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## **Transition Probabilities for One Electron Atoms**

Jonathan Baker

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U.S. Department of Commerce  
*Carlos M. Gutierrez, Secretary*

National Institute of Standards and Technology  
*Patrick D. Gallagher, Deputy Director*

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## Abstract

A procedure for calculating transition probabilities for one electron atoms using the fully relativistic Dirac wave function is described in this technical note. Transition probabilities are calculated for Hydrogen transitions between states with  $n \leq 6$ , and presented in the appendix.

## I. INTRODUCTION

A fortran program was written to compute transition probabilities for one electron atoms using the fully relativistic Dirac wave function. The program can evaluate any transition where the sum of the principal quantum numbers for the initial and final states is less than about 80. The transition rate  $\Gamma_{12}$  to go from the initial state  $\phi_1(\mathbf{r})$  with energy  $E_1$  to final state  $\phi_2(\mathbf{r})$  with energy  $E_2$  is given by [1-3]

$$\Gamma_{12} = (\alpha\omega/2\pi) \int_{\Omega} \left| \langle \phi_1(\mathbf{r}) | \boldsymbol{\alpha} \cdot \boldsymbol{\epsilon} e^{i\mathbf{k}\cdot\mathbf{r}} | \phi_2(\mathbf{r}) \rangle \right|^2 d\Omega, \quad (1)$$

where  $\boldsymbol{\alpha}$  is the vector whose components are the Dirac matrices,  $\alpha$  is the fine-structure constant,  $\mathbf{k}$  is the photon wave vector, and  $\boldsymbol{\epsilon}$  is the photon polarization vector. The photon energy is

$$\hbar\omega = E_1 - E_2. \quad (2)$$

The Dirac wave functions can be expressed as follows

$$\begin{aligned} \phi_1(\mathbf{r}) &= \frac{1}{r} \begin{pmatrix} G_1(r)\chi_1^+(\hat{\mathbf{r}}) \\ iF_1(r)\chi_1^-(\hat{\mathbf{r}}) \end{pmatrix}, \\ \phi_2(\mathbf{r}) &= \frac{1}{r} \begin{pmatrix} G_2(r)\chi_2^+(\hat{\mathbf{r}}) \\ iF_2(r)\chi_2^-(\hat{\mathbf{r}}) \end{pmatrix}. \end{aligned} \quad (3)$$

Where the functions  $\chi^+$  and  $\chi^-$  are two component spinors.

When  $e^{i\mathbf{k}\cdot\mathbf{r}}$  is expressed as an expansion in spherical harmonics it can be shown [1-3] that equation (1) can be expressed as a sum of products of functions

$$\begin{aligned} \Gamma_{12} &= 2\alpha\omega(2j_2 + 1) \sum_L \left( B^2(\kappa_1, \kappa_2, L) R_L^2(e) + B^2(-\kappa_1, \kappa_2, L) R_L^2(m) \right) \\ &|j_1 - j_2| \leq L \leq (j_1 + j_2), \end{aligned} \quad (4)$$

where  $l$  and  $j$  are quantum numbers associated with orbital angular momentum and total angular momentum respectively, and  $\kappa$  is related to  $l$  and  $j$  by

$$\begin{aligned} j &= |\kappa| - \frac{1}{2} \quad \text{and} \\ l &= \left| \kappa + \frac{1}{2} \right| - \frac{1}{2}. \end{aligned} \quad (5)$$

The function  $B(\kappa_1, \kappa_2, L)$  is defined as follows,

$$B(\kappa_1, \kappa_2, L) = (-1)^{(j_2+l+\frac{1}{2})} \sqrt{\frac{(2l_1+1)(2l_2+1)(2L+1)}{L(L+1)}} \times \begin{Bmatrix} L & l_2 & l_1 \\ \frac{1}{2} & j_1 & j_2 \end{Bmatrix} \begin{pmatrix} L & l_2 & l_1 \\ 0 & 0 & 0 \end{pmatrix}, \quad (6)$$

where  $\begin{pmatrix} a & b & c \\ d & e & f \end{pmatrix}$  and  $\begin{Bmatrix} a & b & c \\ d & e & f \end{Bmatrix}$  are respectively Wigner 3-j and Wigner 6-j symbols.

