidentally small because of the detailed intermediate-coupling nature of the 4 f wavefunctions (this factor being ~ 0.07 for pure jK-coupling functions).

In contrast to the above results, the values given by Armstrong and Liebermann and by Warner are mostly much poorer. Since least-squares eigen-vectors were used in these calculations also, the much larger oscillator strengths are presumably due to the different values which they used for the radial dipole integrals. A partial verification of this is given by

TABLE VI

Oscillator strengths for Si I 3 p 3 d(+ sp³ + 3 p 4 d) ³D⁰-3 p 4 f

3 d	4 f[a]	λ[b]	$10^3\,gf$				
			Exp[c]	LS-HF[d]	A-L[e]	W[f]	W$_{ave}$[g]
	—	—	—	—	—	—	—
³D₁⁰	3/2[5/2]₂	7 226.2	39.2	55.0	60	285	170
	3/2[3/2]₁	7 184.9 }	20.2	37.8	40	62.9	114
	3/2[3/2]₂	7 184.6 }		7.0	9.1	11.6	23.3
	1/2[5/2]₂	7 405.8 }	484	373	414	1 480	1 133
³D₂⁰	1/2[7/2]₃	7 409.1 }		183	568	748	554
	1/2[5/2]₃	7 415.9 }	365	319	—	1 130	965
	1/2[5/2]₂	7 415.3 }		28.3	92	155	87.3
	3/2[7/2]₃	7 275.3	99.2	104	383	509	335
	3/2[5/2]₃	7 235.8 }	68.7	33.0	96	228	95.4
	3/2[5/2]₂	7 235.3 }		63.8	215	201	198
	3/2[3/2]₁	7 193.9 }	20.2	12.5	40	22.8	38.1
	3/2[3/2]₂	7 193.6 }		38.9	117	69.3	115
³D₃⁰	1/2[5/2]₃	(7 431.6) }	....	0.01	—	18.9	0.10
	1/2[5/2]₂	(7 430.9) }		0.01	0.07	1.3	0.05
	1/2[7/2]₃	7 424.6 }	485	17.9	56	79	54.5
	1/2[7/2]₄	7 423.5 }		498	1 517	1 990	1 500
	3/2[7/2]₃	7 290.3 }	635	12.6	46	60.3	40.6
	3/2[7/2]₄	7 289.2 }		392	1 313	1 770	1 223
	3/2[5/2]₃	7 250.6 }	90.8	150	485	345	461
	3/2[5/2]₂	7 250.1 }		7.0	23	16.3	21.8
	3/2[9/2]₄	(7 239.1)	—	1.1	—	2.6	2.4
	3/2[3/2]₂	7 208.2	—	8.1	27	14.4	25.0

(a) Levels designated in jK-coupling notation, $j_1[K]_j$.

(b) Radziemski and Andrew [35]. Wavelengths in parentheses are computed values for unobserved lines.

(c) Schulz-Gulde [30].

(d) This investigation ; least-squares eigenvectors, with Hartree-Fock radial dipole integrals.

(e) Armstrong and Liebermann [34] ; least-squares eigenvectors, with dipole integrals from scaled Hartree-Fock-Slater wavefunctions.

(f) Warner [32] ; least-squares eigenvectors, with dipole integrals from scaled Thomas-Fermi-Dirac wavefunctions.

(g) This investigation ; least-squares eigenvectors, using the averages of Warner's dipole integrals given in Table V.

column « W_{ave} » in Table VI, which we computed using the weighted averages of Warner's radial integrals given in Table V ; compared with our values obtained with HF integrals, use of the « W_{ave} » values decreases the degree of cancellation sufficiently to increase all line strengths by a factor of about three, giving oscillator strengths comparable with Warner's and Armstrong's. The importance of using accurate dipole integrals is evident.

Completely *ab initio* HF calculations (for eigenvectors as well as dipole integrals) give oscillator strengths of an accuracy comparable to the LS-HF values, provided interactions with several additional 3 pnd configurations are included. However, this fact must be considered largely accidental since the computed sp³ energy levels agree comparatively

poorly with experiment, and in particular the sp³ ³D⁰ is computed to lie below the 3 d ³D⁰ term.

