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THE CALCULATION OF THE ABSOLUTE STRENGTHS OF SPECTRAL LINES

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It is shown that in calculating transition integrals it is permissible to neglect the departure of the potential of an atom or ion from its asymptotic Coulomb form. This enables a general analytical expression for the transition integral to be derived. Tables are compiled from which the absolute strengths of large numbers of spectral lines can at once be obtained if the term values of the upper and lower levels are known. *s–p*, *p–d* and *d–f* transitions are all treated. Comparison with experimental data shows that for the simpler systems (i.e. systems with a single electron outside closed shells) the method gives remarkably accurate results; indeed, it appears superior to the normal rather laborious procedure involving the computation of the necessary wave functions, in each individual case, by solution of the appropriate Hartree or Fock differential equation. The method (in its most elementary form) may not be so satisfactory for complex systems (i.e. systems with unclosed shells) owing to difficulties associated with the identification of certain energy parameters. However, the rather scanty comparison data available suggest that even for such systems it yields useful (and in some cases precise) information on the line strengths.

Incidentally, in the course of the work the accuracy of a few wave functions based on the self-consistent field approximation (including exchange) was tested by using them to evaluate line strengths from both the dipole moment and the dipole velocity formulae. Appreciable defects were revealed.

1. Introduction

For a number of purposes, particularly in astrophysical applications, it is desirable to know the oscillator strengths f and spontaneous transition probabilities A associated with spectral lines. These related quantities can be expressed in terms of the line strengths S: thus

$$f=\frac{8\pi^2mc}{3he^2}\frac{1}{g_1\lambda}S, \tag{1}$$

$$A=\frac{64\pi^4}{3h}\frac{1}{g_2\lambda^3}S\,\text{sec.}^{-1}. \tag{2}$$

m, e, c and h have here their standard significance, λ is the wave-length of the radiation absorbed or emitted, and g_1 and g_2 are the respective statistical weights of the lower and upper levels concerned in the transition (see Condon & Shortley 1935). It is convenient to have these formulae in numerical form. Substituting for the various constants it can readily be seen that with λ in Ångström units (10^{-8} cm.) and S in atomic units ($a_0^2e^2$), then

$$f=\frac{3{\cdot}04\times10^2}{g_1\lambda}S, \tag{3}$$

and

$$A=\frac{2{\cdot}02\times10^{18}}{g_2\lambda^3}S\,\text{sec.}^{-1}. \tag{4}$$

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Now it can be shown that $S = \mathscr{S}(\mathscr{M})\,\mathscr{S}(\mathscr{L})\,\sigma^2,$

where $\mathscr{S}(\mathscr{M})$ is a factor depending on the particular multiplet of the transition array, $\mathscr{S}(\mathscr{L})$ is a factor depending on the particular line of the multiplet, and σ^2 is simply

$$\frac{1}{(4l^2-1)}\left(\int_0^\infty R_i R_f r\,dr\right)^2, \tag{5}$$

l being the *greater* of the two azimuthal quantum numbers involved in the transition and R_i/r and R_f/r being respectively the initial and final radial wave functions of the active electron normalized in atomic units. $\mathscr{S}(\mathscr{M})$ can be obtained from two sets of tables published by Goldberg (1935, 1936), and $\mathscr{S}(\mathscr{L})$ can be obtained from the papers either of White & Eliasen (1933) or of Russell (1936). The calculation of S, and hence of f and A, therefore requires only the evaluation of σ^2. The procedure usually adopted has been to treat each individual case of interest separately, the determination of the wave functions, and the evaluation of the integral occurring in (5), being carried out by numerical methods except for hydrogen-like systems. As the work is laborious and is now of little intrinsic interest to the theoretician (except perhaps in the developing of methods for improving the accuracy) the demand of the astrophysicists, that many transitions should be treated, does not seem likely to be met. The object of the present paper is to compile tables from which approximate results for large numbers of transitions in both neutral atoms and positive ions can be derived rapidly.

2. METHOD

In the standard central field model the functions R_i and R_f satisfy a differential equation of the form

$$\frac{d^2R}{dr^2}+\left(2v-\frac{l(l+1)}{r^2}-\epsilon\right)R=0, \tag{6}$$

v being the potential, l the azimuthal quantum number and ϵ the energy parameter. Here (and throughout the remainder of the paper) all quantities are expressed in atomic units. The normal method of solving such an equation is by integrating numerically outwards from the origin, ϵ being adjusted to be an eigenvalue. The disadvantage of this is that a knowledge of v is required; furthermore, systematization of the calculation to cover the different levels of a number of atoms and ions is scarcely feasible.

An examination of the central fields that have been computed shows that v approximates closely to its asymptotic form before the region is reached which gives the dominant contribution to the transition integral. This can be demonstrated by comparing $\int_0^{r_c} R_i R_f r\,dr$ and $\int_{r_c}^\infty R_i R_f r\,dr$, where r_c is the value of r at which v is within some factor F (differing but little from unity) of its asymptotic form. Table 1 gives the relevant data for two representative cases of s–p transitions, F being arbitrarily chosen to be 1·01. As can be seen the ratios of the outer to the inner integrals are considerable. For p–d and d–f transitions the corresponding ratios are naturally even larger.

TABLE 1

system	transition	r_c	$\int_0^{r_c} R_i R_f r dr$	$\int_{r_c}^{\infty} R_i R_f r dr$	references
Na I	$3s$–$4p$	1·5	0·004	0·386	Fock & Petrashen (1934, 1935)
O II	$3s$–$3p$	2·0	0·05	4·02	Hartree, Hartree & Swirles (1939); Bates & Damgaard (1948)

It is clear therefore that the wave functions appearing in (5) need only be accurate at moderate and large radial distances; and for determining such wave functions it would appear sufficient to replace v by its asymptotic form C/r, C being the excess charge on the nucleus when the active electron is removed. The differential equation for R thus becomes

$$\frac{d^2R}{dr^2}+\left(\frac{2C}{r}-\frac{l(l+1)}{r^2}-\epsilon\right)R=0. \tag{7}$$

A solution of this satisfying the boundary condition

$$R\to 0 \quad \text{as} \quad r\to\infty, \tag{8}$$

can be written down for any given ϵ. Since in general ϵ is not an eigenvalue of the differential equation as modified the solution normally diverges at the origin; but as will be seen later this causes no difficulty. The form of solution chosen as most appropriate for the present purpose is that given by Eddington (1927) and Suguira (1927),

$$R=W_{n^*,l+\frac{1}{2}}(2Cr/n^*), \tag{9}$$

n^* being the quantity $(C/\epsilon^{\frac{1}{2}})$ and $W_{n^*,l+\frac{1}{2}}$ being the confluent hypergeometric function defined as the solution of the equation

$$d^2W_{n^*,l+\frac{1}{2}}/dr^2+\left[\frac{2C}{r}-\frac{C^2}{(n^*)^2}-\frac{l(l+1)}{r^2}\right]W_{n^*,l+\frac{1}{2}}=0,$$

which has the asymptotic expansion

$$W_{n^*,l+\frac{1}{2}}(2Cr/n^*)=[\exp(-rC/n^*)]\,(2rC/n^*)^{n^*}\left\{1+\sum_{t=1}^{\infty}\frac{a_t}{r^t}\right\}, \tag{10}$$

with

$$a_1=\frac{n^*}{2C}[l(l+1)-n^*(n^*-1)], \tag{11}$$

and

$$a_t=a_{t-1}\left\{\frac{n^*}{2tC}[l(l+1)-(n^*-t)\,(n^*-t+1)]\right\}. \tag{12}$$

The a-coefficients can readily be tabulated systematically for a wide range of n^*.

Hartree (1927) has discussed the normalization and has suggested (without giving a proof) that the confluent hypergeometric function should be multiplied by the factor

$$1/[n^{*2}\Gamma(n^*+l-1)\,\Gamma(n^*-l)/C]^{\frac{1}{2}}. \tag{13}$$

This is certainly the correct factor for integral values of n^* (Waller 1926) and, as Hartree pointed out, it satisfies the necessary recurrence relation for values of n^* differing by integers. Further, in several particular cases of non-integral n^*, Hartree checked by numerical methods that it provides an excellent approximation; and this was confirmed by the present authors. The factor was therefore adopted.

Consider now the evaluation of

$$\int_0^\infty R_i R_f r\,dr. \tag{14}$$

Let the values of n^* and l associated with R_i be $n^{*\prime}$ and l', and let those associated with R_f be $n^{*\prime\prime}$ and l''. The general terms in the normalized expansion of R_i and R_f may then be written in the form

$$\sum_{p'=0}^{\infty} c_{p'}(n^{*\prime}, l')\, C^{\frac{1}{2}}(Cr)^{n^{*\prime}-p'} \exp\left(-Cr/n^{*\prime}\right) \tag{15}$$

and

$$\sum_{p''=0}^{\infty} c_{p''}(n^{*\prime\prime}, l'')\, C^{\frac{1}{2}}(Cr)^{n^{*\prime\prime}-p''} \exp\left(-Cr/n^{*\prime\prime}\right), \tag{16}$$

respectively, the coefficients $c_{p'}(n^{*\prime}, l')$ and $c_{p''}(n^{*\prime\prime}, l'')$ being known constants. It follows that

$$\int_0^\infty R_i R_f r\,dr = \sum_{p'}\sum_{p''}\int_0^\infty c_{p'}(n^{*\prime}, l')\, c_{p''}(n^{*\prime\prime}, l'')\, (Cr)^{n^{*\prime}+n^{*\prime\prime}+1-p'-p''} \exp\left[-Cr\left(\frac{n^{*\prime}+n^{*\prime\prime}}{n^{*\prime}n^{*\prime\prime}}\right)\right] dr, \tag{17}$$

$$= \frac{1}{C}\sum_{p'}\sum_{p''} c_{p'}(n^{*\prime}, l')\, c_{p''}(n^{*\prime\prime}, l'')\left(\frac{n^{*\prime}+n^{*\prime\prime}}{n^{*\prime}n^{*\prime\prime}}\right)^{n^{*\prime}+n^{*\prime\prime}+2-p'-p''} \Gamma(n^{*\prime}+n^{*\prime\prime}+1-p'-p''). \tag{18}$$

This series terminates if $n^{*\prime}$ and $n^{*\prime\prime}$ are integers, but in general is of the form of an asymptotic expansion. It can, however, be evaluated with sufficient accuracy by ignoring terms for which

$$p'+p'' < n^{*\prime}+n^{*\prime\prime}-1. \tag{19}$$ †

The first omitted term is in fact unimportant, except when the sum of the others is passing through a zero. The significance of condition (19) can perhaps most clearly be visualized by noting that it corresponds to neglecting in the integrals of (17) powers of r less than 2. The main contribution from these comes from the region close to the origin. Thus the maximum of

$$r^s \exp\left[-Cr\left(\frac{n^{*\prime}+n^{*\prime\prime}}{n^{*\prime}n^{*\prime\prime}}\right)\right] \tag{20}$$

occurs at a radial distance r_m given by

$$r_m = \frac{s n^{*\prime} n^{*\prime\prime}}{C(n^{*\prime}+n^{*\prime\prime})}. \tag{21}$$

The limitation imposed on s (that it should be below 2) is a compromise aimed at keeping r_m as small as possible (it can be seen from (21) that it is always much less than the total extent of the wave function), without at the same time causing it to lie within the region where the true potential departs too seriously from a Coulomb potential. For the two transitions Na I ($3s$–$4p$) and O II ($3s$–$3p$) (used as illustrations in table 1), the values of r_m are 1·9 and 1·2 respectively.