The Wigner 3-j and Wigner 6-j symbols in equation (6) have closed form expressions [7].

Let  $J = L + l_1 + l_2$ , then  $B^2(\kappa_1, \kappa_2, L) = 0$  for odd  $J$  and

$$B^2(\kappa_1, \kappa_2, L) = \frac{(2l_1+1)(2l_2+1)(2L+1)}{L(L+1)} \left| \frac{(L+\kappa_1+\kappa_2+1)(\kappa_1+\kappa_2-L)}{4\kappa_1\kappa_2(2\kappa_1+1)(2\kappa_2+1)} \right| \times \frac{(J-2L)!(J-2l_1)!(J-2l_2)!}{(J+1)!} \left( \frac{(\frac{J}{2})!}{(\frac{J}{2}-L)!(\frac{J}{2}-l_1)!(\frac{J}{2}-l_2)!} \right)^2 \quad (7)$$

when  $J$  is even [1].

The radial integrals  $R_L(e)$  and  $R_L(m)$  corresponding to the allowed electric and magnetic multipole moments for the transition are

$$R_L(e) = \int \frac{dr}{kr} \left[ \left( F_2(r)G_1(r) - G_2(r)F_1(r) \right) L(L+1)j_L(kr) + (\kappa_1 + \kappa_2) \left( F_2(r)G_1(r) - G_2(r)F_1(r) \right) \left( r \frac{d}{dr} j_L(kr) + j_L(kr) \right) \right] \\ R_L(m) = (\kappa_1 + \kappa_2) \int dr j_L(kr) \left( F_2(r)G_1(r) + G_2(r)F_1(r) \right), \quad (8)$$

where  $F_1(r)$ ,  $F_2(r)$ ,  $G_1(r)$  and  $G_2(r)$  are the radial parts of the wave function defined in equation (3), and  $j_L(r)$  are spherical Bessel functions.

Scofield provides a more complete derivation of equation (4) and the definitions in equations (6) and (8) in reference [3].

Numerical evaluation is structured around equation (4). Prior to performing the sum, the functions  $B^2(\kappa_1, \kappa_2, L)$  are tabulated and separately,  $R_L(e)$  and  $R_L(m)$  are also tabulated for all values of  $L$  in the sum. The energies of the two states are computed from equation (11) described in the next section where the radial functions  $F(r)$  and  $G(r)$  are discussed;  $\omega$  is computed from equation (2).

After the sum in equation (4) is computed the value  $\Gamma_{12}$  is scaled by the reduced mass ratio  $\frac{m_N}{m_N+m_e}$  where  $m_N$  and  $m_e$  are the nuclear mass and the electron mass respectively.

## II. THE $R_L(e)$ AND $R_L(m)$ INTEGRALS

The radial wave functions  $F(r)$  and  $G(r)$  are computed recursively following Appendix A in reference [4].

$$\begin{aligned} F(r) &= \sqrt{N}\sqrt{1+E} \sum_{m=0}^{n_r} (C_1^{(m)} + C_2^{(m)}) (2ar)^{m+\lambda-1} e^{-ar} \\ G(r) &= \sqrt{N}\sqrt{1-E} \sum_{m=0}^{n_r} (C_1^{(m)} - C_2^{(m)}) (2ar)^{m+\lambda-1} e^{-ar} \end{aligned} \quad (9)$$

where

$$\begin{aligned} n_r &= n - |\kappa| \\ \lambda &= \sqrt{\kappa^2 - (Z\alpha)^2} \\ a &= \frac{Z\alpha}{\sqrt{(n_r + \lambda)^2 + (Z\alpha)^2}} \\ N &= \frac{2a^5}{Z\alpha(Z\alpha - \kappa a)} \frac{\Gamma(2\lambda + 1 + n_r)}{\Gamma(2\lambda + 1)^2 \Gamma(n_r + 1)}. \end{aligned} \quad (10)$$