5. Si I 3 p 4 s-3 p 5 p. — Most of the remaining lines measured by Schulz-Gulde [30] belong to the 4 s-5 p array. Mixing of 4 s and 5 p with other configurations is very small, and single-configuration oscillator strengths computed from least-squares eigenvectors and a HF dipole integral are given in column « LS-HF » of Table VII ; agreement with experiment is reasonably good for all except the 4 s ³P⁰-5 p ³D lines. Note that though we have fairly good LS coupling (the average purities being 99 % and 87 % for the 4 s and 5 p configurations, respectively), there are nonetheless numerous lines with small computed cancellation factors, resulting

TABLE VII

Oscillator strengths for Si 1 3 p 4 s-3 p 5 p

4 s	5 p	$\lambda^{(a)}$	$10^3\ gf$ Exp[b]	LS-HF[c]	A-L[d]	W[e]	HF[f]	HF(ci)[g]
$^3P_0^0$	$^1P_1$	(5 847)	—	1.7(0.38)	—	0.89	2.1	0.2
$^3P_1^0$		5 874	—	5.8(1.00)	—	4.27	5.0	0.8
$^3P_2^0$		(5 942)	—	0.0(0.03)	—	0.00	0.0	0.0
$^1P_1^0$		6 332	5	16.7(0.83)	—	0.00	16.8	18.6
$^3P_0^0$	$^3D_1$	5 780	3.09	17.4(1.00)	17.5	16.9	14.6	4.5
$^3P_1^0$	$^3D_1$	(5 806)	—	3.1(0.20)	2.9	1.67	4.8	0.1
	$^3D_2$	5 793	6.19	38.6(1.00)	38.6	34.5	35.5	8.4
$^3P_2^0$	$^3D_1$	(5 873)	—	0.2(0.05)	0.1	0.15	0.6	0.0
	$^3D_2$	(5 859)	—	4.4(0.25)	4.2	2.08	7.5	0.0
	$^3D_3$	5 798	9.45	60.5(1.00)	60.3	47.9	6.03	8.9
$^1P_1^0$	$^3D_1$	6 254	—	4.9(0.86)	—	0.07	5.4	7.9
	$^3D_2$	6 238	—	0.1(0.05)	—	1.18	0.0	1.0
$^3P_0^0$	$^3P_1$	5 666	6.50	7.0(0.44)	13.9	15.5	4.3	6.0
$^3P_1^0$	$^3P_0$	5 701	6.28	8.8(1.00)	17.9	15.1	9.0	40.4
	$^3P_1$	5 690	9.60	15.8(0.89)	32.8	30.2	12.2	12.5
	$^3P_2$	5 646	5.72	4.4(0.21)	8.6	10.6	7.9	46.7
$^3P_2^0$	$^3P_1$	5 754	0.89	1.3(0.06)	2.3	0.79	8.8	3.2
	$^3P_2$	5 708	26.50	39.0(1.00)	80.0	61.0	36.7	152
$^1P_1^0$	$^3P_0$	(6 132)	—	0.0(0.02)	—	0.21	0.0	0.1
	$^3P_1$	(6 120)	—	2.1(1.00)	—	0.39	1.0	0.4
	$^3P_2$	6 068	—	0.6(0.29)	—	1.75	0.3	0.4
$^3P_0^0$	$^3S_1$	(5 598)	—	0.0(0.00)	0.1	0.44	5.3	33.3
$^3P_1^0$		5 622	0.88	1.4(0.09)	3.1	5.86	4.3	24.4
$^3P_2^0$		5 684	16.8	24.9(1.00)	64.0	56.0	17.2	57.7
$^1P_1^0$		(6 041)	—	0.1(0.33)	—	0.07	0.1	0.0
$^3P_1^0$	$^1D_2$	(5 542)	— —	0.4(0.10)	—	0.05	0.1	0.0
$^3P_2^0$		5 603	—	0.4(0.19)	—	0.95	0.2	0.9
$^1P_1^0$		5 949	51.2	41.4(1.00)	124	118	42.1	201
$^3P_1^0$	$^1S_0$	(5 389)	—	0.0(0.02)	—	0.02	0.0	0.2
$^1P_1^0$		5 772	12.1	8.7(1.00)	40.8	39.9	8.8	148

[a] Radziemski and Andrew [35] ; wavelengths in parentheses are solar or computed values for lines not observed in the laboratory.
[b] Schulz-Gulde [30], except that the value for $^1P^0$-^1P is a rough estimate from intensities observed in Ref. [35].
[c] Numbers in parentheses are computed cancellation factors.
[d] Armstrong and Liebermann [34].
[e] Warner [32].
[f] *Ab initio* Hartree-Fock, single-configuration results.
[g] *Ab initio* Hartree-Fock results, including 4 s-5 s and 4 p-5 p configuration interactions.

from the intermediate-coupling mixing of the LS-coupled basis states.

The calculations by Warner [32] and by Armstrong and Liebermann [34] were also made with least-squares eigenvectors. However, they used different dipole integrals for different pairs of LS basis functions, and the effect is clearly evident in Table VII : their ^{3}P-^{3}D integrals were about the same as ours, and all other integrals were considerably larger except for Warner's ^{1}P^0-^{1}P integral, which was extremely small. The ^{1}P^0-^{1}P result, particularly, illustrates our remarks at the end of Sec. 1 concerning the use of one vs. many dipole integrals.