The computations involved in the evaluation of the series, though tedious, readily lent themselves to systematic work. They were carried through for s–p, p–d and d–f transitions.

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† An alternative procedure would have been to terminate the series at the minimum term. It was considered, however, that the use of condition (19) was preferable as the object was to obtain transition integrals for actual atomic potentials rather than for the exact Coulomb potential. Further, the extension of the series to the minimum term would have involved additional labour. The distinction between the two alternative criteria is in any case academic, since, as has been stated, the omitted terms are negligible—at most they only seem to affect the final answers in the fourth decimal place.

To enable the results finally obtained to be presented in a reasonably compact form, some care is necessary in the method of tabulation. If $\sigma^2(n^*_{l-1}, l-1;\, n^*_l, l;\, C)$ was merely given for a number of specific values of n^*_{l-1} and n^*_l, very close intervals would be required to permit interpolation to intermediate values. Now in the transition $(n^*, l-1) \rightarrow (n^*, l)$ the integral (14) can be expressed as

$$\frac{3}{2}\frac{n^*}{C}(n^{*2}-l^2)^{\frac{1}{2}}. \tag{22}$$

This suggested the possibility of writing $\sigma(n^*_{l-1}, l-1;\, n^*_l, l;\, C)$ in the form

$$\sigma(n^*_{l-1}, l-1;\, n^*_l, l;\, C) = \frac{1}{C}\mathscr{F}(n^*_l, l)\,\mathscr{I}(n^*_{l-1}, n^*_l, l), \tag{23}$$

where

$$\mathscr{F}(n^*_l, l) = \left[\frac{3n^*_l}{2}\left\{\frac{(n^{*2}_l-l^2)}{(4l^2-1)}\right\}^{\frac{1}{2}}\right], \tag{24}$$

and†

$$\mathscr{I}(n^*_{l-1}, n^*_l, l) = \left[\frac{2C}{3n^*_l}\frac{1}{(n^{*2}_l-l^2)^{\frac{1}{2}}}\right]\int_0^\infty R(n^*_{l-1}, l-1, C)\,R(n^*_l, l, C)\,r\,dr. \tag{25}$$

It was found that such subdivision of $\sigma(n^*_{l-1}, l-1;\, n^*_l, l;\, C)$ greatly facilitated the presentation.

The simple function $\mathscr{F}(n^*_l, l)$ is given in table 2‡ for $l=1$ (i.e. *s–p* transitions), $l=2$ (i.e. *p–d* transitions) and $l=3$ (i.e. *d–f* transitions). The intervals are sufficiently close to allow the value at any n^*_l to be obtained by linear interpolation.

The function $\mathscr{I}(n^*_{l-1}, n^*_l, l)$ presents rather more difficulty, as for it three double-entry tables (corresponding to $l = 1, 2$ and 3) are necessary. Now the variation of $\mathscr{I}(n^*_{l-1}, n^*_l, l)$ along a line of constant $n^*_{l-1}-n^*_l$ is very slow; in particular (as can be seen from (22)) there is no variation along the line $n^*_{l-1}-n^*_l = 0$, the value of the function being unity there. Hence the most suitable variables to use would appear to be, not n^*_{l-1} and n^*_l, but instead $n^*_{l-1}-n^*_l$ and n^*_l. These are employed in tables 3, 4 and 5. The interval for the variable $n^*_{l-1}-n^*_l$ was taken to be 0·1 throughout, and that for the variable n^*_l was taken to be 0·5 in tables 3 and 4 and to be 1·0 in table 5. In reading from the tables linear interpolation is generally sufficient. The reason for taking the intervals of the variable n^*_l as 1·0 in table 5 is that n^*_3 (which, of course, relates to *f*-levels) is always so close to being integral that smaller intervals are superfluous.

Now that the tables have been described it is convenient to discuss in greater detail than hitherto the actual calculations performed. The evaluation of $\mathscr{F}(n^*_l, l)$ was trivial and requires no comment. But the preparation of the tables of $\mathscr{I}(n^*_{l-1}, n^*_l, l)$ was a formidable task, and some mention may be made of the procedure adopted to minimize the labour.

Owing to the gradual nature of the variation of the function across a $n^*_{l-1}-n^*_l$ row it was found that if the computations were carried out for those columns with n^*_l integral, the figures in the intermediate columns could be obtained by interpolation. This was a very important simplification; not only was the number of computations reduced, but also each was made easier, for as a consequence of n^*_l being integral one of the two series occurring in (17) terminated. Though a certain loss of accuracy must be caused, it is unlikely to be at all

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† It will be noted that as the integral occurring in (25) is inversely proportional to C, $\mathscr{I}(n^*_{l-1}, n^*_l, l)$ itself is independent of C.

‡ Tables 2, 3, 4 and 5 are printed at the end of the paper (pp. 120 to 122).

serious. The values interpolated are probably rarely wrong by more than one unit in the last place, except in the case of those in the column furthest to the left (where the variation of the function is most rapid), and even here the fractional error must usually be small. The most dubious interpolated figures occur in table 4 and are enclosed in brackets; fortunately, they are located in a relatively unimportant region.

The computations become more and more laborious as n_l^* increases. It was decided therefore to make a limited use of extrapolation. This might at first appear a somewhat dubious operation, but in fact it is fully justifiable. Thus in the relevant region, at the extreme right of the tables, $\mathscr{I}(n_{l-1}^*, n_l^*, l)$ varies remarkably slowly along a row. In addition, it was possible to lock the extrapolated columns at a number of points by evaluating the function at integral values of both n_{l-1}^* and n_l^* using a formula due to Gordon (1929), who showed that for such values of n_{l-1}^* and n_l^*

$$\int_0^\infty R(n_{l-1}^*, l-1, C)\, R(n_l^*, l, C)\, r\, dr = PU, \tag{26}$$

where
$$P = \frac{(-1)^{(n_{l-1}^*-l)}}{4C(2l-1)!}\left\{\frac{(n_l^*+l)!\,(n_{l-1}^*+l-1)!}{(n_l^*-l-1)!\,(n_{l-1}^*-l)!}\right\}^{\frac{1}{2}}\frac{(4n_l^*n_{l-1}^*)^{(l+1)}\,(n_l^*-n_{l-1}^*)^{(n_l^*+n_{l-1}^*-2l-2)}}{(n_l^*+n_{l-1}^*)^{n_l^*+n_{l-1}^*-1}} \tag{27}$$

and
$$U = \left[F\left(-n_l^*+l+1,\ -n_{l-1}^*+l,\ 2l,\ \frac{-4n_l^*n_{l-1}^*}{(n_l^*-n_{l-1}^*)^2}\right) - \left(\frac{n_l^*-n_{l-1}^*}{n_l^*+n_{l-1}^*}\right)^2 F\left(-n_l^*+l-1,\ -n_{l-1}^*+l,\ 2l,\ \frac{-4n_l^*n_{l-1}^*}{(n_l^*-n_{l-1}^*)^2}\right)\right], \tag{28}$$

the F's being hypergeometric functions.

The extrapolated parts of the tables are as follows:

Table 3: $n_l^* = 5{\cdot}0$; $n_{l-1}^* - n_l^* = +1{\cdot}0$ to $+3{\cdot}0$,
$n_l^* = 6{\cdot}0$; $n_{l-1}^* - n_l^* = -3{\cdot}0$ to $+2{\cdot}0$,
$n_l^* = 7{\cdot}0$; $n_{l-1}^* - n_l^* = -3{\cdot}0$ to $+1{\cdot}0$.

Table 4: $n_l^* = 6{\cdot}0$; $n_{l-1}^* - n_l^* = +1{\cdot}0$ to $+2{\cdot}0$,
$n_l^* = 7{\cdot}0$; $n_{l-1}^* - n_l^* = -3{\cdot}0$ to $+1{\cdot}0$.

Table 5: none.

Gordon's formula (or, where available, the simpler formulae for special series derived by Kupper (1928)) was also used to check the computations at integral n_{l-1}^* and n_l^* throughout the tables.†

When the investigation was well on the way to completion it was discovered that Hylleraas (1945) had published a paper on the same problem. The basic assumptions made were similar, but the wave functions, instead of being represented by series expansions, were represented by contour integrals which led to an elegant mathematical development. However, Hylleraas confined his attention to *s*–*p* transitions, and even for these did not cover as wide a range of n_l^* as does the present work; nor were his results presented in a suitable form for interpolation. None the less the figures he gave provided a valuable check on certain parts of

† It may be mentioned incidentally that the results at these integral values published by earlier workers contain a few numerical errors.

table 3. They were also used to compile the following sections of this table (the computations for which had not been carried through when the existence of Hylleraas's paper was realized):

$$
\begin{aligned}
n^*_l &= 2{\cdot}0, & n^*_{l\;1}-n^*_l &= -2{\cdot}0 \text{ to } -1{\cdot}0,\\
n^*_l &= 3{\cdot}0, & n^*_{l-1}-n^*_l &= -3{\cdot}0 \text{ to } -2{\cdot}0,\\
n^*_l &= 4{\cdot}0, & n^*_{l-1}-n^*_l &= -4{\cdot}0 \text{ to } -3{\cdot}0,\\
n^*_l &= 2{\cdot}0, 3{\cdot}0, 4{\cdot}0, & n^*_{l-1}-n^*_l &= +3{\cdot}0 \text{ to } +4{\cdot}0.
\end{aligned}
$$

The most serious limitation on the range of the tables is that they do not include columns for which n^*_l is less than $l+1$ (i.e. is less than 2 for *p*-levels, less than 3 for *d*-levels and less than 4 for *f*-levels). In some systems these are required in dealing with transitions between the lower levels. They were omitted, as the validity of the approximation is rather uncertain in such cases (cf. § 3·1). Extrapolation to values of n^*_l above about $l+0{\cdot}5$ appears, however, to be justifiable provided n^*_{l-1} is not too small (say for $n^*_{l-1}-n^*_l$ positive).

Thus far the value to be used for the energy parameter ϵ has not been discussed. For systems with a single electron outside closed shells (such as Al I and Mg II) it may reasonably be taken to be the energy required to remove the electron from the particular level concerned, since Hartree & Hartree (1938) have shown that the corresponding parameter in the Fock wave equations is identical with this energy. As will be seen, the accuracy of the values of σ^2 it gives fully vindicates the interpretation adopted. The position regarding complex systems is less certain, but perhaps as a first approximation (which may be improved later) the same significance may be attached to ϵ here also. Some justification for this assumption is provided by the results it appears to yield—though it must be admitted that the comparison data available is not yet as comprehensive as could be desired.

With ϵ as defined, the related quantity n^* (given by $\epsilon^{\frac{1}{2}}/C$) is simply the *effective principal quantum number*. It is, of course, immediately obtainable from tables of term values, such as those by Bacher & Goudsmit (1932).

3. Comparison with results derived by other methods

3·1

It is desirable first to verify the assumption that the departure of the true potential of atoms and ions from the Coulomb form is unimportant as far as the transition integral is concerned. This issue can be separated from others that might arise by comparing the values of σ^2 obtained by self-consistent field calculations with the values obtained by the method described in the present paper (which in future will be termed the Coulomb approximation), *the eigenvalues found in the self-consistent calculations being here used as the energy parameters.* The relevant data for a number of transitions are collected in table 6. It is apparent that for the lighter elements the assumption mentioned causes no significant error; and even for the heavy element mercury (which has a nuclear charge of 80) the inaccuracy introduced by it is remarkably small, particularly for transitions involving the higher levels.

