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# Three-photon transitions from ground state to bound states in atomic hydrogen

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## Abstract

In this paper, we present an efficient alternative method for the evaluation of the three-photon transition matrix element in the dipole approximation from the ground state to bound states in atomic hydrogen. This method is a variation of the Dalgarno–Lewis method for the treatment of the second-order Stark effect in the hydrogen atom. In this approach, the infinite double sum over the complete set of states including the continuum states present in the third-order perturbation theory result is treated exactly. The closed analytical expression obtained for the matrix element, as a function of incident photon energy, clearly displays all singularities present in the original third-order perturbation theory result.

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## 1. Introduction

When perturbative methods are used for the evaluation of multiphoton transition rates, a major difficulty found in such calculations is the infinite sum over the complete set of intermediate states, which includes both discrete and continuum states. Among different methods [1], the differential equation method using the implicit summation technique of Dalgarno and Lewis [2] is more advantageous both in terms of computational efficiency and numerical accuracy than other methods which approximate the summation by various truncation schemes [3]. There are many known ways of calculating these transition matrix elements [4, 5]. The use of the Dalgarno–Lewis method reduces the problem formally to finding the solution of a set of coupled inhomogeneous differential equations. Here we apply this method for the evaluation of the three-photon transition matrix element from the ground state in atomic hydrogen and obtain an alternative analytical expression [6] for the transition matrix element. This is a very useful method if the details of entire intermediate states are not known as in alkali atoms.

## 2. Method of implicit summation

In this paper, we consider the three-photon transitions in atomic hydrogen using a radiation with frequency  $\omega$  polarized along the  $z$ -axis. In the dipole approximation, the three-photon transition rate for the hydrogen atom from an initial ground state  $|g\rangle$  to a final state  $|f\rangle$  can be calculated using the following transition matrix element in the atomic unit [7]:

$$D_{fg}^{(3)} = \sum_{i,i'} \frac{\langle f|z|i\rangle\langle i|z|i'\rangle\langle i'|z|g\rangle}{(E_i - E_g - 2\omega)(E_{i'} - E_g - \omega)} \quad (1)$$

where the summation includes discrete as well as continuum states. Here  $z$  is in units of the Bohr radius  $a$ , and the energies  $E_g$ ,  $E_i$ ,  $E_{i'}$  and  $\omega$  are in units of  $(e^2/a)$ . The main objective of the present work is to obtain an alternative expression for the matrix element given in equation (1) retaining all analytical structure as a function of the incident photon energy  $\omega$ . In order to perform the infinite double summation over the complete set of states including the contribution from continuum states, we extend the Dalgarno–Lewis method by defining two auxiliary dimensionless operator  $D_1$  and  $D_2$  as follows

$$z|g\rangle = (D_1 H_0 - H_0 D_1 + \omega D_1)|g\rangle \quad (2)$$

and

$$z D_1 |g\rangle = (D_2 H_0 - H_0 D_2 + 2\omega D_2)|g\rangle \quad (3)$$

where  $H_0$  is the hydrogen atom Hamiltonian in atomic units and

$$H_0 = \frac{-\nabla^2}{2} - \frac{1}{r}. \quad (4)$$

Now, using the closure relation  $\sum_i |i\rangle\langle i| = I$ , where  $I$  is the unit operator and substituting equations (2) and (3) into equation (1) we can write

$$D_{fg}^{(3)} = \langle f|z D_2 |g\rangle. \quad (5)$$

Thus, the problem of finding an analytical expression for the transition matrix element is reduced to a problem of finding a possible analytical expression for the operator  $D_2$ . It is useful to note that the operator  $D_1$  can be used [8] to express the two-photon transition matrix element  $D_{fg}^{(2)}$  given by

$$D_{fg}^{(2)} = \sum_i \frac{\langle f|z|i\rangle\langle i|z|g\rangle}{E_g - E_i + \omega} \quad (6)$$

as

$$D_{fg}^{(2)} = \langle f|z D_1 |g\rangle. \quad (7)$$

In this way, we can also obtain an alternative analytical expression [9] for the two-photon transition matrix element.