The energy of the bound-state is

$$E = \sqrt{1 - a^2} \quad (11)$$

The coefficients  $C_1^{(m+1)}$  and  $C_2^{(m+1)}$  are defined recursively by the equations

$$\begin{aligned} C_1^{(0)} &= -n_r \\ C_1^{(m+1)} &= \frac{m+1-n_r}{(m+2\lambda+1)(m+1)} C_1^{(m)} \\ C_2^{(0)} &= \frac{Z\alpha}{a} - \kappa \\ C_2^{(m+1)} &= \frac{m-n_r}{(m+2\lambda+1)(m+1)} C_2^{(m)}. \end{aligned} \quad (12)$$

The  $R_L(e)$  and  $R_L(m)$  integrals are performed numerically, using Gauss-Laguerre quadrature which approximates integrals of the form [5]

$$\int_0^\infty x^\sigma e^{-x} f(x) dx \quad (13)$$

Both the exponential term and the fractional power of  $r^\lambda$ , in equation (9) can be absorbed into the weight factor, so that evaluation of  $R_L(e)$  and  $R_L(m)$  requires either

$f(x) \sim j_L(kr)P(x)$ , or  $f(x) \sim \frac{dj_L(kr)}{dx}P(x)$  where  $P(x)$  is a polynomial. Moreover, since the wavelength of radiation for hydrogenic transitions is large compared to the Bohr radius, we expect that  $j_L(kr)$  and the derivative to be well approximated by the first couple of terms in the Taylor series in regions where the wave functions are appreciable. Therefore  $f(x)$  is to good approximation simply a polynomial and since Gauss-Laguerre integration exactly evaluates a polynomial of order  $2m - 1$  with  $m$  knots, highly accurate integration results can be obtained when the number of knots is the sum of the two  $n_r$  values in equation (9) plus a constant (12 in this case). In practice, small variations in the number of knots indicate that our choice of knot number generates transition probabilities good to at least 10 digits over transitions between states where both principal quantum numbers are less than 40.

All Gaussian quadrature schemes choose the  $m$  knots to be the roots of an orthogonal polynomial of degree  $m$ . The root finding algorithm used in this program fails when  $m \geq 95$ . For this reason the sum of the two values of  $n_r$  in equation (9) must not be greater than about 80.

The values of spherical Bessel functions  $j_L(kr)$  at the knots are computed recursively in the stable direction going from large  $L$  downward using Miller's method [6]. In this approach a guess is made for the value of  $j_L(kr)$  for values of  $L$  somewhat larger than the maximum value desired. Recurrence relations for the spherical Bessel function then step downward in  $L$  to  $L = 0$  where the exact value is known. If the original maximum value of  $L$  is large enough, the values produced using the downward recurrence at lower values of  $L$  are directly proportional to the correct values, and knowledge of the exact value at  $L = 0$  allows the constant of proportionality to be determined. Rescaling the tabled values then generates the table of  $j_l(kr)$ .

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#### **Appendix A: Table of Transition Probabilities for Hydrogen**

The table below provides transition probabilities in Hertz for fine structure transitions in Hydrogen through  $n \leq 6$  The atomic mass was 1.0078250321 AMU.