In connexion more especially with certain *s*–*p* transitions one minor reservation must be made. Consider a system for which in its ground configuration the outer electrons are *p*-electrons. The n^*-value associated with them is generally below 2: for example, in Al I ($1s^2, 2s^2, 2p^6, 3s^2, 3p, {}^2\mathrm{P}$) it is only $1{\cdot}50_8$. The *p*-wave function involved is consequently very compact, and a considerable part of it lies within the region where the departure of the potential from the Coulomb form is pronounced (particularly as other electrons have the same principal quantum number as the electron considered). For transitions to *d*-levels this is usually unimportant owing to the minuteness of *d*-wave functions at small radial distances. But for transitions to *s*-levels it may cause considerable error since *s*-wave functions have an antinode close to the origin.

TABLE 6

transition		σ^2 (Coulomb approximation)†	σ^2 (self-consistent field method)	reference
Li I	2*s*–2*p*	6·6	6·7	Hargreaves (1928)
O II	3*s*–3*p*	5·4	5·5	Bates & Damgaard (1948)
	3*p*–3*d*	1·5	1·5	
Si II	4*s*–4*p*	11	11	Bates & Damgaard (1948)
Ca II	4*s*–4*p*	5·6	6·1	Hartree & Hartree (1938)
	4*p*–3*d*	1·2	1·1	
Hg I	6*s*–6*p*	4·0	4·8	Misra (1948)
	7*s*–6*p*	4·3	5·1	
	7*s*–7*p*	30	31	
	6*p*–6*d*	1·2	1·3	
	6*p*–7*d*	0·19	0·21	
	7*p*–6*d*	7·8	8·1	
	7*p*–7*d*	3·4	3·3	

† See text for choice of energy parameters in this particular table.

3·2

It remains to examine whether satisfactory results can be achieved by using term values as the energy parameters. A difficulty is that though a fair amount of comparison data is available the degree of accuracy is usually unknown. This must be borne in mind in the subsequent discussion. Any discrepancies that may appear are not necessarily to be attributed to deficiencies in the Coulomb approximation—they may instead be due (and in some cases they are certainly due) to inaccuracies in the comparison data. It is thus important to view the results as a whole.

The main sources of information may be listed as briefly as follows:

(*a*) *Theory A.* Calculations based on a potential of the Wentzel-Brillouin-Kramers or of the Hartree type with an adjustable polarizability correction‡ which is chosen so that the eigenvalues agree with the observed energy levels. It is realized that this approximation (which has been criticized by McDougall 1932) is in certain respects similar to the one under examination; and, indeed, is superior only in that it uses a more accurate central field. Results based on it will, however, be included in the survey because of the closeness with which they agree with experimental data where this is available. The method has only been applied to systems in which the orbital electron lies outside closed shells where its validity is most plausible (cf. § 2·2).

(*b*) *Theory B.* Purely theoretical calculations not involving any semi-empirical assumptions. A number of techniques have been developed. Of these the direct variational method is only practicable for such special cases as helium. The most generally applicable method is that of the self-consistent field either (i) without, or (ii) with, exchange terms. It is known that the wave functions obtained if exchange is neglected tend to be too diffuse. This would

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‡ 'Adjustable polarizability correction' is, of course, an empirical correction to the basic atomic field designed to cover various defects in it (such as those arising from exchange effects).

lead one to suspect that they would not yield accurate values of the transition integrals. It will be apparent later that the method is, indeed, not in general reliable, approximately correct results only being given when interference effects are unimportant (i.e. when there is not close approach to cancellation of the positive and negative portions). The inclusion of the exchange terms certainly leads to an improvement, but even with them the wave functions may remain rather too diffuse. The extent of the defect is not easy to assess. Owing to the elaborate nature of the basic equations and to the difficulty of refining them further (to allow for such effects as configuration interaction), there is a natural tendency to assume that the final accuracy achieved is satisfactory. This assumption, however, is only partially justified. To investigate the matter some calculations were performed in which the matrix elements, instead of being expressed in the usual dipole length form

$$\left|\int \chi_i \,.\, \mathbf{r} \,.\, \chi_f^* \, d\tau\right| \tag{29}$$

were expressed in the dipole velocity form

$$\left|\frac{1}{h\nu}\int \chi_i \nabla(\chi_f^*)\, d\tau\right| = \left|\frac{1}{h\nu}\int \nabla(\chi_i)\, \chi_f^*\, d\tau\right|, \tag{30}$$

χ_i and χ_f being the initial and final wave functions and the other symbols being as already defined. In connexion with the evaluation of the continuous absorption cross-section of the negative ion of hydrogen Chandrasekhar (1945) has pointed out that, while (29) and (30) are formally equivalent, they are not generally of equal merit in practical computations. With (29) the most important contribution to the matrix element comes from comparatively large radial distances, whereas with (30) it comes from moderate radial distances. Since the wave functions are better determined in this latter region the use of formula (30) might seem to be preferred. However, formula (29) has the advantage that it does not depend on the gradient of the wave functions. It would appear best therefore to use both wherever possible. Unfortunately, for many cases the errors in the values of the transition integral obtained by the two formulae are of the same sign. In consequence the true value does not necessarily lie between the calculated values; nor if these calculated values are approximately equal does it necessarily follow that they are accurate. However, inspection of the way in which the integrand varies with radial distance is usually sufficient to show what is the position.

The reduction of the dipole velocity matrix element to a suitable form for numerical work is elementary. It can readily be shown that in the expression for σ^2 the quantity

$$\int_0^\infty R_{l-1} R_l r \, dr \tag{31}$$

must be replaced by

$$\left\{\frac{2}{E}\int_0^\infty R_{l-1}\left(\frac{l}{r}R_l + R_l'\right) dr\right\} = \left\{\frac{2}{E}\int_0^\infty R_l\left(\frac{l}{r}R_{l-1} - R_{l-1}'\right) dr\right\}, \tag{32}$$

the dashes signifying differentiation with respect to r, and E being the energy (in Rydbergs) of the photons involved in the transitions. These expressions have been evaluated for a few representative transitions using wave functions published by other authors together with the observed values of E. The results are included in the tables to be given later. It is sufficient to mention here that in some instances they differ considerably from the results obtained using the dipole moment matrix element—a result of some general interest in connexion with the accuracy of exchange wave functions.

(*c*) *Experiment.* The earlier experimental work has been reviewed by Korff & Breit (1932) and by Mitchell & Zemansky (1932). Recent developments in technique are described in the papers of Ornstein & Key (1934), Ornstein, van Hengstrum & Brinkman (1938), and King & Stockbarger (1939). No attempt at a critical survey of the field can be made in the present paper.

TABLE 7

				theory B			
				(i) exchange	(ii) exchange included		
transition		Coulomb approx.	theory A	neglected	formula (29)	formula (30)	experiment
Li I	$2s-2p$	5·5	5·5 (1)	6·7 (2)	5·6 (3)	5·9	5·5 (4)
	$2s-3p$	0·018	0·020	0·042	0·011	0·0091	0·020
	$2s-4p$	0·014	0·014	0·050	0·010	0·0087	0·014
	$2s-5p$	0·0069	0·0071	0·016	0·0055	0·0048	0·0088
Na I	$3s-3p$	6·1	6·3 (5)	—	6·7 (6)	5·9	6·5 (7), 6·8 (8, 9)
	$3s-4p$	0·052	0·052	—	0·051	0·039	0·053 (9)
	$3s-5p$	0·0067	0·0069	—	—	—	0·0066
	$4s-3p$	6·1	6·1	—	6·2	6·1	—
	$4s-4p$	34	33	—	38	34	—
	$5s-3p$	0·27	—	—	—	—	0·30 (10)
	$6s-3p$	0·071	—	—	—	—	0·074
	$3p-3d$	2·2	2·2	—	—	—	2·2
	$3p-4d$	0·18	0·20	—	—	—	0·20
	$3p-5d$	0·051	—	—	—	—	0·044
Mg II	$3s-3p$	2·7	2·8 (11)	—	—	—	—
	$3p-3d$	0·86	0·85	—	—	—	—
	$3d-4f$	0·69	0·67	—	—	—	—
Al I	$4s-4p$	17	19 (11)	—	—	—	—
	$4s-5p$	0·24	0·25	—	—	—	—
	$4p-3d$	2·9	3·2	—	—	—	—
Si II	$4s-4p$	8·6	9·2 (11)	11·4 (12)	—	—	—
	$4p-3d$	1·3	1·5	—	—	—	—
	$3d-4f$	0·63	0·64	—	—	—	—
K I	$4s-4p$	8·3	9·0 (11)	10·4 (13)	—	—	8·4 (14, 15, 16)
	$4s-5p$	0·065	0·061	—	—	—	0·040 (15), 0·12 (16)
	$4s-6p$	0·0093	0·0087	—	—	—	0·0033, 0·014
	$4p-6s$	0·36	—	—	—	—	0·49 (14)
	$4p-7s$	0·098	—	—	—	—	0·13
	$4p-3d$	3·4	3·1 (17)	—	—	—	—
	$4p-4d$	0·0001	0·0004	—	—	—	0·0003
	$4p-5d$	0·0058	0·0070	—	—	—	0·0057
Ca II	$4s-4p$	4·3	4·8 (18)	6·1 (19)	5·1 (19)	4·1	—
Cu I	$4s-4p$	2·9	—	—	—	—	3·4 (20)
Cs I	$6s-6p$	9·9	—	—	—	—	9·3 (21)
	$6s-7p$	0·13	—	—	—	—	0·072

References. (1) Trumpy (1930); (2) Hargreaves (1928); (3) Fock & Pedrashen (1935); (4) Filippov (1931); (5) Prokofjew (1929); (6) Fock & Pedrashen (1934); (7) Minkowski (1926); (8) Ladenburg & Thiele (1931); (9) Filippov & Prokofjew (1929); (10) Ornstein & Key (1934); (11) Biermann (1946); (12) Bates & Damgaard (1948); (13) Misra (1948); (14) van der Held & Heierman (1936); (15) Filippov (1934); (16) Schwarz (1940); (17) Coenen & Kramers (1936); (18) Zwaan (1929); (19) Hartree & Hartree (1938); (20) King & Stockbarger (1939); (21) Minkowski & Muhlenbruch (1930).

Note. Some of the original experimental papers gave relative values only. However, if σ^2 for one of the transitions studied is known from other investigations (experimental or theoretical), these relative values can, of course, be converted to absolute values. The following adjustments were made: Li I, in ref. (4), $\sigma^2(2s, 2p)$ is taken from ref. (1). Na I, in ref. (9), $\sigma^2(3s, 3p)$ is taken from ref. (8); and in ref. (10), $\sigma^2(3p, 3d)$ is taken from ref. (5). K I, in refs. (15) and (16), $\sigma^2(4s, 4p)$ is taken from ref. (14).

In the original literature the results obtained are expressed in a variety of ways. For convenience all the data will here be reduced to give the values of σ^2. Transitions in simple systems (i.e. systems with a single electron outside closed shells) and transitions in complex systems (i.e. systems with unclosed shells) will be discussed separately.

3·2·1. *Simple systems*

The information collected on simple systems is shown in table 7. For the lighter systems the excellence of the agreement between the results are given by the Coulomb approximation, and those given by the other methods is at once apparent. Attention may be drawn to the fact that in many of the cases (for example, in all but the resonance transition of the principal series of the alkalies) gross interference occurs in the transition integral, the positive and negative contributions almost exactly cancelling each other.† That even in these cases the results are so satisfactory is very striking. There would seem little doubt that the wave functions obtained by using term value as energy parameters are extremly accurate.