Now using  $|g\rangle = \exp(-r)/\sqrt{\pi}$  as the ground-state wavefunction of the hydrogen atom, the angular separation of the functions  $D_1$  and  $D_2$  can be performed by writing

$$D_1(\mathbf{r}) = r\psi_1(r)P_1(\cos\theta) \quad (8)$$

and

$$D_2(\mathbf{r}) = \psi_0(r) + r^2\psi_2(r)P_2(\cos\theta) \quad (9)$$

where  $P_l(\cdot)$  is the Legendre polynomial of order  $l$ . Substituting equations (8) and (9) into equations (2) and (3) the angular separation can easily be achieved and the following differential equations can be obtained for the unknown radial functions  $\psi_1$ ,  $\psi_0$  and  $\psi_2$ :

$$r \frac{d^2}{dr^2} \psi_1(r) + (4 - 2r) \frac{d}{dr} \psi_1(r) + (2\omega r - 2) \psi_1(r) = 2r \tag{10}$$

$$r \frac{d^2}{dr^2} \psi_0(r) + (2 - 2r) \frac{d}{dr} \psi_0(r) + 4\omega r \psi_0(r) = \frac{2}{3} r^3 \psi_1(r) \tag{11}$$

$$r \frac{d^2}{dr^2} \psi_2(r) + (6 - 2r) \frac{d}{dr} \psi_2(r) + (4\omega r - 4) \psi_2(r) = \frac{4}{3} r \psi_1(r). \tag{12}$$

Using the following notations:

$$\mathcal{D}_{l\lambda} = r \frac{d^2}{dr^2} + (2l + 2 - 2r) \frac{d}{dr} + (1 - \lambda^2) r - 2l. \tag{13}$$

$$\lambda_1 = \sqrt{1 - 2\omega} \tag{14}$$

$$\lambda_0 = \lambda_2 = \sqrt{1 - 4\omega} \tag{15}$$

equations (10)–(12) can be written as a single equation

$$\mathcal{D}_{l\lambda_i} \psi_l(r) = f_l(r) \tag{16}$$

where  $f_1(r) = 2r$ ,  $f_0(r) = (2/3)r^3\psi_1(r)$  and  $f_2(r) = (4/3)r\psi_1(r)$  and equations (10)–(12) can be obtained by taking  $l = 1, 0$  and  $2$ , respectively, in equation (16). The solutions to the differential equations (10)–(12) can be obtained by the method of Laplace transform [10]. This is achieved by using the following definitions:

$$K(p, q, \lambda, s) = \left(\frac{1 - \lambda}{1 + \lambda}\right)^{\frac{1}{\lambda}} (s + \lambda)^{p+\frac{1}{\lambda}} (s - \lambda)^{q-\frac{1}{\lambda}} \tag{17}$$

$$\Phi(p, q, \lambda, t, r) = \int_{\lambda}^t ds e^{-r(s-1)} K(p, q, \lambda, s) \tag{18}$$

where  $p, q$  and  $\lambda$  are real numbers. The integrals in equation (18) are defined only for  $q - 1/\lambda > -1$ . It is easy to analytically continue this definition for  $q - 1/\lambda < -1$  also. This is done by writing  $(s - \lambda)^{q-\frac{1}{\lambda}} = \partial/\partial s \{(s - \lambda)^{q+1-\frac{1}{\lambda}}\} / (q + 1 - \frac{1}{\lambda})$  in equation (18) and performing a partial integration. By neglecting the lower limit contribution of the integrated part we obtain

$$\begin{aligned} \Phi(p, q, \lambda, t, r) = & \frac{1}{q + 1 - \frac{1}{\lambda}} \left\{ e^{-r(t-1)} K(p, q + 1, \lambda, t) \right. \\ & \left. + r \Phi(p, q + 1, \lambda, t, r) - \left(p + \frac{1}{\lambda}\right) \Phi(p - 1, q + 1, \lambda, t, r) \right\}. \end{aligned} \tag{19}$$

