DIPOLE TRANSITION INTEGRALS FOR NON-METAL RESONANCE TRANSITIONS

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ABSTRACT

By formulating a numerical analog of the Bates-Damgaard Coulomb approximation for dipole transition probabilities, but with a Thomas-Fermi potential, transition probabilities are calculated for $p^n - p^{n-1} \cdot s$ transitions as a function of empirical energies. The variation of the calculated values with atomic number is found to be approximately factorable. The formulation obtains radial wavefunctions by solution of an initial value problem. Extension of the Bates-Damgaard tables are given for p ground states and s excited states of neutral atoms. The scaled Thomas-Fermi or quantum defect methods are recommended for ions. For intermediate weight atoms, agreement with experiment is found within 30%. Errors of 40% or more are found in C, N, Pb, and I, where failure of the configuration assignments is the probable cause. The Burgess-Seaton quantum defect method is found to give results - 10% + 80% different from the present formulation.

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I. INTRODUCTION

We present here a simple numerical formulation of the "radial integral" evaluation for atomic dipole transitions with one-electron jumps. The method of Bates and Damgaard (1949), (BD), which uses a Coulomb potential for the central field, is, in essence, duplicated except that a Thomas-Fermi (TF) potential is used. We shall formulate the extension and then mention its relation to the scaled Thomas-Fermi (STF) method of Stewart and Rotenberg (1965), self-consistent field calculations, and experiment.

The present formulation is motivated by a desire to extrapolate the BD tables for use with the resonance-type transitions $(mp^n - mp^{n-1} (m + 1)s)$ of non-metals. For example, Griem (1964) and Kelly and Armstrong (1962) have made such extrapolations. The latter authors used the quantum defect method of Burgess and Seaton (1960) to modify the BD method. This is an important improvement and is described in section V. The tables and specific calculations given here are for the resonance transitions in neutral atoms. Extension of the tables to ions is discussed in section IX.

Our goal for the accuracy of such a formulation is 10% in reproducing other one-electron type calculations for resonance type transitions. Core changes, configuration mixing, spin orbit interaction, etc. are partially or completely ignored in such a formulation. Table 5 gives a comparison with some experimental values. We find discrepancies between theory and experiment of factors of two to three in C and N but only factors of 1.3 or less for intermediate weight elements.

The important parts of the BD theory which are retained in this extension are:

1. The radial wavefunctions at large r are Coulombic (except for normalization) and are determined by the experimental energies. Inaccuracies of the wave functions at small r are ignored, and indeed, are ignorable.

2. The results are presented in such a way that interpolation is possible. The BD format is used.

3. A single potential, asymptotically Coulombic, is used for entries in the tables of the extended BD function, $\mathcal{A}$.

The important differences are:

1. The potential used is a numerical approximation to the TF potential, with an exchange approximation, as given by Latter (1955). This potential is Coulombic at large r out drops faster than $1/r$ at small r. The "universal function"; Latter's equations (5) and (9) are used.

2. The atomic number Z enters the calculation through its appearance in the potential, but its effects are mainly on the BD function $\mathcal{F}$.

3. Divergences of the wavefunctions for $r < .001$ are eliminated by the numerical method used.

II. THEORY AND COMPUTATION

The formulation is a numerical solution of the one-electron central field problem defined by the radial Schroedinger equation:

$$\frac{d^2 P_\ell}{d\rho^2} + \left[\frac{-2}{C^2} V(\rho/C) + \frac{1}{\nu_\ell^2} - \frac{\ell(\ell+1)}{\rho^2} \right] P_\ell \tag{1}$$

where C is the core charge, $\rho = Cr$ with the radius in Bohr radii, ℓ is the orbital angular momentum, V (r) the central potential and ν_ℓ

is the effective quantum number defined in terms of the empirical energy ϵ (in Rydbergs) by $\epsilon_\ell = c^2/\nu_\ell^2$. Set C = 1. We wish to calculate σ or I where,

$$I = \sqrt{4\ell_>^2 - 1} \qquad \sigma = \frac{1}{N_1 N_2} \int_0^\infty r \, P_\ell \, P_{\ell'} \, dr \tag{2}$$

where $\ell_>$ is the largest of the angular momenta of the jumping electron in the transition. The quantity σ is used in BD and I is the quantity used by Shore and Menzel (1965). Here, $\sqrt{4\ell_>^2 - 1} = \sqrt{3}$. The normalization factors, N_ℓ, are given by:

$$N_\ell^2 = \int_0^\infty \left[P_\ell (r) \right]^2 dr. \tag{3}$$

In order to obtain P functions which are correct at large r we write

$$P(r) = F(r) \, r^\nu \, e^{-r/\nu}, \tag{4}$$

which requires that F satisfy

$$\frac{d^2 F}{dr^2} + \frac{dF}{dr} \left[\frac{2\nu}{r} - \frac{2}{\nu} \right] + F \left[\frac{\nu(\nu-1) - \ell(\ell+1)}{r^2} - 2\left(\frac{1}{r} - V(r)\right) \right]. \tag{5}$$