The Coulomb approximation would appear to compare favourably with the other theoretical methods. Thus, inspection of the table shows that it is not appreciably less good than theory A; it would seem to be much superior to theory B (i); and judging from the relative success in reproducing the experimental data for the transitions there is even some suggestion that it is rather superior to theory B (ii)—but perhaps this should be treated with reserve at present.

For the $4s$–$5p$ and $4s$–$6p$ transitions of K I the results obtained by the Coulomb approximation and by theory A are essentially identical, but they do not agree very well with the experimental results. However, as the differences between the two sets of experimental results are even greater than the differences between either set and the theoretical results, it is very difficult to decide what significance should be attached to this. Further laboratory work is clearly required. This is particularly important, as it would not be surprising if the elementary Coulomb approximation tended to become unsatisfactory for the heavier systems;‡ and it is desirable to know whether or not there is already a partial failure for K I. Emphasis must be laid on the fact that for the transitions discussed the values of σ^2 are extremely sensitive to the wave functions—either set of experimental results could be reproduced by altering the values of n^* derived from the term values by little over 1 part in 100. There is little doubt, therefore, that, even for K I, the wave functions themselves are remarkably accurate.§ In consequence the results given by the Coulomb approximation for transitions not subject to interference effects (such as $4s$–$4p$, $5s$–$4p$, $5s$–$5p$, $6s$–$5p$, etc.) must certainly be reliable, no matter what the final conclusion regarding those for the other transitions may be.

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† The interference for the $4p$–$4d$ transition of K I is particularly severe, the representative point on the $(n^*_{i-1}-n^*_i,\ n^*_i)$-plane lying within $0{\cdot}00_5$ of one of the zero lines.

‡ Due to influences other than from the purely electrostatic field of the core.

§ This suggests that Coulomb wave functions can probably be usefully employed in other problems. For example, they are certainly satisfactory for calculating the mean square radii of outer orbitals (which are of interest in connexion with the determination of the effective collision-broadening constant in stellar atmospheres). Indeed, for this purpose it is sufficient to use the simple formula

$$\underset{\text{(atomic units)}}{\overline{r^2}} = \frac{n^{*2}}{2C^2}\{5n^{*2}+1-3l(l+1)\} \quad \text{(notation as in text).}$$

Tl I has a very complicated structure; the nuclear charge is 81, and the core consists of six *s*-shells, four *p*-shells, three *d*-shells and one *f*-shell; the spin-orbit interaction is large. Clearly no attempt should normally be made to apply the Coulomb approximation to such a system. Nevertheless, for the purpose of the present survey it is of interest to use the method and to compare the results obtained with those given by experiment, so as to obtain information on how serious is the failure. Table 8 was therefore compiled for the series $6\,^2P_{\frac{1}{2}}$–$n\,^2S_{\frac{1}{2}}$. As can be seen the agreement is surprisingly good† except for the transition $6\,^2P_{\frac{1}{2}}$–$10\,^2S_{\frac{1}{2}}$. For this, two experimental figures are given: the higher value was obtained by direct measurement and is to some extent suspect, as it lies far above the remarkably smooth curve that can be obtained by plotting σ against n for the series;‡ the lower value (which is in fair agreement with theory) was chosen so that it lies on the curve. Even if the former value should prove to be correct, the latter value is probably more representative, in that it is the one that would be associated with the transition if anomalous influences did not enter.

TABLE 8. σ^2 FOR $6\,^2P_{\frac{1}{2}}$–$n\,^2S_{\frac{1}{2}}$ SERIES OF Tl I

	$n=7$	$n=8$	$n=9$	$n=10$
Coulomb approximation	0·57	0·048	0·015	0·0065
experiment (arbitrary units) (Filippov & Prokofjew 1933)	0·53	0·048	0·015	0·024 0·0080

The absolute values of σ^2 given by the experiment are probably not very reliable. If, however, they are accepted they indicate that the values given by the Coulomb approximation are too low by a factor of about 2. For a system like Tl I this is by no means improbable. Confirmatory measurements are, however, required to establish it.

3·2·2. *Complex systems*

So much theoretical work has been done on transitions in He I that it is profitable to consider these separately.

The most detailed calculations are due to Hylleraas (1937), who used as wave functions linear combinations of Laguerre polynomials with variationally determined coefficients. Unfortunately, there is some evidence (which will be given below) that a number of arithmetical errors were made in the exceedingly laborious computations involved. The greatest care has therefore to be taken in using the published results.

Both the singlet and triplet transitions of the $2s$–np and $2p$–nd series have also been considered by Goldberg (1939), though not by such precise methods. The following wave functions were employed:

series	level	wave function
$2s\,^1S$–$np\,^1P$	$2s\,^1S$	variational (Coolidge & James type)
	$np\,^1P$	either (i) variational (Slater type) or (ii) hydrogenic
$2s\,^3S$–$np\,^3P$	$2s\,^3S$	variational (Slater type)
	$np\,^3P$	either (i) variational (Slater type) or (ii) screened hydrogenic
$2p\,^{1,3}P$–$nd\,^{1,3}D$	$2p\,^{1,3}P$	variational (Slater type)
	$nd\,^{1,3}D$	hydrogenic

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† In spite of the agreement in this instance it is felt that the utmost caution should be used in applying the Coulomb approximation to other heavy systems.

‡ It should be mentioned that the experimental investigation covered members of the series with n greater than 10. These higher members are outside the range covered by the computations, and consequently they are not included in table 8.

Table 9 compares the values of σ^2 obtained by the Coulomb approximation with those given by Hylleraas and by Goldberg. As can be seen the agreement is in general good. However, in a number of instances the results of the Coulomb approximation are seriously different from the results of Hylleraas (though not from the less extensive results of Goldberg). To investigate the significance of the discrepancies the values of the variable $n^*_{l-1}-n^*_l$ required to reproduce Hylleraas's figures were determined.[†] From each of these were subtracted the corresponding values obtained directly from the energy levels in the usual way. The magnitudes of the resulting quantities $\Delta(n^*_{l-1}, n^*_l)$ are given in table 9. If the differences in the two sets of values of σ^2 were due to it being incorrect to identify the energy parameters used in the Coulomb approximation with the term values, then the Δ's associated with *a given type of transition* would exhibit certain characteristics. In particular, they would all be of the same sign and, as functions of n^*_{l-1} and n^*_l, would be slowly and regularly varying. Such behaviour is not followed by the figures in the table. Instead, some are positive and some are negative, and the variation with n^*_{l-1} and n^*_l is erratic; especially striking is the fact that, while most of the figures are small, an occasional one is abnormally large. A possible interpretation is that there are some numerical mistakes in Hylleraas's work. The correctness of this is supported by the ill success of the summation tests he applied.

In spite of the suggested defects in them the results of Hylleraas provide valuable evidence that it is a good approximation to equate the energy parameters to the term values. Thus, in table 10, it is plausible to omit, as unreliable, figures whose modulus is greater than or equal to 0·05. And, as can readily be verified, the remaining figures in each section show no marked tendency to be either positive or negative. Their mean values, $\bar{\Delta}$, are as follows:

$$\begin{aligned}\bar{\Delta}(s\text{–}p,\ \text{singlets}) &= +0{\cdot}00_1,\\ \bar{\Delta}(s\text{–}p,\ \text{triplets}) &= -0{\cdot}00_2,\\ \bar{\Delta}(p\text{–}d,\ \text{singlets}) &= +0{\cdot}00_3,\\ \bar{\Delta}(p\text{–}d,\ \text{triplets}) &= +0{\cdot}01_2.\end{aligned}$$

The corrections to the energy parameters implied by the $\bar{\Delta}$'s have negligible effect.

When more trustworthy comparison data becomes available it is, of course, desirable that the above analysis should be repeated. But in the meantime it can reasonably be assumed that the elementary form of the Coulomb approximation gives satisfactory results for transitions in He I.

Unfortunately, the somewhat scanty comparison data available on other complex systems refer to transitions for which the present method could scarcely be expected to apply. The survey that can be made is therefore rather limited.

The absolute values of σ^2 are only known for a few resonance transitions. As in the ground level the active electron forms part of a shell containing other electrons, and as the excited level is low, it is clear that the fundamental assumptions made in the Coulomb approximation are invalid. Nevertheless, it is of importance to have information on the degree of accuracy that can be obtained.

Examination of table 11 shows that the Coulomb approximation gives values of σ^2 that are at least comparable with those derived by experiment. The tendency for them to be rather too large is understandable. Thus it is probable that the main error is caused by the

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[†] It will be remembered that σ^2 is relatively insensitive to the other variable n^*_l.

TABLE 9. σ^2 FOR He I TRANSITIONS†

transition	method	singlets $n=2$	$n=3$	$n=4$	$n=5$	$n=6$	triplets $n=2$	$n=3$	$n=4$	$n=5$	$n=6$
$2s$–np	Coulomb approx.	8·4	0·84	0·21	0·090	—	6·4	0·27	0·091	0·039	—
	Hylleraas	8·8	0·83	0·27	0·097	—	6·6	0·22	0·107	0·042	—
	Goldberg (i)	8·5	0·65	0·25	0·100	—	6·4	0·35	0·095	0·040	—
	Goldberg (ii)	8·8	0·87	—	—	—	6·4	0·31	—	—	—
$3s$–np	Coulomb approx.	1·2	51	2·5	0·62	—	1·6	42	0·69	0·25	—
	Hylleraas	1·2	52	3·2	0·58	—	1·8	42	0·50	0·031	—
$4s$–np	Coulomb approx.	0·14	7·1	170	5·5	1·5	0·16	10	140	1·4	0·61
	Hylleraas	0·11	8·6	180	10·6	1·3	0·080	8·1	130	1·5	0·020
$5s$–np	Coulomb approx.	0·045	0·80	24	—	—	0·050	0·94	35	—	—
	Hylleraas	0·047	0·86	22	—	—	0·0014	1·77	40	—	—
$6s$–np	Coulomb approx.	0·021	0·25	2·5	—	—	0·023	0·28	2·9	—	—
	Hylleraas	0·014	0·19	2·8	—	—	0·023	0·30	2·2	—	—
$2p$–nd	Coulomb approx.	—	1·6	0·19	0·062	0·029	—	1·2	0·18	0·064	0·027
	Hylleraas	—	1·6	0·21	0·062	0·028	—	1·3	0·12	0·066	0·024
	Goldberg	—	1·7	0·19	0·060	0·027	—	1·1	0·19	0·068	0·033
$3p$–nd	Coulomb approx.	—	6·6	4·1	0·59	0·20	—	6·9	2·7	0·48	0·18
	Hylleraas	—	6·7	4·4	0·56	0·20	—	6·9	2·8	0·68	0·21
$4p$–nd	Coulomb approx.	—	0·093	29	8·8	1·3	—	0·24	29	5·3	1·0
	Hylleraas	—	0·091	29	9·1	1·5	—	0·16	29	6·8	0·83
$5p$–nd	Coulomb approx.	—	0·013	0·52	—	—	—	0·029	1·2	—	—
	Hylleraas	—	0·014	0·49	—	—	—	0·020	0·89	—	—
$6p$–nd	Coulomb approx.	—	—	0·069	—	—	—	—	0·15	—	—
	Hylleraas	—	—	0·071	—	—	—	—	0·11	—	—

† Data on d–f transitions is not included, as for these the results of the Coulomb approximation and of Hylleraas are identical.

