Two-Photon Transitions Between Discrete States

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In this note, we discuss different approximation schemes for the evaluation of the two-photon transition rate between discrete states. Non relativistic atomic hydrogen is used as a test of the reliability of the methods. We consider a one particle system described by a Hamiltonian H_o, whose eigenstates and eigenvalues are denoted by $|n\rangle$ and E_n, respectively. In the gauge with divA = 0, the interaction of the particle with the electromagnetic field has the usual form

$$h_J = \frac{-e}{mc}\mathbf{A}\cdot\mathbf{p} + \frac{1}{2m}\left(\frac{e}{c}\right)^2 A^2 \tag{1}$$

Since we are interested in the two-photon transition rate, we will consider a vector potential

$$A_J = \hat{e}_1\, A_{01} \exp[-i\,\omega_1\, t] + \hat{e}_2\, A_{02} \exp[-i\,\omega_2\, t] + \text{c.c.} \tag{2}$$

The dipole approximation in (2) is justified in all the cases that we will consider [1]. As a consequence of this approximation the term proportional to A^2 in the interaction does not contribute to the two-photon transition rate, which takes in the velocity gauge the well known form

$$W_J^{(2)}(m,n) = \frac{2\pi e^4 |A_{01}A_{02}|^2}{\hbar^4 c^4} |\Omega_J(m,n)|^2 \delta(\Delta\omega)\,, \tag{3}$$

where

$$\Omega_J(m,n) = (1 + P_{12}) \sum_{\mu} \frac{\langle m|\hat{e}_1.p/m|\mu\rangle\langle\mu|\hat{e}_2.p/m|n\rangle}{\omega(\mu) - \omega(n) - \omega_2}\,. \tag{4}$$

In (3) A_{01}, A_{02} are the amplitudes of the vector potentials with frequencies ω_1, ω_2 and polarization unit vectors $\hat{e}_1$, $\hat{e}_2$, the operator P_{12} interchanges $(\hat{e}_1, \omega_1)$ with $(\hat{e}_2, \omega_2)$, $\omega(\mu) = E_\mu/\hbar$, $\Delta\omega = \omega(m) - \omega(n) - \omega_1 - \omega_2$, and $\{|\mu\rangle\}$ represents a complete set of

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eigenstates of H_0 with eigenvalues E_μ. Since rot**A** = 0 in the dipole approximation, the vector potential can be eliminated by a gauge transformation. In the so called length gauge J_o with $A_{J_o} = 0$, the interaction Hamiltonian takes the form

$$h_{J_o} = \frac{e}{c} x . \frac{\partial}{\partial t} A_J \tag{5}$$

The transition rate in the length gauge can be obtained from (3,4) by the substitution $p . \hat{e}_i / m \rightarrow \omega_i x . \hat{e}_i$. It is important to notice that the transition rates between eigenstates of the same free Hamiltonian H_0, evaluated in different gauges are gauge independent, i.e.

$$W^{(2)}_J = W^{(2)}_{J_o} . \tag{6}$$

For the special case of non relativistic Hydrogen, the multiphoton transition rate can be obtained exactly using methods based on Green function techniques, which avoid summations over intermediate states. This approach was introduced in order to treat time independent problems, and later extended to time dependent ones [2]. In the Green function method, the evaluation of the infinite sums over intermediate states is reduced to the solution of a linear differential equation. For systems other than Hydrogen, this method can also be used, but the associated differential equation has to be integrated numerically. The two-photon transition rate can also be evaluated exactly by performing explicitly the summation over the intermediate states.

We present exact calculations of the two-photon transition rates between discrete states of the non relativistic Hydrogen atom and we compare these results with those obtained with various approximation schemes. We plot in Fig. 1 the 1s-3s resonant transition amplitude D^3_1 as a function of one of the photon frequencies [3], where

$$D^3_1[J_0] = \frac{3}{2} \frac{2\pi R}{a_0^2 \omega_1 \omega_2} \Omega_{J0}(1s, 3s) \tag{7}$$

and a_0 and R are the Bohr radius and the Rydberg frequency, respectively.

The transition amplitude exhibits dramatic structure over the entire frequency range. Besides the resonance enhancement for $\omega_1 = 2\pi R [1 - 1/\mu^2]$ with $\mu = 2, 3$, the plot clearly shows the two-photon transparency. We refer to [3, 4] for the behavior of the transition rate $W^{(2)}$ to higher excited s and d states and for the dependence of $W^{(2)}$ on the polarization of the incoming radiation. A detailed discussion of the transparencies for different transitions is also given in a recent paper by Florescu et al [4]. In Table 1, we reproduce some of their results, showing in particular that the position of the transparencies are almost independent of the final state.