This is an important recurrence relation and it can be used to analytically continue the function  $\Phi(p, q, \lambda, t, r)$  for  $q - 1/\lambda > -2$ , since the right-hand side of the equation is well defined for  $q - 1/\lambda > -2$ . It also clearly displays the singularities of  $\Phi(\cdot)$  as a function of  $\lambda$ . The function  $\Phi(\cdot)$  has simple poles at  $q + 1 = 1/\lambda$ . By repeating this procedure we can see that the function  $\Phi(\cdot)$  has simple poles for those values of  $\lambda$  such that  $q + n = 1/\lambda$  where  $n = 1, 2, 3, \dots$ . The transition matrix element can be expressed in terms of this function with  $q$  as a positive integer. Since  $\lambda$  is related to the photon frequency  $\omega$ , these values of  $\lambda$  correspond to one- and two-photon intermediate resonance singularities present in equation (1). Now using the following relations:

$$\frac{d}{dr} \Phi(p, q, \lambda, t, r) = \int_{\lambda}^t ds e^{-r(s-1)} K(p, q, \lambda, s) (1 - s)$$

$$r \Phi(p, q, \lambda, t, r) = - \int_{\lambda}^t ds \frac{\partial}{\partial s} \{e^{-r(s-1)}\} K(p, q, \lambda, s)$$

and by taking  $p = q = l$  in equation (18) and operating  $\mathcal{D}_{l\lambda}$  given by equation (13) on it, after performing a partial integration and rearranging the expressions, we obtain an important relation

$$\mathcal{D}_{l\lambda}\Phi(l, l, \lambda, t, r) = -e^{-r(t-1)}K(l+1, l+1, \lambda, t) \quad (20)$$

where we have assumed  $q+1-1/\lambda > 0$ . For an arbitrary function  $\psi(r)$ , we have the following relations also:

$$\mathcal{D}_{l\lambda}(r\psi) = r\mathcal{D}_{l\lambda}\psi + 2r\frac{d}{dr}\psi + (2l+2-2r)\psi \quad (21)$$

$$\mathcal{D}_{0\lambda_0}\psi = \mathcal{D}_{1\lambda_1}\psi - 2\frac{d}{dr}\psi + (2\omega r + 2)\psi \quad (22)$$

$$\mathcal{D}_{2\lambda_2}\psi = \mathcal{D}_{1\lambda_1}\psi + 2\frac{d}{dr}\psi + (2\omega r - 2)\psi. \quad (23)$$

Now using the relations in equations (20)–(23) and after some algebra we can show that the following are the solutions to equations (10)–(12):

$$\psi_1(r) = \frac{1}{\omega} - \frac{1}{2\omega^3}\Phi(1, 1, \lambda_1, 1, r) \quad (24)$$

$$\begin{aligned} \psi_0(r) = & \frac{2}{3\omega^2} \left\{ \frac{r^2}{4} + \frac{1}{4\omega^2}(1-2\lambda_1) - \frac{3}{8\omega} \right\} - \frac{1}{3\lambda_1\omega^4}\Phi(0, 0, \lambda_2, 1, r) \\ & - \frac{1}{6\omega^4} \left\{ r^2 + \frac{\lambda_1}{\omega}r - \frac{1}{\omega} \left( 1 + \frac{1}{\lambda_1} \right) \right\} \Phi(1, 1, \lambda_1, 1, r) \\ & - \frac{1}{3\omega^4} \left( 1 + \frac{1}{\lambda_1} \right) \int_{\lambda_1}^1 dt \frac{K(1, 1, \lambda_1, t)}{K(1, 1, \lambda_2, t)} \\ & \times \left\{ \frac{1-2\omega}{\omega(1+\lambda_1)} - \frac{t}{\omega} - \frac{2}{t+\lambda_1} + \frac{2}{(t+\lambda_1)^2} \right\} \Phi(0, 0, \lambda_2, t, r) \end{aligned} \quad (25)$$