TABLE 10. $\Delta(n^*_{l-1}, n^*_l)$ FOR He I

transition	singlets $n=2$	$n=3$	$n=4$	$n=5$	$n=6$	triplets $n=2$	$n=3$	$n=4$	$n=5$	$n=6$
$2s$–np	+0·05	0·00	+0·03	+0·01	—	+0·02	−0·01	+0·01	+0·01	—
$3s$–np	0·00	+0·03	+0·02	−0·01	—	−0·02	0·00	−0·02	−0·10	—
$4s$–np	+0·04	−0·03	+0·05	+0·06	−0·02	+0·16	+0·04	−0·10	+0·01	−0·12
$5s$–np	−0·01	−0·02	+0·01	—	—	+0·37	†	−0·03	—	—
$6s$–np	+0·08	+0·07	−0·03	—	—	0·00	−0·03	+0·09	—	—
$2p$–nd	—	+0·01	†	0·00	0·00	—	+0·03	−0·18	0·00	−0·04
$3p$–nd	—	0·00	+0·02	−0·03	0·00	—	0·00	+0·01	+0·16	+0·16
$4p$–nd	—	0·00	−0·01	+0·01	+0·04	—	+0·04	0·00	+0·04	−0·04
$5p$–nd	—	−0·01	+0·01	—	—	—	+0·04	+0·03	—	—
$6p$–nd	—	—	0·00	—	—	—	—	+0·03	—	—

† Indicates that no value of $n^*_{l-1} - n^*_l$ gives Hylleraas's result.

identification of the energy parameters associated with the s-orbitals with the term values of the ground levels; since the energy necessary to remove an electron from an s^2-shell is partially provided by the other electron, it is likely that the true energy parameter is greater; and this would lead to a decrease in σ^2.

Table 11. σ^2 for some resonance transitions in complex systems

			theory B			
				(ii) exchange included		
transition		Coulomb approximation	(i) exchange neglected	formula (29)	formula (30)	experiment
Be I	$2s\,{}^1\mathrm{S}$–$2p\,{}^1\mathrm{P}$	2·0	—	2·4 (1)	1·3	—
Ca I	$4s\,{}^1\mathrm{S}$–$4p\,{}^1\mathrm{P}$	4·3	—	5·5 (2)	2·7	—
Zn I	$4s\,{}^1\mathrm{S}$–$4p\,{}^1\mathrm{P}$	1·8	—	—	—	1·4 (3), 1·1 (4)
Cd I	$5s\,{}^1\mathrm{S}$–$5p\,{}^1\mathrm{P}$	1·9	—	—	—	1·5 (5)
Hg I	$6s\,{}^1\mathrm{S}$–$6p\,{}^1\mathrm{P}$	1·5	4·8 (6)	—	—	1·2 (7)

References. (1) Hartree & Hartree (1935, 1936); (2) Hartree & Hartree (1938); (3) Prokofjew (1929); (4) Auslander (1938); (5) Zemansky (1931); (6) Misra (1948); (7) Wolfsohn (1933).

Regarding theory B it will be noted that, with exchange neglected, it appears to be much less satisfactory than the Coulomb approximation. As will be recalled, the same conclusion was reached in § 3·2·1 in connexion with simple systems. The values of σ^2, obtained with exchange included, are of interest in that they demonstrate clearly that the alternative formulae that can be used in the computation of the transition integral may lead to very different results. It is gratifying that for both Be I and Ca I they bracket the result derived from the Coulomb approximation. Judging from the general trend in the table it would seem likely that the true value of σ^2 lies nearer that given by formula (30) than that given by formula (29).

Measurements have been made on the *relative* values of σ^2 for a number of transitions in Mg I, Ca I, Zn I, Sr I and Cd I. The main series studies are as follows:

Mg I:	$3p\,{}^3\mathrm{P}$–$ns\,{}^3\mathrm{S}$; $3p\,{}^3\mathrm{P}$–$nd\,{}^3\mathrm{D}$	(Kersten & Ornstein 1941).
Ca I:	$4p\,{}^3\mathrm{P}$–$ns\,{}^3\mathrm{S}$; $4p\,{}^3\mathrm{P}$–$nd\,{}^3\mathrm{D}$	(Schuttevaer, de Bont & van den Broek 1943).
Zn I:	$4p\,{}^3\mathrm{P}$–$ns\,{}^3\mathrm{S}$; $4p\,{}^3\mathrm{P}$–$nd\,{}^3\mathrm{D}$	(Schuttevaer & Smit 1943).
Sr I:	$5p\,{}^3\mathrm{P}$–$ns\,{}^3\mathrm{S}$; $5p\,{}^3\mathrm{P}$–$nd\,{}^3\mathrm{D}$	(Schuttevaer, de Bont & van den Broek 1943).
Cd I:	$5p\,{}^3\mathrm{P}$–$ns\,{}^3\mathrm{S}$; $5p\,{}^3\mathrm{P}$–$nd\,{}^3\mathrm{D}$	(Ornstein, van Hengstrum & Brinkman 1938).

All involve the configuration with the deepest p-orbital. Now for such a configuration the separation of the singlet and triplet terms is a considerable fraction of the term value of their centre of gravity.† In view of this evidence of large exchange forces the series are clearly not altogether suitable for treatment by the Coulomb approximation; further, Zn I, Sr I and Cd I are rather heavy systems. But there is no observational data for more ideal cases. Table 12 compares the values of σ^2 given by the theory with those obtained by measurement—those latter are given in arbitrary units, chosen so that the product of the figures in each series is about equal to the product of the corresponding theoretical figures. The agreement between the two sets of data is remarkably good in spite of the fact that in most cases a high degree of cancellation occurs in the transition integrals so that the values

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† The mean value of the fraction for the five elements under discussion is about 0·3.

of σ^2 are sensitive to the precise form of the wave functions. The *p–d* transitions in Sr I are the only ones for which any serious difference appears. In the original paper giving the experimental results it was mentioned that these transitions seemed abnormal, in that the apparent ratio of the strength of the first line of the series to that of the second is much greater than the corresponding ratio for the other similar atoms.‡ This suggests that if the discrepancy is real it is due to some special perturbing influence. Undue concern need not be felt about it at present.

TABLE 12

Mg I

transition	σ^2 Coulomb approx.	σ^2 experiment†
$3p\ {}^3P$–$4s\ {}^3S$	1·2	1·2
$3p\ {}^3P$–$5s\ {}^3S$	0·092	0·091
$3p\ {}^3P$–$6s\ {}^3S$	0·028	0·030

Ca I

transition	σ^2 Coulomb approx.	σ^2 experiment†
$4p\ {}^3P$–$5s\ {}^3S$	1·6	1·7
$4p\ {}^3P$–$6s\ {}^3S$	0·12	0·12
$4p\ {}^3P$–$7s\ {}^3S$	0·036	0·034
$4p\ {}^3P$–$4d\ {}^3D$	0·44	0·42
$4p\ {}^3P$–$5d\ {}^3D$	0·10	0·10

Zn I

transition	σ^2 Coulomb approx.	σ^2 experiment†
$4p\ {}^3P$–$5s\ {}^3S$	1·1	0·82
$4p\ {}^3P$–$6s\ {}^3S$	0·077	0·077
$4p\ {}^3P$–$7s\ {}^3S$	0·023	0·027
$4p\ {}^3P$–$8s\ {}^3S$	0·011	0·012
$4p\ {}^3P$–$5d\ {}^3D$	0·093	0·091
$4p\ {}^3P$–$6d\ {}^3D$	0·039	0·039

Sr I

transition	σ^2 Coulomb approx.	σ^2 experiment†
$5p\ {}^3P$–$6s\ {}^3S$	2·1	2·4
$5p\ {}^3P$–$7s\ {}^3S$	0·15	0·12
$5p\ {}^3P$–$8s\ {}^3S$	0·045	0·050
$5p\ {}^3P$–$5d\ {}^3D$	0·42	0·83
$5p\ {}^3P$–$6d\ {}^3D$	0·097	0·049

Cd I

transition	σ^2 Coulomb approx.	σ^2 experiment†
$5p\ {}^3P$–$6s\ {}^3S$	1·1	1·0
$5p\ {}^3P$–$7s\ {}^3S$	0·086	0·098
$5p\ {}^3P$–$8s\ {}^3S$	0·026	0·025
$5p\ {}^3P$–$6d\ {}^3D$	0·11	0·11
$5p\ {}^3P$–$7d\ {}^3D$	0·038	0·034

† The experimental results are in arbitrary units (see text).

The success of the Coulomb approximation in predicting relative values of σ^2 within a series, though encouraging, does not necessarily mean that it also yields the correct absolute values. For the variable $n^*_{l-1}-n^*_l$ must clearly change in steps of about unity in passing along a series; and as can be seen from tables 3, 4 and 5, $\mathscr{I}(n^*_{l-1}, n^*_l, l)$, regarded as a function of $n^*_{l-1}-n^*_l$, happens to have about unity as its semi-wave-length except in the region near the central line, $n^*_{l-1}-n^*_l = 0$. Hence the relative values of σ^2 are less affected by small errors in n^*_{l-1} and n^*_l than are the absolute values (provided of course all the members of the series considered lie well to either side of the central line—say beyond the region bounded by $n^*_{l-1}-n^*_l = \pm 0·6$).§

The experimental data used in table 11 actually does provide evidence that absolute values of σ^2 are not very accurate. For, though the measurements gave the relative values for the *p–s* and *p–d* series in the same units, different multiplying factors had to be used to

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‡ The ratios for Mg I, Zn I and Cd I are about the same as that for Ca I. Table 12 gives the σ^2's only for those transitions lying within the range of the computations; experimental data for a number of other transitions are available.

§ It should be noted, however, that if the representative point on the $(n^*_{l-1}-n^*_l,\ n^*_l)$-plane lies very close to a zero line small errors in the variable $n^*_{l-1}-n^*_l$ would affect even the relative values of the σ^2's. Another example of the Coulomb approximation giving accurate relative values of the σ^2's, but not necessarily accurate absolute values, is provided by the $6\ {}^2P_{\frac{1}{2}}$–$n\ {}^2S_{\frac{1}{2}}$ series in Tl I (cf. Table 8).

bring them into conformity with the theoretical results, the ratio of the multiplying factors for the *s–p* and *p–d* series ranging from 0·7 for Ca I to 0·5 for Cd I. Having regard to the nature of the transitions involved the magnitude of the error suggested is not excessive.

4. The use of the Coulomb approximation

Apart from the minor reservation indicated at the end of § 3·1 it would appear that the Coulomb approximation may be employed with confidence for all transitions in the *lighter, simple* systems. For the *heavier, simple* systems it is probably necessary to restrict the use of the method to those transitions for which the interference is small. Unfortunately, there are not sufficient comparison data available to indicate clearly which systems should, in the present connexion, be regarded as light and which as heavy. It can, however, be stated that in the case of *s–p* transitions the rather ill-defined boundary is located at, or beyond, potassium; and in the case of *p–d* and *d–f* transitions it must lie even farther down the Periodic Table. The issue can only be finally decided by further experimental work. It is particularly desirable that future investigations should include confirmatory measurements on a few *s–p* transitions in K I together with a few measurements on *s–p*, *p–d* and (less important) *d–f* measurements in heavier systems. These should establish the range of validity of the method.

For *complex* systems the Coulomb approximation (even in the present elementary form) also appears to meet with considerable success. It is not possible to lay down comprehensive, and yet not over-elaborate, rules to give the circumstances under which it may be applied; each case must be examined separately. As a guide, however, table 13 was compiled. The classification of levels in it is as follows:

Class I: levels for which the active electron is in a shell by itself and for which the exchange forces are relatively small (the moderately and highly excited levels);

Class II: levels for which the active electron is in a shell containing other electrons *or* for which the exchange forces are relatively large (the ground and usually the lower excited levels).