The asymptotic form of F is taken from BD:

$$F \xrightarrow[r \to \infty]{} 1 + \sum_{t=1}^\infty a_t / r^t, \tag{6}$$

where

$$a_1 = \nu/2 \left[\ell(\ell+1) - \nu(\nu-1) \right] .$$

The numerical solution of the radial wave equation was accomplished by stepwise integration of Eq. 5, starting at r_0 = 38.001 and stopping at r = .001 with Δr = -0.05. The initial conditions were F (r_0) = 1.0 and F' (38.001) = $-a_1 / r_0^2$. A Runge-Kutte method by Gill (1951) was used.[1]

In the range of values included here, the step size, starting radius and initial slope condition were determined to be appropriate to give σ^2 values within 1% of those given by exact solutions of the equations. Such a formulation is limited to small ν values because of starting radius limitations. If Z is set $= 1$ and ν an integer, the proper normalized hydrogenic P functions are obtained within 0.001.

The true solution to the problem defined above will, in general, diverge at the origin because the experimentally determined ν values are not eigen values of the approximate potential used. This divergence is found to begin in F (r) for $r \lesssim$ 0.1 but the r^{ν} factor in Eq. 4 makes its effect quite small. For a typical resonance transition as listed in Table 5, we find $\approx$ 2% increase in the calculated values of σ^2 if the wave functions are arbitrarily truncated shortwards of r = 0.1. Thus the solution is not strongly dependent upon cut-off radius.

The potential used is accurate enough that solutions for the transition arrays of Table 5 have the proper number of nodes except for the misbehavior at the origin.

III. PRESENTATION OF THE DATA

Tables 3 and 4 are arranged as extensions of the BD tables for $0.5 \lesssim \nu_p$ $\lesssim 2.0$ and $\nu_p \lesssim \nu_s \lesssim 2.8$. We obtain σ from

$$\sigma (Z) = \left(1/c \right) \overline{\sigma_Z} \left(\nu_p \right) \, \mathcal{A} \left(\nu_s, \nu_p \right), \tag{8}$$

where

$$\overline{\sigma_Z} \left(\nu_p \right) \equiv \sigma \left(\nu_s = \nu_p, Z \right).$$

Now strictly speaking, $\mathcal{A}$ is a function of Z but was found to vary only by $\pm$ .03 for Z between 7 and 33. A "medium" value of Z = 15 was chosen. Hence,

one interpolates between Z values only in finding $\tilde{\mathcal{F}}$. Interpolation of

$\mathcal{d}$ is best done linearly while $\tilde{\mathcal{F}}$ varies approximately exponentially with

$\mathcal{V}_p$. The specific examples in column 5 of Table 5 were interpolated from

graphs of ln $\tilde{\mathcal{F}}$ vs $\mathcal{V}_p$ and of $\mathcal{d}$ vs ($\mathcal{V}_s - \mathcal{V}_p$). A comparison with the

directly calculated values in column 6 shows that the error involved in taking

$\mathcal{d} = \mathcal{d}$ (Z = 15) is not serious.

IV. VARIATION WITH THE POTENTIAL

We ask now, how crucial is the choise of potential? The value of Z is

a convenient parameter for varying the potential. As pointed out above, most

of the variation in the calculated value of σ is isolated in the function

$\tilde{\mathcal{F}}_{z} \left(\mathcal{V}_p \right)$ which is tabulated in Table 3. Examination of the entries shows

that at Z $\cong$ 26, d ln σ /d ln Z = 0.26, 0.21, 0.10 and 0.02 for V_p = 0.75,

1, 1.5, and 2, respectively. As a rather drastic example, if we use $\mathcal{V}_p = 1$,

we find in going from Z = 15 to Z = 82 that σ has increased only 34% while the

p wave function has gained approximately 3 nodes. At Z = 7, however, σ is some-

what more sensitive to Z.