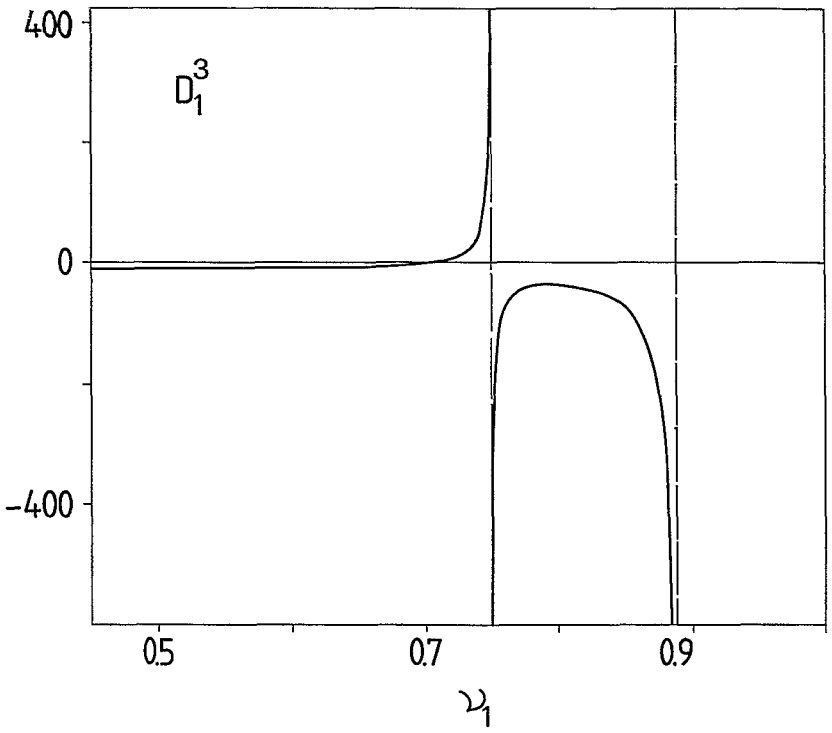

Fig. 1. Two-photon resonant transition amplitude D_1^3 for 1s-3s transitions in Hydrogen has a function of ν_1, for $\frac{4}{9} \leq \nu_1 < \frac{8}{9}$ [Rydberg units]

Frequency interval	0.3750 0.7500	0.7500 0.8899	0.8899 0.9375	0.9375 0.9600	0.9600 0.9720	0.9720 0.9796
1s-3s	0.6936					
1s-4s	0.6912	0.8714				
1s-4d		0.8381				
1s-5s	0.6905	0.8707	0.9299			
1s-5d		0.8307	0.9215			
1s-6s	0.6901	0.8705	0.9295	0.9560		
1s-6d		0.8274	0.9192	0.9529		
1s-10s	0.6897	0.8704	0.9294	0.9557	0.9697	0.9780
1s-10d		0.8232	0.9163	0.9510	0.9676	0.9767
1s-20s	0.6895	0.8703	0.9293	0.9557	0.9697	0.9780
1s-20d		0.8216	0.9160	0.9505	0.9672	0.9766
1s-∞s	0.6894	0.8703	0.9293	0.9557	0.9697	0.9780
1s-∞d		0.8211	0.9157	0.9503	0.9671	0.9765

Table 1. Two-photon transparency frequencies for several 1s-ns and 1s-nd transitions (frequencies in Rydberg units), from Ref. [4]

We turn now to the evaluation of $W^{(2)}$ using various approximation schemes. Problems that one has to consider in an approximate calculation are the rate of convergence of the sum over intermediate states, the importance of the contribution from the continuum and the gauge independence of the final result. For frequencies out of the condition of resonance enhancement, a heuristic approximation generally adopted, is to consider only a limited number of intermediate states, choosing those close to initial and final states because of their smaller energy denominators. As an example, we present in Table 2 the resonant 1s-3s two-photon transition amplitude in atomic Hydrogen, for various values of the incident frequencies, in the length and velocity gauges. We notice that both gauges give the same final result, but the respective contribution from the intermediate states are dramatically different.