Reference to the earlier tables giving the comparison results will indicate the significance that is attached to the adjectives (accurate, fair, etc.) used. It need scarcely be emphasized that, to enable the useful range of the method to be fully established, further experimental results are urgently required. Such results should also be helpful in any attempt at modifying and improving the present elementary form of the Coulomb approximation.

Table 13

degree of interference	class of levels involved	comment on results expected
small	both I	accurate
small	either or both II	fair
gross	both I	fair to accurate for lighter systems (the authors tentatively suggest up to at least Mg I for *s–p* transitions and to Ca I for *p–d* and *d–f* transitions)
gross	either or both II	probably unreliable

Finally, it is perhaps worth recalling that, even when conditions are unsuitable for using the Coulomb approximation to obtain the absolute values of σ^2, it may often still be used to obtain the relative values of σ^2 within a series. This is discussed in more detail in § 3·2·2.

In conclusion, we must express our gratitude to the Council of the Royal Society for awarding us a grant which enabled the professional assistance of the Scientific Computing Service Ltd. to be engaged for part of the very heavy numerical work involved. This was supervised by the Technical Director, Dr J. C. P. Miller, whom we thank for the personal interest he took in the problem. We wish also to express our appreciation of the encouragement given us by Professor H. S. W. Massey, F.R.S., during the course of the tedious calculations we ourselves performed.

APPENDIX

The principles to be followed in evaluating line strengths from the tables contained in this paper are described in the main text, but to ensure that the practical procedure is clear it is worth working through an individual example in detail.

Consider the transition Mg II ($3s\,^2S$–$3p\,^2$P). The n^* values for the two levels concerned have first to be determined. For the $3s\,^2$S-level the term value is $1{\cdot}213_0 \times 10^5$ cm.$^{-1}$ (Bacher & Goudsmit 1932). Expressing this in Rydbergs gives the energy parameter ϵ to be $1{\cdot}106$. For a singly charged ion C is 2. Substituting in the expression $C/\epsilon^{\frac{1}{2}}$ gives

$$n^*_{l-1} = 1{\cdot}90_2.$$

Similarly for the $3p\,^2$P level, $$n^*_l = 2{\cdot}26_4.$$

Thus $$n^*_{l-1} - n^*_l = -0{\cdot}36_2.$$

From table 2 the value of $\mathscr{F}\,(2{\cdot}26_4, 1)$ is $3{\cdot}98_5$ and from table 3† the value of $\mathscr{I}\,(1{\cdot}90_2, 2{\cdot}26_4, 1)$ is $0{\cdot}83_0$. Hence from the general formula,

$$\sigma(n^*_{l-1}, l-1;\, n^*_l, l;\, C) = \frac{1}{C}\mathscr{F}(n^*_l, l)\,\mathscr{I}(n^*_{l-1}, n^*_l, l),$$

it follows that $$\sigma(1{\cdot}90_2, 0;\, 2{\cdot}26_4, 1;\, 2) = \tfrac{1}{2} \times 3{\cdot}98_5 \times 0{\cdot}83_0$$
$$= 1{\cdot}65.$$

Finally, therefore, the value of σ^2 for the transition Mg II ($3s\,^2$S–$3p\,^2$P) is $2{\cdot}7$, which gives the total line strength of the doublet to be 16 (the multiplying factor $\Sigma\mathscr{S}(\mathscr{M})\,\mathscr{S}(\mathscr{L})$ being 6).

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† This table is, of course, arranged with $n^*_{l-1} - n^*_l$ and n^*_l as the variables.

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TABLE 2. $\mathscr{F}(n_l^*, l)$

n_l^*	$l = 1$	$l = 2$	$l = 3$
1·5	1·452	—	—
1·6	1·731	—	—
1·7	2·024	—	—
1·8	2·333	—	—
1·9	2·658	—	—
2·0	3·000	—	—
2·1	3·358	—	—
2·2	3·734	—	—
2·3	4·126	—	—
2·4	4·535	—	—
2·5	4·961	1·452	—
2·6	5·404	1·673	—
2·7	5·864	1·897	—
2·8	6·342	2·125	—
2·9	6·837	2·359	—
3·0	7·348	2·598	—
3·1	7·878	2·844	—
3·2	8·424	3·096	—
3·3	8·988	3·355	—
3·4	9·568	3·621	—
3·5	10·17	3·894	1·600
3·6	10·78	4·174	1·816
3·7	11·41	4·461	2·032
3·8	12·06	4·755	2·247
3·9	12·73	5·057	2·464
4·0	13·42	5·367	2·683
4·1	14·12	5·683	2·905
4·2	14·84	6·008	3·130
4·3	15·57	6·339	3·359
4·4	16·33	6·679	3·591
4·5	17·10	7·026	3·827
4·6	17·89	7·380	4·067
4·7	18·69	7·742	4·311
4·8	19·52	8·112	4·560
4·9	20·36	8·489	4·813
5·0	21·21	8·874	5·071
5·1	22·09	9·267	5·333
5·2	22·98	9·667	5·600
5·3	23·89	10·07	5·871
5·4	24·82	10·49	6·147
5·5	25·76	10·91	6·428
5·6	26·72	11·34	6·714
5·7	27·70	11·78	7·004
5·8	28·70	12·23	7·300
5·9	29·71	12·68	7·600
6·0	30·74	13·15	7·905
6·1	31·79	13·61	8·215
6·2	32·85	14·09	8·529
6·3	33·94	14·58	8·849
6·4	35·04	15·07	9·174
6·5	36·15	15·57	9·503
6·6	37·29	16·08	9·838
6·7	38·44	16·59	10·18
6·8	39·61	17·12	10·52
6·9	40·80	17·65	10·87
7·0	42·00	18·19	11·22

Table 3. $\mathscr{I}(n^*_{l-1}, n^*_l, l)$ for $l = 1$ (i.e. s–p transitions)

n^*_l \ $-n^*_l$	2·0	2·5	3·0	3·5	4·0	4·5	5·0	5·5
−4·0	—	—	—	—	0	(−0·003)	$-0{\cdot}005_7$	—
−3·9	—	—	—	—	+0·000	−0·003	$-0{\cdot}006_3$	—
−3·8	—	—	—	—	0·000	−0·003	$-0{\cdot}006_4$	—
−3·7	—	—	—	—	0·000	−0·002	$-0{\cdot}005_6$	—
−3·6	—	—	—	—	0·001	−0·001	$-0{\cdot}003_9$	—
−3·5	—	—	—	—	0·002	+0·000	$-0{\cdot}001_3$	—
−3·4	—	—	—	—	0·004	0·003	$+0{\cdot}002_3$	—
−3·3	—	—	—	—	0·006	0·006	$0{\cdot}006_8$	—
−3·2	—	—	—	—	0·008	0·010	$0{\cdot}011_8$	—
−3·1	—	—	—	—	0·011	0·014	0·017	—
−3·0	—	—	0	+0·007	0·013	0·018	0·021	+0·023
−2·9	—	—	−0·000	0·008	0·015	0·020	0·024	0·027
−2·8	—	—	−0·000	0·008	0·015	0·021	0·025	0·028
−2·7	—	—	−0·001	0·007	0·014	0·020	0·024	0·027
−2·6	—	—	−0·003	+0·004	0·010	0·015	0·019	0·021
−2·5	—	—	−0·006	−0·001	+0·004	+0·008	+0·011	0·013
−2·4	—	—	−0·010	−0·008	−0·005	−0·002	−0·000	+0·001
−2·3	—	—	−0·016	−0·016	−0·016	−0·015	−0·014	−0·014
−2·2	—	—	−0·024	−0·027	−0·029	−0·029	−0·030	−0·031
−2·1	—	—	−0·032	−0·038	−0·042	−0·044	−0·046	−0·048
−2·0	0	−0·025	−0·041	−0·049	−0·055	−0·059	−0·062	−0·064
−1·9	+0·000	−0·029	−0·048	−0·058	−0·066	−0·072	−0·075	−0·077
−1·8	0·001	−0·030	−0·051	−0·063	−0·072	−0·079	−0·083	−0·085
−1·7	0·004	−0·028	−0·050	−0·063	−0·073	−0·080	−0·084	−0·087
−1·6	0·012	−0·019	−0·041	−0·055	−0·064	−0·071	−0·076	−0·079
−1·5	0·026	−0·003	−0·024	−0·037	−0·046	−0·053	−0·058	−0·061
−1·4	0·048	+0·023	+0·004	−0·007	−0·015	−0·022	−0·026	−0·029
−1·3	0·080	0·060	0·045	+0·035	+0·028	+0·022	+0·018	+0·016
−1·2	0·123	0·109	0·098	0·090	0·084	0·080	0·077	0·074
−1·1	0·180	0·170	0·163	0·158	0·154	0·151	0·148	0·146
−1·0	0·248	0·244	0·241	0·238	0·235	0·233	0·232	0·230
−0·9	0·329	0·329	0·328	0·328	0·327	0·326	0·325	0·324
−0·8	0·418	0·422	0·424	0·425	0·425	0·425	0·425	0·425
−0·7	0·514	0·520	0·524	0·526	0·527	0·528	0·528	0·528
−0·6	0·612	0·619	0·624	0·627	0·629	0·630	0·631	0·632
−0·5	0·708	0·715	0·720	0·723	0·725	0·727	0·728	0·729
−0·4	0·797	0·804	0·808	0·811	0·813	0·815	0·816	0·817
−0·3	0·875	0·880	0·884	0·887	0·888	0·890	0·891	0·892
−0·2	0·937	0·941	0·943	0·945	0·946	0·947	0·948	0·949
−0·1	0·980	0·981	0·983	0·984	0·984	0·985	0·985	0·985
0	1·000	1·000	1·000	1·000	1·000	1·000	1·000	1·000
+0·1	0·996	0·995	0·994	0·993	0·992	0·992	0·992	0·992
0·2	0·967	0·965	0·964	0·962	0·961	0·961	0·960	0·960
0·3	0·915	0·913	0·911	0·909	0·908	0·907	0·907	0·906
0·4	0·842	0·839	0·837	0·836	0·835	0·834	0·833	0·832
0·5	0·749	0·748	0·747	0·746	0·745	0·744	0·744	0·743
0·6	0·643	0·643	0·643	0·643	0·642	0·642	0·642	0·642
0·7	0·528	0·530	0·531	0·531	0·531	0·532	0·532	0·532
0·8	0·409	0·412	0·415	0·416	0·417	0·418	0·419	0·420
0·9	0·292	0·297	0·300	0·303	0·304	0·306	0·307	0·308
1·0	0·181	0·187	0·192	0·196	0·198	0·200	0·202	0·203
1·1	+0·081	0·088	0·094	0·099	0·102	0·104	0·106	0·107

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5	6·0	6·5	7·0
	—	—	—
	—	—	—
	—	—	—
	—	—	—
	—	—	—
	—	—	—
	—	—	—
	—	—	—
	—	—	—
	—	—	—
23	+0·025	+0·027	+0·028
27	0·029	0·031	0·032
28	0·030	0·032	0·033
27	0·029	0·031	0·032
21	0·023	0·024	0·025
13	0·014	0·015	0·016
01	+0·002	+0·003	+0·003
14	−0·014	−0·014	−0·014
31	−0·032	−0·033	−0·034
48	−0·049	−0·050	−0·051
64	−0·065	−0·066	−0·067
77	−0·079	−0·080	−0·081
85	−0·087	−0·088	−0·089
87	−0·089	−0·090	−0·091
79	−0·081	−0·082	−0·083
61	−0·063	−0·064	−0·065
29	−0·031	−0·032	−0·033
16	+0·014	+0·013	+0·012
74	0·072	0·071	0·070
46	0·145	0·144	0·143
30	0·229	0·228	0·228
24	0·323	0·322	0·322
25	0·425	0·424	0·424
28	0·528	0·528	0·528
32	0·632	0·633	0·633
29	0·730	0·731	0·731
17	0·818	0·819	0·819
92	0·892	0·893	0·893
49	0·949	0·949	0·949
85	0·985	0·986	0·986
00	1·000	1·000	1·000
92	0·992	0·991	0·991
60	0·960	0·959	0·959
06	0·906	0·906	0·906
32	0·831	0·830	0·830
43	0·743	0·743	0·743
42	0·642	0·642	0·642
32	0·532	0·532	0·532
20	0·420	0·421	0·421
08	0·309	0·310	0·311
03	0·204	0·205	0·206
07	0·108	—	—
24	+0·025		