Let us examine the source of the variation with Z. The TF potential is

non-Coulombic only for $r \tilde{<} 1$ so that changes in P (r) occur only for

$r \tilde{<}$ 1. The r factor in Eq. (2) thus practically eliminates changes in

the radial integral with Z. This leaves the variation in the normalization

factors, N_ℓ . Table 1 illustrates the variation with Z of the radial integral,

N_s, and N_p of Eq. (2) for energies appropriate to the 2p - 3s transition in N I.

N_s does not vary much because the peak of the s-orbital occurs at r = 4.2 where

the potential is 1/r . The relatively strong variation in N_p occurs because

P_p is localized near r = 1. As Z increases the potential steepens, causing

the electron to spend less time at small r . Since the un-normalized wave-

functions are Z-independent at large r , the normalization factor N_p decreases, thus increasing the calculated value of σ^2.

For the specific cases treated in Table 5, a change in Z of only one or two was sufficient to cause convergence at the origin. From this study, a rough limit of 5% can be set on the error due to ignoring the partial divergence at the origin.

V. VARIATION WITH ENERGY

The effective quantum numbers, ν_p, of the non-metal ground states vary from ≈ 0.8 to ≈ 1.4 so that in using a Coulomb potential one is dealing with something like a "1p" Coulomb function - which diverges strongly at the origin. This divergence appears as a factor, $\Gamma(\nu - \ell)$, in the normalization factor N_p inherent in BD. The large normalization factor near $\nu_p = 1$ causes an incorrectly small σ^2. The use of the numerical integration only to $r = .001$ eliminates this divergence. The use of the appropriate Z in the Thomas-Fermi potential then gives more nearly correct absolute values. Except for the non-zero σ at $\nu_p = 1$, Tables 3 and 4 are qualitatively similar to the BD tables.

VI. OTHER METHODS

Burgess and Seaton (1960), in the process of developing their quantum defect method, in effect proposed an extended $\sigma(\nu_p)$ function good for all Z. The dependence on Z is eliminated through the approximate dependence of ν_p on Z. They proposed that the BD normalization factor, N_p^2, be multiplied by $(\nu - 1) \cdot (\nu + 2) / (\nu^2 + \nu)$ for np^q configurations. This factor is derived from the observation that the extrapolated quantum defect, $\mu = n - \nu$, is a nearly

linear function of ϵ between $|\epsilon| = 1$ and the ground state energy, and that the value of μ at $|\epsilon| = 1$ is n - 1. Using this renormalization, we obtain a modified form of the BD function $\mathcal{F}(\nu_p)$:

$$\mathcal{F}_{QD}(\nu_p) = \frac{1}{2}\sqrt{3}\ \nu_p(\nu_p+1)(\nu_p/[\nu_p+2])^{1/2} \tag{9}$$

Some points of this function are tabulated under QD in Table 4 and corresponding σ^2 values are listed in Table 5 under σ^2 (Q D). The values of $\mathcal{F}_{QD}(\nu_p)$ are generally 10-30% larger than the corresponding $\mathcal{F}(\nu_p, Z)$ values though the major variation from high to low Z is followed.

Scaled Thomas-Fermi potentials have been used by Stewart and Rotenberg (1965). They solve the radial equation (3) as the usual boundary value, eigen value problem, adjusting the radial scale of the Thomas-Fermi potential until the eigen value matches the experimental energy. A TF potential somewhat more physical than Latter's is used. Because of the small effect of changes in Z, this STF method will give similar results in so far as their numerical solution (Numerov's method) is "accurate" at large r . That is, consistent with the energy and asymptotic potential.

Similarly, self-consistent field calculations will give the same answers (approximately) if the calculated energies are near the experimental ones, and if the wavefunctions are approximated so as to be accurate at large r .

VII. CHOICE OF EXPERIMENTAL ENERGIES

One can formally obtain σ^2 for transition arrays (nℓ - n'ℓ') or for multiplets (L - L ') by putting in appropriate energies.

For an entire transition array, one averages the energies of the terms in a configuration, weighting by statistical weight. The ionization energy is the average of the ground state terms of the core. These averages remove (to

1st order in perturbation theory) the perturbations due to electrostatic and spin orbit interaction.