Completely *ab initio* single-configuration *HF* results are approximately the same as our least-squares values, except for three weak lines which have small cancellation factors. The factor-of-six error is still present for the ^{3}P^0-^{3}D lines (which have a *CF* of unity), and this prompted us to look for an explanation through configuration interaction effects. An obvious candidate is mixing of 3 p 5 p with 3 p 4 f because the only terms common to these configurations are ^{1,3}D. However, the computed mixing is very small, and effects on computed oscillator strengths are negligible.

Series-type mixing is also very small (for 4 s-5 s, less than 0.2 % ; and for 4 p-5 p, less than 1 %, except 4 % for ^{1}D and 13 % for ^{1}S). However, Table VII shows that inclusion of 4 s-5 s and 4 p-5 p interactions has very large effects on computed oscillator strengths — the ^{3}P^0-^{3}D values are greatly improved, but most other values are ruined. The reason for these large (and generally meaningless) effects may be seen from Table V to lie in the fact that the value of $(4 \text{ s} \parallel r \parallel 5 \text{ p})$ is an order of magnitude smaller than the other three dipole elements involved. Thus, for example, a 1 % admixture of 4 p into a 5 p state means eigenvector components of about ($\pm$ 0.1, 0.995), which together with the 4 s-4 p and 4 s-5 p dipole elements give (if the angular factors are equal) a value of $S^{1/2}$ proportional to $\pm$ 0.1 × 7 + 0.995 × 0.7 = $\pm$ 0.7 + 0.7 and therefore an oscillator strength equal to either zero or four times the single-configuration value, depending on the phase relations.

A large number of different calculations have been made, using different configuration-interaction parameter values and dipole-element values, and including various additional configurations. In no case was a good overall set of oscillator strengths obtained. The conclusion — not surprisingly — is that in a case of this type it is not safe to attempt a calculation in anything more than the single-configuration approximation, even though configuration-interaction effects may in fact be important so far as oscillator strengths are concerned. (Nor are cancellation factors computed as defined in Sec. 1 any guide to the reliability of computed configuration-interaction effects in such cases ; in the present example, the apparently-improved ^{3}P^0-^{3}D values are small as the result of *CF*'s < 0.008,

whereas the very poor values for other lines are large because of   *CF*'s > 0.3.)

6. **Summary.** — The discussion and examples given above may be summarized by listing the following set of conditions which are conducive to maximum reliability of computed transition probabilities.

A. *Conditions involving the entire transition array.*

1. Highly stable radial wavefunctions ; e. g., high ionization stages, and no d function near the start of a transition series nor f function near the start of a rare earth series.

2. No interactions with arrays having much larger magnitudes of radial dipole element $(nl \parallel r \parallel n' \, l')$.

3. Large overlap of radial wavefunctions (e. g., nearly equal values of $< r >_{nl}$ and $< r >_{n'l'}$), and little cancellation between positive and negative contributions to the radial dipole element $(nl \parallel r \parallel n' \, l')$

4. Small configuration mixing.

5. Pure coupling in each configuration.

6. Lowest configuration of a Rydberg series (maximum separation from other configurations, and minimum phase uncertainties in eigenvector components of perturbing configurations).

B. *Conditions on individual lines.*

1. Little cancellation in the double sum over eigenvector components (large value of the *CF*).

2. Extreme values of J and J' (small-sized energy matrices, and hence few eigenvector components).

3. Lines involving levels each of which has an energy, relative to other levels of the same parity and J value, that is insensitive to modest variation in relative values of the energy parameters F^k, G^k, ζ, and R^k. (This criterion is pertinent particularly to ab initio calculations, as opposed to least-squares fitting of experimental levels.)

C. *Calculational procedure.*

1. Use both theory and experiment (i. e., make judicious compromise between theoretical energy parameter values, and parameter values which give the best agreement with experimental energy levels and g-values — particularly noting discrepancies which may indicate neglected configuration-interaction effects, etc.).

2. In complex transition arrays, or when there are appreciable departures from LS-coupling conditions, calculate radial dipole integrals from configuration-average wavefunctions rather than from wavefunctions for specific LS terms.

For practical applications of computed oscillator strengths, many of the above criteria are automatically met. For example, in astrophysical applications one tends to employ only the strongest lines, and this implies lines without serious cancellation effects, and

lines of large (J, J') from low-lying configurations. Still, when wavelength or similar restraints limit the choice. one needs to beware of cases such as Si I 3 d $^3D^0$-4 f where an entire set of lines suffers strong cancellation effects, and good agreement between computed and observed *relative* line strengths is no indication whatever of the accuracy of the computed *absolute* values.

7. **Acknowledgements.** — The author's interest in the Si I arrays discussed above was first aroused by L. J. Radziemski. Jr. and D. C. Griffin, who made a number of the preliminary calculations. He is indebted also to D. C. Griffin [36] for providing a numerical *HF* program capable of handling the *nd* configurations of Ga I, In I and Tl I, and to L. Minnhagen for providing unpublished observations on K II.

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