1·0	0·181	0·187	0·192	0·196	0·198	0·200	0·202	0·203
1·1	+0·081	0·088	0·094	0·099	0·102	0·104	0·106	0·107
1·2	−0·004	+0·004	+0·011	+0·016	+0·019	+0·021	+0·023	+0·024
1·3	−0·071	−0·063	−0·056	−0·051	−0·047	−0·044	−0·042	−0·041
1·4	−0·120	−0·112	−0·105	−0·100	−0·096	−0·093	−0·091	−0·090
1·5	−0·149	−0·142	−0·136	−0·132	−0·128	−0·126	−0·124	−0·123
1·6	−0·160	−0·155	−0·150	−0·146	−0·142	−0·140	−0·138	−0·137
1·7	−0·155	−0·151	−0·148	−0·145	−0·142	−0·140	−0·138	−0·137
1·8	−0·137	−0·135	−0·133	−0·131	−0·128	−0·126	−0·124	−0·123
1·9	−0·108	−0·108	−0·108	−0·107	−0·105	−0·103	−0·102	−0·101
2·0	−0·074	−0·075	−0·076	−0·077	−0·077	−0·077	−0·077	−0·077
2·1	−0·036	−0·039	−0·041	−0·043	−0·044	−0·045	−0·045	—
2·2	+0·000	−0·004	−0·007	−0·009	−0·011	−0·012	−0·013	—
2·3	0·032	+0·027	+0·024	+0·021	+0·019	+0·018	+0·017	—
2·4	0·058	0·053	0·049	0·046	0·044	0·043	0·042	—
2·5	0·076	0·071	0·067	0·064	0·062	0·060	0·059	—
2·6	0·085	0·081	0·078	0·075	0·073	0·071	0·070	—
2·7	0·085	0·082	0·080	0·078	0·076	0·075	0·074	—
2·8	0·077	0·075	0·074	0·072	0·071	0·070	0·070	—
2·9	0·063	0·062	0·062	0·061	0·061	0·060	0·060	—
3·0	0·044	0·045	0·045	0·045	0·045	+0·045	+0·045	—
3·1	0·022	0·024	0·025	0·026	0·026	—	—	—
3·2	+0·000	+0·003	+0·005	+0·006	+0·007	—	—	—
3·3	−0·020	−0·017	−0·014	−0·012	−0·011	—	—	—
3·4	−0·037	−0·034	−0·031	−0·028	−0·027	—	—	—
3·5	−0·049	−0·046	−0·043	−0·041	−0·039	—	—	—
3·6	−0·056	−0·053	−0·051	−0·049	−0·047	—	—	—
3·7	−0·057	−0·055	−0·053	−0·051	−0·050	—	—	—
3·8	−0·052	−0·051	−0·050	−0·048	−0·047	—	—	—
3·9	−0·043	−0·042	−0·042	−0·041	−0·041	—	—	—
4·0	−0·030	−0·031	−0·031	−0·031	−0·031	—	—	—

PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

03	0·204	0·205	0·206
07	0·108	—	—
24	+0·025	—	—
41	−0·040	—	—
90	−0·089	—	—
23	−0·122	—	—
37	−0·136	—	—
37	−0·136	—	—
23	−0·122	—	—
01	−0·101	—	—
77	−0·077	—	—
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Table 4. $\mathscr{I}(n_{l-1}^*, n_l^*, l)$ for $l = 2$ (i.e. p–d transitions)

n_l^* / $n_{l-1}^* - n_l^*$	3·0	3·5	4·0	4·5	5·0	5·5	6·0	6·5	7·0
−4·0	—	—	—	—	—	—	−0·013	—	—
−3·9	—	—	—	—	—	—	−0·012	—	—
−3·8	—	—	—	—	—	—	−0·009	—	—
−3·7	—	—	—	—	—	—	−0·005	—	—
−3·6	—	—	—	—	—	—	−0·000	—	—
−3·5	—	—	—	—	—	—	+0·006	—	—
−3·4	—	—	—	—	+0·019	+0·015	0·012	—	—
−3·3	—	—	—	—	0·023	0·022	0·019	—	—
−3·2	—	—	—	—	0·026	0·026	0·026	—	—
−3·1	—	—	—	—	0·028	0·030	0·031	—	—
−3·0	—	—	—	—	0·028	0·031	0·034	+0·036	+0·037
−2·9	—	—	—	—	0·026	0·030	0·035	0·037	0·038
−2·8	—	—	—	—	0·022	0·028	0·032	0·034	0·035
−2·7	—	—	—	—	0·014	0·021	0·026	0·028	0·029
−2·6	—	—	—	—	+0·004	+0·011	0·016	0·018	0·019
−2·5	—	—	−0·036	(−0·020)	−0·009	−0·002	+0·003	+0·005	+0·006
−2·4	—	—	−0·047	(−0·034)	−0·025	−0·018	−0·014	−0·012	−0·011
−2·3	—	—	−0·059	−0·049	−0·042	−0·037	−0·033	−0·031	−0·030
−2·2	—	—	−0·069	−0·063	−0·059	−0·055	−0·052	−0·050	−0·049
−2·1	—	—	−0·077	−0·075	−0·074	−0·072	−0·070	−0·069	−0·068
−2·0	—	—	−0·082	−0·085	−0·086	−0·086	−0·086	−0·086	−0·085
−1·9	—	—	−0·082	−0·089	−0·093	−0·095	−0·097	−0·098	−0·099
−1·8	—	—	−0·074	−0·086	−0·093	−0·097	−0·100	−0·103	−0·105
−1·7	—	—	−0·058	−0·073	−0·083	−0·089	−0·094	−0·098	−0·101
−1·6	+0·091	(+0·008)	−0·032	−0·051	−0·063	−0·071	−0·077	−0·082	−0·086
−1·5	0·131	(0·047)	+0·006	−0·016	−0·030	−0·040	−0·048	−0·054	−0·059
−1·4	0·182	(0·097)	0·055	+0·032	+0·016	+0·005	−0·004	−0·011	−0·016
−1·3	0·242	(0·159)	0·117	0·092	0·075	0·063	+0·053	+0·046	+0·040
−1·2	0·311	0·232	0·190	0·164	0·146	0·133	0·123	0·115	0·109
−1·1	0·388	0·315	0·273	0·247	0·229	0·215	0·205	0·197	0·190
−1·0	0·472	0·405	0·364	0·338	0·321	0·308	0·298	0·290	0·283
−0·9	0·559	0·499	0·461	0·436	0·420	0·408	0·398	0·390	0·383
−0·8	0·648	0·595	0·560	0·537	0·522	0·511	0·501	0·493	0·486
−0·7	0·734	0·688	0·657	0·637	0·623	0·613	0·604	0·597	0·590
−0·6	0·814	0·776	0·750	0·732	0·720	0·711	0·703	0·697	0·691
−0·5	0·885	0·854	0·833	0·818	0·808	0·801	0·794	0·789	0·784
−0·4	0·944	0·919	0·903	0·892	0·884	0·878	0·872	0·868	0·864
−0·3	0·987	0·969	0·957	0·949	0·943	0·939	0·935	0·932	0·929
−0·2	1·011	1·000	0·993	0·988	0·984	0·981	0·978	0·976	0·974
−0·1	1·016	1·010	1·007	1·005	1·003	1·001	1·000	0·999	0·998
0	1·000	1·000	1·000	1·000	1·000	1·000	1·000	1·000	1·000
+0·1	0·963	0·968	0·971	0·973	0·975	0·976	0·977	0·978	0·978
0·2	0·907	0·915	0·921	0·925	0·928	0·931	0·933	0·934	0·935
0·3	0·834	0·844	0·852	0·858	0·862	0·866	0·868	0·870	0·871
0·4	0·746	0·758	0·767	0·774	0·779	0·783	0·786	0·788	0·790
0·5	0·646	0·660	0·670	0·677	0·683	0·687	0·691	0·694	0·696
0·6	0·540	0·554	0·564	0·572	0·578	0·583	0·587	0·590	0·593
0·7	0·431	0·445	0·455	0·463	0·469	0·475	0·479	0·482	0·485
0·8	0·324	0·336	0·346	0·354	0·360	0·365	0·369	0·372	0·375
0·9	0·222	0·233	0·242	0·249	0·255	0·260	0·264	0·267	0·270
1·0	0·129	0·139	0·147	0·153	0·158	0·163	0·166	0·169	0·172
1·1	+0·049	+0·057	+0·063	+0·068	0·073	0·077	0·080	—	—
1·2	−0·017	−0·011	−0·006	−0·002	+0·002	+0·005	+0·008	—	—
1·3	−0·067	−0·063	−0·060	−0·057	−0·054	−0·052	−0·050	—	—
1·4	−0·101	−0·099	−0·097	−0·095	−0·093	−0·092	−0·091	—	—
1·5	−0·120	−0·119	−0·119	−0·118	−0·117	−0·116	−0·116	—	—
1·6	−0·124	−0·125	−0·126	−0·126	−0·126	−0·126	−0·126	—	—
1·7	−0·117	−0·119	−0·120	−0·121	−0·122	−0·123	−0·123	—	—
1·8	−0·099	−0·102	−0·104	−0·106	−0·107	−0·108	−0·109	—	—
1·9	−0·076	−0·079	−0·082	−0·084	−0·085	−0·087	−0·088	—	—
2·0	−0·048	−0·051	−0·054	−0·056	−0·058	−0·060	−0·061	—	—

TABLE 5. $\mathscr{I}(n^*_{l-1}, n^*_l, l)$ FOR $l = 3$ (I.E. d–f TRANSITIONS)