$$\psi_2(r) = \frac{1}{3\omega^2} - \frac{1}{3\omega^4}\Phi(1, 1, \lambda_1, 1, r) + \frac{2}{3\omega^4} \int_{\lambda_1}^1 dt \frac{K(1, 1, \lambda_1, t)t}{K(3, 3, \lambda_2, t)} \Phi(2, 2, \lambda_2, t, r) \quad (26)$$

where we have used the identity  $K(l, l, \lambda, 1) = (1 - \lambda^2)^l$ , and  $\lambda_1$  and  $\lambda_2$  are given in equations (14) and (15).

The transition matrix element from the ground state to a final state  $|f\rangle$  with principle quantum number  $n$  and orbital angular momentum  $l$  can be calculated by taking [11]

$$|f\rangle = |nl\rangle = \sqrt{\frac{2l+1}{4\pi}} R_{nl}(r) P_l(\cos\theta) \quad (27)$$

where

$$R_{nl}(r) = \frac{2}{n^{l+2}(2l+1)!} \sqrt{\frac{(n+l)!}{(n-l-1)!}} (2r)^l \exp\left(-\frac{r}{n}\right) F\left(l+1-n, 2l+2, \frac{2r}{n}\right) \quad (28)$$

and  $F(\cdot)$  is the confluent hypergeometric function. Substituting equations (27), (8) and (9) into equation (5) and using the orthogonality relation for Legendre polynomials, we can see that the transitions are possible only for  $l = 1$  and  $l = 3$  states, which are the well-known selection rules for three-photon transitions. Now we denote  $D_{fg}^{(3)}$  by  $D_{nl}^{(3)}$  and matrix element for the  $l = 1$  transition can be written as

$$D_{n1}^{(3)} = \frac{2}{\sqrt{3}} \int_0^\infty dr R_{n1}(r) e^{-r} \left\{ r^3\psi_0(r) + \frac{2}{5}r^5\psi_2(r) \right\}. \quad (29)$$

Similarly the matrix element for the  $l = 3$  transition is

$$D_{n3}^{(3)} = \frac{6}{5\sqrt{7}} \int_0^\infty dr R_{n3}(r) r^5 e^{-r} \psi_2(r). \tag{30}$$

Using equations (25) and (26) in equations (29) and (30), the  $r$  integration can be performed exactly. For its evaluation, the following definitions are very useful:

$$I_{nl}(s, k) = \int_0^\infty dr R_{nl}(r) e^{-rs} r^k \tag{31}$$

$$\begin{aligned} \mathcal{I}_{nl}(p, q, \lambda, t, k) &= \int_0^\infty dr R_{nl}(r) e^{-r} r^k \Phi(p, q, \lambda, t, r) \\ &= \int_\lambda^t ds K(p, q, \lambda, s) I_{nl}(s, k). \end{aligned} \tag{32}$$

The following relations [12] are also useful for the numerical evaluation of the transition matrix elements:

$$I_{nl}(s, l + 1) = \frac{2^{l+1}}{n^{l+2}} \sqrt{\frac{(n+l)!}{(n-l-1)!}} \frac{(s - \frac{1}{n})^{n-l-1}}{(s + \frac{1}{n})^{n+l+1}} \tag{33}$$

$$I_{nl}(s, k + 1) = -\frac{\partial}{\partial s} I_{nl}(s, k). \tag{34}$$

With these we can write

$$\begin{aligned} \int_0^\infty dr R_{nl}(r) e^{-r} r^5 \psi_2(r) &= \frac{1}{3\omega^2} I_{nl}(1, 5) - \frac{1}{3\omega^4} \mathcal{I}_{nl}(1, 1, \lambda_1, 1, 5) \\ &+ \frac{2}{3\omega^4} \int_{\lambda_1}^1 dt \frac{K(1, 1, \lambda_1, t)t}{K(3, 3, \lambda_2, t)} \mathcal{I}_{nl}(2, 2, \lambda_2, t, 5) \end{aligned} \tag{35}$$