For individual multiplets we can attempt to use the philosophy inherent in the Chicago SCF program of Roothaan and Bagus (1963). They say, in effect, let us calculate the energy of a term, variationally, by finding the "best" radial wavefunctions consistent with the central field angular functions appropriate to the term. So, then, let us find the radial wavefunction consistent with the energy of the term and its ℓ value.

However, in the more complex spectra we have difficulty identifying the unique ionization limit for our "equivalent" one-electron central field problem. Let us use a term of the NI ground state to show the problem and illustrate a possible solution. The ^2P term has three (parent + 2p) ion terms, ^1S, ^1D, and ^3P. We can express the expectation value of the ion limit energy by

$$\langle E\ ^2P\ \text{limit} \rangle = 2/9\ E(^1S) + 1/2\ E(^3P) + 5/18\ E(^1D),$$

where the weighting factors are squared coefficients of fractional parentage as given, for example, by Racah (1943). Table 2 lists σ^2 for multiplets in the $2p^3 = 2p^2 3s$ transition array of NI obtained in this fashion. These σ^2 values are compared with the values obtained by Kelly (1964) using the much more complicated Chicago SCF program of Roothaan and Bagus (1963). Exact agreement is not obtained though the general trend down the column is followed.

However, experimental values obtained from the arc intensity measurements of Labuhn (1965), assuming pure configurations, disagree by factors of one to three. Indeed, calculating individual σ values for each multiplet worsens the agreement. Labuhn's measurements have received support from the radiative lifetime determinations of Lawrence and Savage (1966). Analytical

self-consistent field calculations with extensive configuration mixing made for these transitions by Weiss (1966) give better agreement with experiment. Thus, one cannot expect a-priori that central field calculations for individual multiplets will give better transition probabilities than a calculation for the entire array.

VII. COMPARISON WITH EXPERIMENT

Table 5 gives specific calculations for the $mp^n - mp^{n-1}$ $(m + 1)$ s transition arrays of most of the neutral non-metals, excluding the inert gases. The effective quantum numbers ν_s and ν_p are obtained from the average energies, estimating the position of a few unobserved terms. The energies are taken from Moore (1949-58). Values of σ^2 obtained both from Eq. 8 and from direct calculation with the correct Z are listed.

The "experimental" values of σ^2 listed under σ^2 (IC) are mostly derived from radiative lifetime measurements and are discussed by Lawrence (1967). The necessary branching ratios and angular factors were calculated using intermediate coupling theory. The experimental values of σ^2 are generally based on only one or two measurements. The data suggest that these values can be considered accurate to $\pm$ 20% except in cases such as C and N and I where configuration mixing makes such values of σ^2 meaningless within factors of two or three.

The last column in Table 5 gives the ratio of σ^2 (Z) to the experimental value.

IX. EXTENSION TO IONS

Values of σ^2 for the 2p - 3s transitions of OII, OIII, IV, NII, and NIII were calculated, using Tables 3 and 4 and Eq. (8) with $q \neq 1$. The ground state effective quantum numbers, ν_p, range from 1.3 to 1.7. The σ^2's were

compared with the corresponding values given in Table V of STF. The present
values were within 20% of the extrapolated BD given in STF and thus approximately
a factor of two lower than the STF values.

This reproduction of the BD values can be explained in terms of the
potential implicit in the use of Eq. (8). It can be shown from Eq. (3) that
Eq. (8) implies an ion potential $V_I(r) = C^2 V_{TF}(rC)$; where
$V_{TF}(r)$ is Latter's potential as used in the numerical solution. Examina-
tion of $V_I(r)$ and comparison with the ion potentials of STF shows that
although it is asymptotically correct, the scale of the screening is approximately
a factor C too small. Thus the potential serves largely to provide a small cut-off
radius for the BD formulation.

A more correct TF potential for use in Eq. (3), with screening further
out, could be obtained from Gombás (1949) or from STF. The additional screening
will increase the calculated values of σ^2. The numerical calculations required
are not done here.

The ground state quantum defects are closer to their asymptotic value
in ions than neutrals so that the quantum defect method would be expected to
give more accurate results for ions. Thus Eq. 9, Eq. 8 and Table 3 can be used
for the corresponding calculations in ions.

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TABLE 1

RADIAL INTEGRAL AND NORMALIZATION FACTORS FOR NI
VS. Z. ν_p = 1.015; ν_s = 1.79.