transition	rate	transition	rate	transition	rate
$1s_{\frac{1}{2}} 2p_{\frac{3}{2}}$	626482607.00	$1s_{\frac{1}{2}} 2p_{\frac{1}{2}}$	626494236.00	$1s_{\frac{1}{2}} 3p_{\frac{3}{2}}$	167251765.00
$1s_{\frac{1}{2}} 3p_{\frac{1}{2}}$	167251326.00	$1s_{\frac{1}{2}} 4p_{\frac{3}{2}}$	68186317.40	$1s_{\frac{1}{2}} 4p_{\frac{1}{2}}$	68185609.30
$1s_{\frac{1}{2}} 5p_{\frac{3}{2}}$	34375152.50	$1s_{\frac{1}{2}} 5p_{\frac{1}{2}}$	34374660.00	$1s_{\frac{1}{2}} 6p_{\frac{3}{2}}$	19728237.80
$1s_{\frac{1}{2}} 6p_{\frac{1}{2}}$	19727908.60	$2s_{\frac{1}{2}} 3p_{\frac{3}{2}}$	22447988.20	$2s_{\frac{1}{2}} 3p_{\frac{1}{2}}$	22449083.00
$2s_{\frac{1}{2}} 4p_{\frac{3}{2}}$	9668046.04	$2s_{\frac{1}{2}} 4p_{\frac{1}{2}}$	9668339.74	$2s_{\frac{1}{2}} 5p_{\frac{3}{2}}$	4948324.58
$2s_{\frac{1}{2}} 5p_{\frac{1}{2}}$	4948438.61	$2s_{\frac{1}{2}} 6p_{\frac{3}{2}}$	2858331.76	$2s_{\frac{1}{2}} 6p_{\frac{1}{2}}$	2858386.37
$2p_{\frac{3}{2}} 3s_{\frac{1}{2}}$	4209659.65	$2p_{\frac{1}{2}} 3s_{\frac{1}{2}}$	2104596.86	$2p_{\frac{3}{2}} 3d_{\frac{5}{2}}$	64650898.90
$2p_{\frac{3}{2}} 3d_{\frac{3}{2}}$	10775136.90	$2p_{\frac{1}{2}} 3d_{\frac{3}{2}}$	53877072.60	$2p_{\frac{3}{2}} 4s_{\frac{1}{2}}$	1719000.45
$2p_{\frac{1}{2}} 4s_{\frac{1}{2}}$	859410.93	$2p_{\frac{3}{2}} 4d_{\frac{5}{2}}$	20625192.20	$2p_{\frac{3}{2}} 4d_{\frac{3}{2}}$	3437496.42
$2p_{\frac{1}{2}} 4d_{\frac{3}{2}}$	17188279.10	$2p_{\frac{3}{2}} 5s_{\frac{1}{2}}$	859196.94	$2p_{\frac{1}{2}} 5s_{\frac{1}{2}}$	429554.59
$2p_{\frac{3}{2}} 5d_{\frac{5}{2}}$	9425363.31	$2p_{\frac{3}{2}} 5d_{\frac{3}{2}}$	1570871.66	$2p_{\frac{1}{2}} 5d_{\frac{3}{2}}$	7854783.94
$2p_{\frac{3}{2}} 6s_{\frac{1}{2}}$	490062.52	$2p_{\frac{1}{2}} 6s_{\frac{1}{2}}$	245006.41	$2p_{\frac{3}{2}} 6d_{\frac{5}{2}}$	5144980.72
$2p_{\frac{3}{2}} 6d_{\frac{3}{2}}$	857482.92	$2p_{\frac{1}{2}} 6d_{\frac{3}{2}}$	4287663.85	$3s_{\frac{1}{2}} 4p_{\frac{3}{2}}$	3065039.74
$3s_{\frac{1}{2}} 4p_{\frac{1}{2}}$	3065217.09	$3s_{\frac{1}{2}} 5p_{\frac{3}{2}}$	1637691.42	$3s_{\frac{1}{2}} 5p_{\frac{1}{2}}$	1637758.34
$3s_{\frac{1}{2}} 6p_{\frac{3}{2}}$	955079.63	$3s_{\frac{1}{2}} 6p_{\frac{1}{2}}$	955111.99	$3p_{\frac{3}{2}} 4s_{\frac{1}{2}}$	1223772.46
$3p_{\frac{1}{2}} 4s_{\frac{1}{2}}$	611824.69	$3p_{\frac{3}{2}} 4d_{\frac{5}{2}}$	7037596.66	$3p_{\frac{3}{2}} 4d_{\frac{3}{2}}$	1172942.86
$3p_{\frac{1}{2}} 4d_{\frac{3}{2}}$	5864673.81	$3p_{\frac{3}{2}} 5s_{\frac{1}{2}}$	603198.36	$3p_{\frac{1}{2}} 5s_{\frac{1}{2}}$	301571.13
$3p_{\frac{3}{2}} 5d_{\frac{5}{2}}$	3391477.00	$3p_{\frac{3}{2}} 5d_{\frac{3}{2}}$	565246.73	$3p_{\frac{1}{2}} 5d_{\frac{3}{2}}$	2826268.54
$3p_{\frac{3}{2}} 6s_{\frac{1}{2}}$	338151.22	$3p_{\frac{1}{2}} 6s_{\frac{1}{2}}$	169060.23	$3p_{\frac{3}{2}} 6d_{\frac{5}{2}}$	1877787.93
$3p_{\frac{3}{2}} 6d_{\frac{3}{2}}$	312963.94	$3p_{\frac{1}{2}} 6d_{\frac{3}{2}}$	1564851.13	$3d_{\frac{5}{2}} 4p_{\frac{3}{2}}$	312799.86
$3d_{\frac{3}{2}} 4p_{\frac{3}{2}}$	34753.98	$3d_{\frac{3}{2}} 4p_{\frac{1}{2}}$	347592.59	$3d_{\frac{5}{2}} 4f_{\frac{7}{2}}$	13787949.40
$3d_{\frac{5}{2}} 4f_{\frac{5}{2}}$	919194.57	$3d_{\frac{3}{2}} 4f_{\frac{5}{2}}$	12868844.00	$3d_{\frac{5}{2}} 5p_{\frac{3}{2}}$	134589.59
$3d_{\frac{3}{2}} 5p_{\frac{3}{2}}$	14953.74	$3d_{\frac{3}{2}} 5p_{\frac{1}{2}}$	149559.57	$3d_{\frac{5}{2}} 5f_{\frac{7}{2}}$	4542144.19