OMEGA(1) = 0.44444 OMEGA(2) = 0.44444		
N	D[J0,N]	D[J,N]
2	3.96259	2.08965
3	-10.83427	2.08965
4	-7.45560	1.31014
5	-6.54089	0.99402
6	-6.14107	0.83003
7	-5.92520	0.73293
8	-5.79366	0.67034
9	-5.70690	0.62749
10	-5.64637	0.59682
11	-5.60233	0.57408
12	-5.56921	0.55674
13	-5.54364	0.54320
14	-5.52347	0.53243
15	-5.50726	0.52372
DD	-5.39815	0.46363
DC	2.18723	-3.67456
D	-3.21093	-3.21093

OMEGA(1) = 0.21389 OMEGA(2) = 0.67500		
N	D[J0,N]	D[J,N]
2	9.20118	6.63866
3	-11.04357	6.63866
4	-6.71940	5.27370
5	-5.57604	4.73307
6	-5.08192	4.45579
7	-4.81685	4.29266
8	-4.65598	4.18792
9	-4.55015	4.11642
10	-4.47647	4.06533
11	-4.42292	4.02751
12	-4.38270	3.99869
13	-4.35168	3.97622
14	-4.32721	3.95835
15	-4.30756	3.94389
DD	-4.17555	3.84442
DC	2.50625	-5.51372
D	-1.66930	-1.66930

OMEGA(1) = 0.12389 OMEGA(2) = 0.76500		
N	D[J0,N]	D[J,N]
2	-39.39279	-43.29640
3	-70.23253	-43.29640
4	-64.38017	-46.11053
5	-62.88897	-47.18464
6	-62.25544	-47.72621
7	-61.91877	-48.04184
8	-61.71562	-48.24332
9	-61.58251	-48.38032
10	-61.49007	-48.47796
11	-61.42303	-48.55011
12	-61.37274	-48.60499
13	-61.33400	-48.64774
14	-61.30347	-48.68171
15	-61.27898	-48.70916
DD	-61.11479	-48.89761
DC	2.91474	-9.30244
D	-58.20004	-58.20004

Table 2. Two-photon transition amplitude D_1^3 for 1s-3s transitions in Hydrogen for three different values of the incident photon frequency in the length and velocity gauges J_0 and J respectively. D[J_0, N] (D[J; N]) denotes the contribution from the discrete spectrum in the length (velocity) gauge up to the N-th intermediate state. The total contribution from the discrete and continuum spectrum are denoted by DD and DC, respectively

Robinson [5] has shown how to obtain gauge-independent results for the two-photon transition rates in cases when only a limited number of intermediate states are used. Following Robinson, we first transform the transition amplitudes in a more compact form

$$D[J_0] = \frac{3}{2\nu_1\nu_2} \sum_{\mu} F_\mu C_\mu \qquad (8a)$$

and

$$D[J] = -\frac{3}{2\nu_1\nu_2}\sum_{\mu} F_\mu C_\mu \qquad (8b)$$

where

$$C_\mu = (1+P_{12})\langle m|\hat{e}_1 . x/a_0|\mu\rangle\langle\mu|\hat{e}_2 . x/a_0|n\rangle[\nu(\mu)-\nu(n)-\nu_1] \qquad (9)$$

$$F_\mu = \frac{\nu_1\nu_2}{[\nu(\mu)-\nu(n)-\nu_2]\,[\nu(\mu)-\nu(n)-\nu_1]} \qquad (10a)$$

$$F'_\mu = \frac{[\nu(\mu)-\nu(m)]\,[\nu(\mu)-\nu(n)]}{[\nu(\mu)-\nu(n)-\nu_2]\,[\nu(\mu)-\nu(n)-\nu_1]}. \qquad (10b)$$

Using energy conservation, i.e. $\nu(m)-\nu(n) = \nu_1+\nu_2$, one has

$$F'_\mu = 1 - F_\mu. \qquad (11)$$

From the equality of the transition amplitudes in different gauges one obtains the sum rule

$$\sum_{\mu} C_\mu = 0 . \qquad (12)$$

The sum rule (12) can be used in order to have a gauge independent approximation scheme. The transition amplitude $D[J_0]$ is split into two parts :

$$D[J_0] = \sum_{\mu}^{(c)} F_\mu C_\mu + \sum_{\mu}^{(u)} F_\mu C_\mu , \qquad (13)$$

in the first term, the summation extends over states which are exactly known or for which a good approximation is available (characterized states), while the states in the second summation are supposed to be unknown (uncharacterized states). In the approximation scheme proposed by Robinson, the coefficients F_μ under the sum over the uncharacterized states in (13) are replaced by a constant coefficient F_K, which is obtained from F_μ replacing $\nu(\mu)$ with an averaged frequency $\nu(K)$. Using then the sum rule (12), we obtain an approximate expression for the transition amplitude :

$$D[R;J_0] = \sum_{\mu}^{(c)} (F_\mu - F_K)\, C_\mu . \qquad (14)$$

In the velocity gauge an analogous expression holds for the transition amplitude, and it can be shown [5] that the approximate results obtained in the length and velocity gauges are equal.