$$\begin{aligned} \int_0^\infty dr R_{nl}(r) e^{-r} r^3 \psi_0(r) &= \frac{1}{6\omega^2} I_{nl}(1, 5) + \frac{2}{3\omega^2} \left\{ \frac{1}{4\omega^2} (1 - 2\lambda_1) - \frac{3}{8\omega} \right\} I_{nl}(1, 3) \\ &- \frac{1}{3\lambda_1\omega^4} \mathcal{I}_{nl}(0, 0, \lambda_2, 1, 3) - \frac{1}{6\omega^4} \left\{ \mathcal{I}_{nl}(1, 1, \lambda_1, 1, 5) + \frac{\lambda_1}{\omega} \mathcal{I}_{nl}(1, 1, \lambda_1, 1, 4) \right. \\ &- \left. \frac{1}{\omega} \left( 1 + \frac{1}{\lambda_1} \right) \mathcal{I}_{nl}(1, 1, \lambda_1, 1, 3) \right\} - \frac{1}{3\omega^4} \left( 1 + \frac{1}{\lambda_1} \right) \int_{\lambda_1}^1 dt \frac{K(1, 1, \lambda_1, t)}{K(1, 1, \lambda_2, t)} \\ &\times \left\{ \frac{1 - 2\omega}{\omega(1 + \lambda_1)} - \frac{t}{\omega} - \frac{2}{t + \lambda_1} + \frac{2}{(t + \lambda_1)^2} \right\} \mathcal{I}_{nl}(0, 0, \lambda_2, t, 3). \end{aligned} \tag{36}$$

By choosing proper values for  $l$  in equations (35) and (36) the transition matrix elements  $D_{n1}^{(3)}$  and  $D_{n3}^{(3)}$  in equations (29) and (30) can be calculated.

### 3. Numerical results and conclusions

The integrals in equations (35) and (36) can be numerically evaluated for various values for  $n$ . Since we are considering the three-photon transition from the ground state to an excited state with principle quantum number  $n$ , the corresponding  $\omega = (1 - n^{-2})/6$ . Repeated use of the recurrence relation given in equation (19) also has to be appropriately used for the evaluation of  $\mathcal{I}_{nl}(l, l, \lambda, t, k)$  if  $l - 1/\lambda < -1$ . The simple poles of the function  $\Phi(l, l, \lambda, t)$  at  $l + k - 1/\lambda = 0$  where  $l$  and  $k$  are positive integers are due to intermediate state resonances. For example, if  $\lambda = \lambda_1$  these poles correspond to one-photon intermediate state resonance. Similarly if  $\lambda = \lambda_2$  the photon energy corresponds to two-photon intermediate state resonance. This is a

**Table 1.** Three-photon transition matrix element  $D_{n1}^{(3)}$  and  $D_{n3}^{(3)}$  for atomic hydrogen in atomic units.

$n$	2	3	4	5	6	7	8	9	10
$D_{n1}^{(3)}$	182.0	-107.5	-85.23	-65.35	-51.58	-41.87	-34.80	-29.47	-25.36
$D_{n3}^{(3)}$	-	-	45.32	36.66	29.08	23.53	19.47	16.43	14.09

very important property of the solution we have obtained because any analytical expression equivalent to equation (1) should exhibit this behaviour. Also, these simple poles as a function of  $\omega$  present in the original expression given in equation (1) are clearly manifested in our solution by repeated application of the recurrence relation given in equation (19). If integrable singularities are present, a standard method such as subtraction procedure has to be employed for the numerical evaluation of the integrals in equations (35) and (36). Numerical values for  $D_{n1}^{(3)}$  and  $D_{n3}^{(3)}$  given in equations (29) and (30) are presented in table 1 in atomic units for various values of  $n$ . It is also easy to analytically continue these solutions and obtain the three-photon transition amplitude in the hydrogen atom above the one photon threshold.

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