Z	I	N_s	N_p
1	1.235	1.89	3.22
7	1.378	1.868	1.034
15	1.382	1.865	0.7314
33	1.318	1.857	0.5608
51	1.266	1.849	0.4847
82	1.202	1.837	0.4374

TABLE 2

VALUES OF σ^2 FOR N I

λ	$2p^3$	$2p^2\ 3s$	ν_p	ν_s	Eq. (8)	OTHER	QD	EXP[c]
1200	^4S	^4P	0.967	1.795	0.132	0.131[a]	0.230	0.34
1495	^2D	^2P	1.018	1.875	.138	.159[a]	.240	.26
1243	^2D	^2D	1.018	1.823	.168	.168[a]	.303	.18
1742	^2P	^2P	1.047	1.875	.174	.187[a]	.304	.26
1412	^2P	^2D	1.047.	1.823	.230	.198[a]	.404	0.20
-	Entire array		1.015	1.79	0.208	0.197[b]	0.360	

a. Kelly (1964) SCF

b. Stewart and Rotenberg (1966) STF

c. From Labuhn (1965) Arc, multiplied by 0.75 as recommended by Lawrence and
Savage (1966).

TABLE 3

$$d\ (\nu_s\ ,\ \nu_p\ );\ Z=15$$

$\nu_s - \nu_p$ \ ν_p	0.5	0.75	1.0	1.5	2.0	BD
0	1.0	1.0	1.0	1.0	1.0	1.0
0.2	0.948	0.988	1.001	1.0	0.968	0.967
0.4	0.784	0.895	0.928	0.899	0.837	0.842
0.6	0.593	0.745	0.779	0.701	0.636	0.643
0.8	0.403	0.551	0.565	0.447	0.402	0.409
1.0	0.223	0.329	0.306	0.191	0.176	0.181
1.2	0.065	0.108	0.062	-0.017		
1.4	-0.055	-0.069	-0.117	-0.147		
1.6	-0.121	-0.171	-0.206	-0.191		
1.8	-0.129	-0.189	-0.205			

TABLE 4

$$\mathcal{F}_{\mathbf{z}} \, (\mathcal{V}_\mathrm{p}, \, \mathrm{z})$$

$\mathcal{V}_\mathrm{p}$	QD	BD	z = 1	7	15	33	51	82
0.5	0.291	-	0.063	0.195	0.470	0.606	0.670	0.739
0.75	0.596	-	0.143	0.461	0.717	0.880	0.956	1.031
1.0	1.0	0	0.264	0.745	0.976	1.15	1.23	1.31
1.5	2.12	1.45	0.866	1.54	1.69	1.83	1.90	1.97
2.0	3.68	3	3.00	3.03	3.07	3.12	3.14	3.17

TABLE 5

SPECIFIC CALCULATIONS COMPARED WITH EXPERIMENT

	ν_s	ν_p	QD σ^2 Eq.8&9	σ^2 Eq. 8	EXT BD $\sigma^2(z)$	EXP. $\sigma^2(IC)$	$\dfrac{\sigma^2(z)}{\text{EXP.}}$
C	1.91	1.13	.29	0.15	0.170	0.362[b]	0.47
Si	2.065	1.32	.90	0.58	0.583	0.65[a]	0.90
Ge	2.06	1.35	1.16	0.88	1.03	0.80[a]	1.29
Sn	2.12	1.39	1.22	0.96	1.17	1.1[a]	1.07
Pb	2.07	1.41	1.74	1.52	1.76	1.25[a]	1.4
N	1.79	1.015	.36	0.21	0.170	Table 2	0.36
P	1.85	1.16	0.68	0.57	0.603	0.60[a]	1.0
As	1.97	1.22	0.71	0.66	0.780	-	
Sb	2.02	1.27	0.80	0.80	0.977	-	
O[d]	1.76	0.93	0.21	0.12	0.127	0.115[c]	1.10
S	1.80	1.08	0.55	0.48	0.494	0.50[a]	0.99
Se	1.81	1.12	0.64	0.74	0.842	-	
F	1.97	0.881	0.06	0.04	0.016	-	
Cl	1.84	0.996	0.24	0.24	0.266	0.202[a]	1.33
Br	1.90	0.994	0.17	0.23	0.407	-	
I	1.87	1.101	0.52	0.70	0.758	0.40[a]	

a. Intermediate coupling + lifetimes, Lawrence (1967).

b. 1656A, τ = 3.1 nsec., Lawrence and Savage (1966).

c. from 1302 Å, τ = 2.4 nsec., Savage and Lawrence (1967).

d. STF gives σ^2 = 0.137.