$n^*_{l-1} - n^*_l$ \ n^*_l	4	5	6	7
−4·0	—	—	—	−0·018
−3·9	—	—	—	−0·014
−3·8	—	—	—	−0·008
−3·7	—	—	—	−0·001
−3·6	—	—	—	+0·007
−3·5	—	—	—	0·016
−3·4	—	—	+0·037	0·024
−3·3	—	—	0·041	0·032
−3·2	—	—	0·043	0·039
−3·1	—	—	0·042	0·043
−3·0	—	—	0·038	0·044
−2·9	—	—	0·032	0·041
−2·8	—	—	0·021	0·035
−2·7	—	—	+0·008	0·024
−2·6	—	—	−0·009	+0·009
−2·5	—	−0·073	−0·028	−0·010
−2·4	—	−0·087	−0·048	−0·031
−2·3	—	−0·100	−0·069	−0·053
−2·2	—	−0·109	−0·087	−0·074
−2·1	—	−0·113	−0·102	−0·093
−2·0	—	−0·111	−0·111	−0·107
−1·9	—	−0·100	−0·112	−0·114
−1·8	—	−0·080	−0·104	−0·111
−1·7	—	−0·050	−0·084	−0·098
−1·6	+0·183	−0·007	−0·052	−0·072
−1·5	0·244	+0·047	−0·007	−0·032
−1·4	0·313	0·113	+0·051	+0·021
−1·3	0·389	0·190	0·123	0·089
−1·2	0·471	0·276	0·206	0·169
−1·1	0·557	0·370	0·298	0·259
−1·0	0·644	0·469	0·397	0·358
−0·9	0·731	0·569	0·500	0·462
−0·8	0·813	0·668	0·603	0·567
−0·7	0·888	0·761	0·703	0·669
−0·6	0·952	0·845	0·794	0·764
−0·5	1·004	0·916	0·874	0·848
−0·4	1·040	0·972	0·938	0·918
−0·3	1·058	1·010	0·985	0·970
−0·2	1·058	1·028	1·012	1·001
−0·1	1·038	1·024	1·017	1·012
0	1·000	1·000	1·000	1·000
+0·1	0·944	0·955	0·962	0·967
0·2	0·872	0·892	0·904	0·912
0·3	0·786	0·813	0·829	0·840
0·4	0·691	0·722	0·740	0·753
0·5	0·588	0·621	0·641	0·655
0·6	0·483	0·515	0·535	0·550
0·7	0·379	0·409	0·428	0·442
0·8	0·279	0·305	0·323	0·335
0·9	0·186	0·209	0·224	0·235
1·0	0·105	0·122	0·134	0·143
1·1	+0·035	+0·047	+0·057	—
1·2	−0·020	−0·013	−0·007	—
1·3	−0·061	−0·059	−0·055	
1·4	−0·088	−0·089	−0·088	—
1·5	−0·101	−0·105	−0·107	—
1·6	−0·103	−0·109	−0·113	—
1·7	−0·095	−0·102	−0·106	—
1·8	−0·079	−0·087	−0·092	—
1·9	−0·059	−0·066	−0·071	—
2·0	−0·036	−0·042	−0·046	—

TABLE 3. $\mathscr{S}(n^*_{l-1}, n^*_l, l)$ FOR $l = 1$ (I.E. s–p TRANSITIONS)

$n^*_{l-1} - n^*_l$ \ n^*_l	2·0	2·5	3·0	3·5	4·0	4·5	5·0	5·5	6·0	6·5	7·0
−4·0	—	—	—	—	0	(−0·003)	$-0{\cdot}005_7$	—	—	—	—
−3·9	—	—	—	—	+0·000	−0·003	$-0{\cdot}006_3$	—	—	—	—
−3·8	—	—	—	—	0·000	−0·003	$-0{\cdot}006_4$	—	—	—	—
−3·7	—	—	—	—	0·000	−0·002	$-0{\cdot}005_6$	—	—	—	—
−3·6	—	—	—	—	0·001	−0·001	$-0{\cdot}003_9$	—	—	—	—
−3·5	—	—	—	—	0·002	+0·000	$-0{\cdot}001_3$	—	—	—	—
−3·4	—	—	—	—	0·004	0·003	$+0{\cdot}002_3$	—	—	—	—
−3·3	—	—	—	—	0·006	0·006	$0{\cdot}006_8$	—	—	—	—
−3·2	—	—	—	—	0·008	0·010	$0{\cdot}011_8$	—	—	—	—
−3·1	—	—	—	—	0·011	0·014	0·017	—	—	—	—
−3·0	—	—	0	+0·007	0·013	0·018	0·021	+0·023	+0·025	+0·027	+0·028
−2·9	—	—	−0·000	0·008	0·015	0·020	0·024	0·027	0·029	0·031	0·032
−2·8	—	—	−0·000	0·008	0·015	0·021	0·025	0·028	0·030	0·032	0·033
−2·7	—	—	−0·001	0·007	0·014	0·020	0·024	0·027	0·029	0·031	0·032
−2·6	—	—	−0·003	+0·004	0·010	0·015	0·019	0·021	0·023	0·024	0·025
−2·5	—	—	−0·006	−0·001	+0·004	+0·008	+0·011	0·013	0·014	0·015	0·016
−2·4	—	—	−0·010	−0·008	−0·005	−0·002	−0·000	+0·001	+0·002	+0·003	+0·003
−2·3	—	—	−0·016	−0·016	−0·016	−0·015	−0·014	−0·014	−0·014	−0·014	−0·014
−2·2	—	—	−0·024	−0·027	−0·029	−0·029	−0·030	−0·031	−0·032	−0·033	−0·034
−2·1	—	—	−0·032	−0·038	−0·042	−0·044	−0·046	−0·048	−0·049	−0·050	−0·051
−2·0	0	−0·025	−0·041	−0·049	−0·055	−0·059	−0·062	−0·064	−0·065	−0·066	−0·067
−1·9	+0·000	−0·029	−0·048	−0·058	−0·066	−0·072	−0·075	−0·077	−0·079	−0·080	−0·081
−1·8	0·001	−0·030	−0·051	−0·063	−0·072	−0·079	−0·083	−0·085	−0·087	−0·088	−0·089
−1·7	0·004	−0·028	−0·050	−0·063	−0·073	−0·080	−0·084	−0·087	−0·089	−0·090	−0·091
−1·6	0·012	−0·019	−0·041	−0·055	−0·064	−0·071	−0·076	−0·079	−0·081	−0·082	−0·083
−1·5	0·026	−0·003	−0·024	−0·037	−0·046	−0·053	−0·058	−0·061	−0·063	−0·064	−0·065
−1·4	0·048	+0·023	+0·004	−0·007	−0·015	−0·022	−0·026	−0·029	−0·031	−0·032	−0·033
−1·3	0·080	0·060	0·045	+0·035	+0·028	+0·022	+0·018	+0·016	+0·014	+0·013	+0·012
−1·2	0·123	0·109	0·098	0·090	0·084	0·080	0·077	0·074	0·072	0·071	0·070
−1·1	0·180	0·170	0·163	0·158	0·154	0·151	0·148	0·146	0·145	0·144	0·143
−1·0	0·248	0·244	0·241	0·238	0·235	0·233	0·232	0·230	0·229	0·228	0·228
−0·9	0·329	0·329	0·328	0·328	0·327	0·326	0·325	0·324	0·323	0·322	0·322
−0·8	0·418	0·422	0·424	0·425	0·425	0·425	0·425	0·425	0·425	0·424	0·424
−0·7	0·514	0·520	0·524	0·526	0·527	0·528	0·528	0·528	0·528	0·528	0·528
−0·6	0·612	0·619	0·624	0·627	0·629	0·630	0·631	0·632	0·632	0·633	0·633
−0·5	0·708	0·715	0·720	0·723	0·725	0·727	0·728	0·729	0·730	0·731	0·731
−0·4	0·797	0·804	0·808	0·811	0·813	0·815	0·816	0·817	0·818	0·819	0·819
−0·3	0·875	0·880	0·884	0·887	0·888	0·890	0·891	0·892	0·892	0·893	0·893
−0·2	0·937	0·941	0·943	0·945	0·946	0·947	0·948	0·949	0·949	0·949	0·949
−0·1	0·980	0·981	0·983	0·984	0·984	0·985	0·985	0·985	0·985	0·986	0·986
0	1·000	1·000	1·000	1·000	1·000	1·000	1·000	1·000	1·000	1·000	1·000
+0·1	0·996	0·995	0·994	0·993	0·992	0·992	0·992	0·992	0·992	0·991	0·991
0·2	0·967	0·965	0·964	0·962	0·961	0·961	0·960	0·960	0·960	0·959	0·959
0·3	0·915	0·913	0·911	0·909	0·908	0·907	0·907	0·906	0·906	0·906	0·906
0·4	0·842	0·839	0·837	0·836	0·835	0·834	0·833	0·832	0·831	0·830	0·830
0·5	0·749	0·748	0·747	0·746	0·745	0·744	0·744	0·743	0·743	0·743	0·743
0·6	0·643	0·643	0·643	0·643	0·642	0·642	0·642	0·642	0·642	0·642	0·642
0·7	0·528	0·530	0·531	0·531	0·531	0·532	0·532	0·532	0·532	0·532	0·532
0·8	0·409	0·412	0·415	0·416	0·417	0·418	0·419	0·420	0·420	0·421	0·421
0·9	0·292	0·297	0·300	0·303	0·304	0·306	0·307	0·308	0·309	0·310	0·311
1·0	0·181	0·187	0·192	0·196	0·198	0·200	0·202	0·203	0·204	0·205	0·206
1·1	+0·081	0·088	0·094	0·099	0·102	0·104	0·106	0·107	0·108	—	—
1·2	−0·004	+0·004	+0·011	+0·016	+0·019	+0·021	+0·023	+0·024	+0·025	—	—
1·3	−0·071	−0·063	−0·056	−0·051	−0·047	−0·044	−0·042	−0·041	−0·040	—	—
1·4	−0·120	−0·112	−0·105	−0·100	−0·096	−0·093	−0·091	−0·090	−0·089	—	—
1·5	−0·149	−0·142	−0·136	−0·132	−0·128	−0·126	−0·124	−0·123	−0·122	—	—
1·6	−0·160	−0·155	−0·150	−0·146	−0·142	−0·140	−0·138	−0·137	−0·136	—	—
1·7	−0·155	−0·151	−0·148	−0·145	−0·142	−0·140	−0·138	−0·137	−0·136	—	—
1·8	−0·137	−0·135	−0·133	−0·131	−0·128	−0·126	−0·124	−0·123	−0·122	—	—
1·9	−0·108	−0·108	−0·108	−0·107	−0·105	−0·103	−0·102	−0·101	−0·101	—	—
2·0	−0·074	−0·075	−0·076	−0·077	−0·077	−0·077	−0·077	−0·077	−0·077	—	—
2·1	−0·036	−0·039	−0·041	−0·043	−0·044	−0·045	−0·045	—	—	—	—
2·2	+0·000	−0·004	−0·007	−0·009	−0·011	−0·012	−0·013	—	—	—	—
2·3	0·032	+0·027	+0·024	+0·021	+0·019	+0·018	+0·017	—	—	—	—
2·4	0·058	0·053	0·049	0·046	0·044	0·043	0·042	—	—	—	—
2·5	0·076	0·071	0·067	0·064	0·062	0·060	0·059	—	—	—	—
2·6	0·085	0·081	0·078	0·075	0·073	0·071	0·070	—	—	—	—
2·7	0·085	0·082	0·080	0·078	0·076	0·075	0·074	—	—	—	—
2·8	0·077	0·075	0·074	0·072	0·071	0·070	0·070	—	—	—	—
2·9	0·063	0·062	0·062	0·061	0·061	0·060	0·060	—	—	—	—
3·0	0·044	0·045	0·045	0·045	0·045	+0·045	+0·045	—	—	—	—
3·1	0·022	0·024	0·025	0·026	0·026	—	—	—	—	—	—
3·2	+0·000	+0·003	+0·005	+0·006	+0·007	—	—	—	—	—	—
3·3	−0·020	−0·017	−0·014	−0·012	−0·011	—	—	—	—	—	—
3·4	−0·037	−0·034	−0·031	−0·028	−0·027	—	—	—	—	—	—
3·5	−0·049	−0·046	−0·043	−0·041	−0·039	—	—	—	—	—	—
3·6	−0·056	−0·053	−0·051	−0·049	−0·047	—	—	—	—	—	—
3·7	−0·057	−0·055	−0·053	−0·051	−0·050	—	—	—	—	—	—
3·8	−0·052	−0·051	−0·050	−0·048	−0·047	—	—	—	—	—	—
3·9	−0·043	−0·042	−0·042	−0·041	−0·041	—	—	—	—	—	—
4·0	−0·030	−0·031	−0·031	−0·031	−0·031	—	—	—	—	—	—