transition	rate	transition	rate	transition	rate
$3d_{\frac{3}{2}} 5f_{\frac{5}{2}}$	302807.29	$3d_{\frac{3}{2}} 5f_{\frac{5}{2}}$	4239379.41	$3d_{\frac{3}{2}} 6p_{\frac{3}{2}}$	70420.77
$3d_{\frac{3}{2}} 6p_{\frac{3}{2}}$	7824.18	$3d_{\frac{3}{2}} 6p_{\frac{1}{2}}$	78253.43	$3d_{\frac{3}{2}} 6f_{\frac{7}{2}}$	2146034.86
$3d_{\frac{3}{2}} 6f_{\frac{5}{2}}$	143067.54	$3d_{\frac{3}{2}} 6f_{\frac{5}{2}}$	2002989.84	$4s_{\frac{1}{2}} 5p_{\frac{3}{2}}$	737159.14
$4s_{\frac{1}{2}} 5p_{\frac{1}{2}}$	737205.16	$4s_{\frac{1}{2}} 6p_{\frac{3}{2}}$	445610.50	$4s_{\frac{1}{2}} 6p_{\frac{1}{2}}$	445631.12
$4p_{\frac{3}{2}} 5s_{\frac{1}{2}}$	430099.22	$4p_{\frac{1}{2}} 5s_{\frac{1}{2}}$	215029.15	$4p_{\frac{3}{2}} 5d_{\frac{5}{2}}$	1485778.34
$4p_{\frac{3}{2}} 5d_{\frac{3}{2}}$	247632.93	$4p_{\frac{1}{2}} 5d_{\frac{3}{2}}$	1238135.61	$4p_{\frac{3}{2}} 6s_{\frac{1}{2}}$	238852.00
$4p_{\frac{1}{2}} 6s_{\frac{1}{2}}$	119415.62	$4p_{\frac{3}{2}} 6d_{\frac{5}{2}}$	862191.17	$4p_{\frac{3}{2}} 6d_{\frac{3}{2}}$	143699.41
$4p_{\frac{1}{2}} 6d_{\frac{3}{2}}$	718493.39	$4d_{\frac{5}{2}} 5p_{\frac{3}{2}}$	169620.91	$4d_{\frac{3}{2}} 5p_{\frac{3}{2}}$	18846.01
$4d_{\frac{3}{2}} 5p_{\frac{1}{2}}$	188485.39	$4d_{\frac{5}{2}} 5f_{\frac{7}{2}}$	2584411.60	$4d_{\frac{5}{2}} 5f_{\frac{5}{2}}$	172294.46
$4d_{\frac{3}{2}} 5f_{\frac{5}{2}}$	2412123.52	$4d_{\frac{5}{2}} 6p_{\frac{3}{2}}$	84755.43	$4d_{\frac{3}{2}} 6p_{\frac{3}{2}}$	9416.90
$4d_{\frac{3}{2}} 6p_{\frac{1}{2}}$	94181.21	$4d_{\frac{5}{2}} 6f_{\frac{7}{2}}$	1286982.51	$4d_{\frac{5}{2}} 6f_{\frac{5}{2}}$	85798.63
$4d_{\frac{3}{2}} 6f_{\frac{5}{2}}$	1201190.73	$4f_{\frac{7}{2}} 5d_{\frac{5}{2}}$	48074.58	$4f_{\frac{5}{2}} 5d_{\frac{5}{2}}$	2403.67
