

Transition probabilities for two-photon $H(1s-2s)$ and $He(1^1s-2^1s)$ transitions: A partial-closure approach

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Abstract. Transition amplitudes and transition probabilities for the two-photon $1s-2s$ transition in the hydrogen atom and 1^1s-2^1s transition in helium atom have been calculated using a partial-closure approach. The dominant term is calculated exactly and the remaining sum over intermediate states is calculated using a mean excitation energy. Our value of the transition amplitudes agree within 2% with the exact results for the hydrogen case. Our value of the transition probability for hydrogen is 8.50 s^{-1} which is in good accord with its known value 8.226 s^{-1} . For helium, the photon energy distribution of the metastable 2^1s state is in good agreement with the accurate values. The corresponding transition probability is 53.7 s^{-1} which is in good agreement with the accurate value 51.3 s^{-1} .

Keywords. Transition probability; two-photon transition; closure approximation; mean excitation energy.

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1. Introduction

In the last few years, the two-photon transitions have become an useful tool for experimental studies of various spectroscopic characteristics in atoms [1–3]. Two-photon spectroscopy is an useful tool for the study of the excitation levels of various systems [4]. It is now possible to measure two-photon absorption coefficients for the hydrogen transitions from its ground state to excited states by employing synchrotron radiation along with a powerful laser beam. The study of the metastable states of hydrogen atom is useful in the determination of fine-structure constant, measurement of the Lamb-shift and in testing Bell's inequality. Two-photon $1s-2s$ transition in hydrogen has been studied experimentally [5,6]. The calculation of the transition amplitudes for the $1s-2s$ two-photon transition in H atom involves a summation over discrete and continuum states of conventional second-order perturbation theory. Different methods can be employed to evaluate this sum exactly. The rate of convergence in various gauges over the intermediate states has been discussed earlier [7,8]. The contribution from discrete and continuum spectrum are nearly the same. The intermediate states can also be replaced by a finite set of pseudostates [9], in which convergence is obtained by retaining twenty pseudostates. Another efficient analytic

approach for the evaluation of transition amplitude is a differential equation approach [10] which has been used to study the second-order Stark effect in the hydrogen atom [11]. In this approach the sum over intermediate states is completely absent and one has to solve a differential equation. This approach [10] has been used to study the two-photon transition in hydrogen atom from its ground state to the $n = 3$ state. There exists a comprehensive review [12,13] concerning the metastability and decay mechanism of hydrogen-like ions. The spectral distribution of the two emitted photons has been measured by Fourier spectroscopy [14].

The 2^1s state of the helium atom can decay to the ground state only by the simultaneous emission of two electric dipole photons. The decay proceeds via virtual $1p$ states. In the second-order perturbation theory, the sum is taken over the discrete and continuum p states. In this case, the $1s$ electron is merely a spectator, and the transition is basically $1s-2s$ transition just like in the hydrogen case. For very high value of nuclear charge of a He-like ion, the decay rate is almost twice the decay rate for hydrogen case. The factor of two is due to the Pauli principle. Therefore, we expect the He decay rate to be much faster than the H decay rate. The two-photon decay rate of the 2^1s state of He was estimated by Dalgarno [15] using oscillator strength sum rules. Dalgarno and Victor [16] used uncoupled Hartree–Fock method and Victor [17] used coupled Hartree–Fock method to calculate the decay rates. A variational calculation by Drake *et al* [18] yields the decay rate equal to 51.3 s^{-1} .

In this present work, we present a simple and accurate analytical approach for the evaluation of frequency-dependent transition amplitudes for $1s-2s$ two-photon transition in H-atom and 1^1s-2^1s transition in He-atom by employing a partial closure approach. We evaluate the contribution of dominant intermediate $2p$ state explicitly and the sum remaining over intermediate states by replacing the energy denominators by a mean excitation energy.

2. Theory

We are interested in evaluating the second-order perturbation sum involved in the two-photon $1s-2s$ transition in the hydrogen atom and 1^1s-2^1s transition in helium-atom. In the length gauge, we can write the sum as

$$D(\omega) = \frac{1}{2} \sum_{N \neq 1,2} \left[\frac{1}{E_n - E_1 + \omega} + \frac{1}{E_n - E_2 + \omega} \right] R_1^N R_2^N, \quad (1)$$

where E_1 and E_2 are the energies of the $1s$ and $2s$ states for H atom and 1^1s and 2^1s states of He-atom respectively. R_1^N is the radial dipole matrix element between the ground state and the intermediate state, and R_2^N is the radial dipole matrix element between the metastable state and the intermediate state. The energy of one of the emitted photon is ω . The energy conservation requires the other photon to have an energy equal to $(\delta E - \omega)$, where δE is the excitation energy between the ground state and the metastable state.

For H-atom case, we write eq. (1) as

$$D(\omega) = D_1(\omega) + D_2(\omega), \quad (2)$$

where $D_1(\omega)$ represents the dominant contribution of the intermediate $2p$ state and is written as

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$$D_1(\omega) = \frac{1}{2} \left[\frac{1}{E_{2p} - E_{1s} - \omega} + \frac{1}{E_{2p} - E_{2s} + \omega} \right] R_{1s}^{2p} R_{2s}^{2p}. \quad (3)$$

Now $D_2(\omega)$ in the partial closure approximation becomes

$$D_2(\omega) = \frac{1}{2} \left[\frac{1}{\Delta - \omega} + \frac{1}{\Delta - (3/4) + \omega} \right] \left(\langle \phi_{1s} | r^2 | \phi_{2s} \rangle - R_{1s}^{2p} R_{2s}^{2p} \right), \quad (4)$$

where ϕ_{ns} is the wave function of ns state.