The approximation can be tested for the 1s-2s transition in Hydrogen. All p-states with $\mu > 2$ are taken as uncharacterized, the average frequency $\nu(K)$ is determined by fitting (14) to the exact transition amplitude D_1^2 [J_0] from [2] at $\nu_1 = 0.375$, leading to $\nu(K) = 0.0171$. In Table 3 we compare at various frequencies the exact amplitude D_1^2 with the amplitudes D_1^2 [R, J_0 2] and D_1^2 [J_0, 2], where only the 2p intermediate state is included. We notice that the error in D_1^2 [R, J_0 2] is less than 2%, and much smaller than the error in D_1^2 [J_0, 2]. The gauge invariant approximation partially overcomes the major difficulty encountered in any approximate calculation; this scheme, however, relies on free parameters which must be determined independently and hence its application is not straightforward.

ν_1	D_1^2 [J_o]	D_1^2 [R; J_o 2]	% error	D_1^2 [J_o 2]	% error
0.3750	- 11.7805			17.8785	(61.8)
0.5250	- 14.7319	- 14.8339	(0.69)	- 21.2839	(44.5)
0.6750	- 41.1484	- 41.8616	(1.73)	- 49.6624	(20.7)
0.6875	- 49.6878	- 50.5207	(1.68)	- 58.5113	(17.8)
0.7000	- 62.6595	- 63.6348	(1.56)	- 71.8331	(14.6)
0.7125	- 84.5252	- 85.6713	(1.36)	- 94.0971	(11.3)
0.7250	- 128.683	- 130.037	(1.05)	- 138.712	(7.79)
0.7375	- 262.165	- 263.772	(0.61)	- 272.722	(4.03)
0.7475	- 1334.33	- 1336.18	(0.14)	- 1345.37	(0.83)

Table 3. Comparison of theoretical transition amplitudes for various ν_1 using only the 2p-state as intermediate state. D_1^2 [J_o] is the exact theoretical value, D_1^2 [R; J_o 2] is from the modified Eq. (14) and D_1^2 [J_o 2] is from Eq. (8a), where in both cases only the 2p intermediate state has been included. The errors relative to the exact results are given in parenthesis. The average frequency $\nu(K) = 0.0171$ is determined by setting D_1^2 [R; J_o 2] = D_1^2 [J_o 2] = - 11.7805 for $\nu_1 = 0.375$. (From ref. [1])

Finally, we propose an alternative approach based on the representation of the Hamiltonian over a finite basis set. In general, the lowest variational states are close to the true states, but this is not the case for the high energy eigenstates, in particular for those with positive energy representing the continuous spectrum. In our approach, we still use the finite set of eigenfunctions to evaluate the sum over the intermediate states, including the continuum. Since the exact result can in principle be obtained with an infinite basis set, the accuracy of the procedure can be checked through the convergence of the transition rate versus basis size. For Hydrogen, we find fast convergence using real exponentional or Gaussian radial basis functions. As an example, we show in Table 4 the 1s-3s two-photon transition rate, at selected

frequencies. The calculations were performed for both beams polarized in the z-direction, in the length and velocity gauges. Convergence tests showed that the basis size (24 Gaussian functions) is sufficient to provide results with 1% accuracy.

ν_1	LENGTH GAUGE D(1s-3s)	VELOCITY GAUGE D(1s-3s)	EXACT D(1s-3s)
0.4444	-3.2108	-3.2104	-3.2109
0.6750	-1.6699	-1.6693	-1.6693
0.7000	0.9832	0.9838	0.9847
0.7250	11.211	11.212	11.216
0.7475	226.71	226.71	226.81
0.7650	-58.184	-58.183	-58.200
0.8000	-38.301	-38.300	-38.310
0.8250	-46.571	-46.569	-46.580
0.8500	-74.412	-74.409	-74.420
0.8750	-219.98	-219.96	-219.98
0.8860	-1116.0	-1116.0	-1117.2

Table 4. 1s-3s Two-photon transition amplitude calculated with variational states. The radial basis set for s an p states are of the form $\varphi_s = c_\alpha \exp - \alpha r^2$ and $\varphi_p = c'_\alpha\, r \exp - \alpha r^2$ respectively. Twenty four different exponents α, with $10^{-3} \leq \alpha \leq 10^{-5}$ (a.u.) in geometrical sequency have been used.

Variational energies : (Rydberg units)

s-states - 1.0000 / - 0.1111

p-states - 0.2500 / - 0.1111 / - 0.0625/- 0.0397 / - 0.0214 / + 0.0821 / ...

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