$4f_{\frac{5}{2}} 5d_{\frac{3}{2}}$	50479.79	$4f_{\frac{7}{2}} 5g_{\frac{9}{2}}$	4254173.90	$4f_{\frac{7}{2}} 5g_{\frac{7}{2}}$	151934.49
$4f_{\frac{5}{2}} 5g_{\frac{7}{2}}$	4102251.69	$4f_{\frac{7}{2}} 6d_{\frac{5}{2}}$	20428.90	$4f_{\frac{5}{2}} 6d_{\frac{5}{2}}$	1021.42
$4f_{\frac{5}{2}} 6d_{\frac{3}{2}}$	21450.98	$4f_{\frac{7}{2}} 6g_{\frac{9}{2}}$	1372778.80	$4f_{\frac{7}{2}} 6g_{\frac{7}{2}}$	49027.54
$4f_{\frac{5}{2}} 6g_{\frac{7}{2}}$	1323757.13	$5s_{\frac{1}{2}} 6p_{\frac{3}{2}}$	242945.70	$5s_{\frac{1}{2}} 6p_{\frac{1}{2}}$	242961.55
$5p_{\frac{3}{2}} 6s_{\frac{1}{2}}$	178801.61	$5p_{\frac{1}{2}} 6s_{\frac{1}{2}}$	89392.60	$5p_{\frac{3}{2}} 6d_{\frac{5}{2}}$	449482.39
$5p_{\frac{3}{2}} 6d_{\frac{3}{2}}$	74914.89	$5p_{\frac{1}{2}} 6d_{\frac{3}{2}}$	374561.87	$5d_{\frac{3}{2}} 6p_{\frac{3}{2}}$	86343.65
$5d_{\frac{3}{2}} 6p_{\frac{3}{2}}$	9593.38	$5d_{\frac{3}{2}} 6p_{\frac{1}{2}}$	95945.64	$5d_{\frac{3}{2}} 6f_{\frac{7}{2}}$	723255.40
$5d_{\frac{3}{2}} 6f_{\frac{5}{2}}$	48217.24	$5d_{\frac{3}{2}} 6f_{\frac{5}{2}}$	675038.13	$5f_{\frac{7}{2}} 6d_{\frac{5}{2}}$	37219.66
$5f_{\frac{5}{2}} 6d_{\frac{5}{2}}$	1860.94	$5f_{\frac{5}{2}} 6d_{\frac{3}{2}}$	39081.66	$5f_{\frac{7}{2}} 6g_{\frac{9}{2}}$	1105692.38
$5f_{\frac{7}{2}} 6g_{\frac{7}{2}}$	39489.03	$5f_{\frac{5}{2}} 6g_{\frac{7}{2}}$	1066205.00	$5g_{\frac{9}{2}} 6f_{\frac{7}{2}}$	11057.13
$5g_{\frac{7}{2}} 6f_{\frac{7}{2}}$	315.91	$5g_{\frac{7}{2}} 6f_{\frac{5}{2}}$	11373.19	$5g_{\frac{9}{2}} 6h_{\frac{11}{2}}$	1644831.07
$5g_{\frac{9}{2}} 6h_{\frac{9}{2}}$	36551.75	$5g_{\frac{7}{2}} 6h_{\frac{9}{2}}$	1608281.86		