Noting the values $E_{1s} = -1$ Ryd, $E_{2s} = E_{2p} = -(1/4)$ Ryd, $R_{1s}^{2p} = \sqrt{5/3}$, $R_{2s}^{2p} = -\sqrt{27}$ and $\langle \phi_{1s} | r^2 | \phi_{2s} \rangle = -(512/243)\sqrt{2}$, we get

$$D_1(\omega) = -10.0623/[\omega(3 - 4\omega)] \quad (5)$$

and

$$D_2(\omega) = 1.86423 \left[\frac{8\Delta - 3}{(\Delta - \omega)(4\Delta - 3 + 4\omega)} \right]. \quad (6)$$

All the matrix elements are in atomic units (with $a_0 = 1$). In eqs (5) and (6), ω is expressed in Ryd. Making the transformation $y = \omega/\delta E$, where δE is the excitation energy in Ryd, we get the following expression [19] for the two-photon transition probability W_{1s}^{2s} ,

$$W_{1s}^{2s} \text{ (in s}^{-1}\text{)} = \left(\frac{\alpha^7 c}{216\pi a_0} \right) (\delta E)^5 \int_0^1 d^2(y) y^3 (1 - y)^3 dy, \quad (7)$$

where δE is expressed in Ryd, and where $d(y)$ is given by

$$D(y) = \frac{2}{3} d(y), \quad (8)$$

$$D(y) = \frac{2}{3} \left[\frac{-6.7082}{y(1-y)} + \frac{3.7292 \left(\frac{2\Delta}{\delta E} - 1 \right)}{\left(\frac{\Delta}{\delta E} - y \right) \left(\frac{\Delta}{\delta E} - 1 + y \right)} \right]. \quad (9)$$

W_{1s}^{2s} can now be evaluated if Δ is known.

To enhance the scope of the present formulation, we have also evaluated the transition probability of the two-photon process 2^1s-1^1s of helium. The analytic Hartree-Fock wave functions of the 1^1s , 2^1s and 2^1p are employed to evaluate the relevant matrix elements. These wave functions are from Byron and Joachain [20]. The ground state wave function is

$$\phi_{1^1s}(r_1, r_2) = u_{1s}(r_1)u_{1s}(r_2), \quad (10)$$

where the normalized orbital $u_{1s}(r)$ is given by

$$u_{1s}(r) = \sqrt{\frac{8}{\pi}} (Ae^{-\alpha r} + Be^{-\beta r}), \quad (11)$$

where $A = 2.60505$, $B = 2.08144$, $\alpha = 1.41$ and $\beta = 2.61$. This wave function yields the Hartree-Fock ground state energy equal to $E_{1s} = -2.86167$ a.u.

The space-symmetric wave function for the 2^1s state is given by

$$\phi_{2^1s}(r_1, r_2) = [u'_{1s}(r_1)v_{2s}(r_2) + v_{2s}(r_1)u'_{1s}(r_2)], \quad (12)$$

where the normalized orbitals $u'_{1s}(r)$ and $v_{2s}(r)$ are given by

$$u'_{1s}(r) = \sqrt{\frac{8}{\pi}} e^{-2r}, \quad (13)$$

$$v_{2s}(r) = \frac{0.6193}{\sqrt{4\pi}} [e^{-\tau_1 r} - c r e^{-\tau_2 r}] \quad (14)$$

with $\tau_1 = 0.865$, $\tau_2 = 0.522$, $c = 0.432784$. The energy of the 2^1s state is $E_{2^1s} = -2.143$ a.u. The wave function for the 2^1s state is orthogonal to the 1^1s state.

The space-symmetric wave function for the 2^1p state is given by

$$\phi_{2^1p}(\vec{r}_1, \vec{r}_2) = [u'_{1s}(r_1)v_{2pm}(\vec{r}_2) + v_{2pm}(\vec{r}_1)u'_{1s}(r_2)], \quad (15)$$

where the normalized orbitals $u'_{1s}(r)$ and $v_{2pm}(r)$ are given by

$$u'_{1s}(r) = \sqrt{\frac{8}{\pi}} e^{-2r}, \quad (16)$$

$$v_{2pm}(\vec{r}) = \frac{Z_0^{5/2}}{\sqrt{96\pi}} r e^{-z_0 r/2} \quad (17)$$

with $Z_0 = 0.97$. The corresponding energy of the 2^1p state is $E_{2^1p} = -2.123$ a.u. For our matrix elements only $m = 0$ term survive.

With these wave functions, the relevant matrix elements (in atomic units) $\langle 1^1s|r|2^1p\rangle$, $\langle 2^1s|r|2^1p\rangle$ and $\langle 1^1s|r^2|2^1s\rangle$ can be easily evaluated. Their values are

$$\langle 1^1s|r|2^1p\rangle = 0.5088078, \quad (18)$$

$$\langle 2^1s|r|2^1p\rangle = -5.20208, \quad (19)$$

$$\langle 1^1s|r^2|2^1s\rangle = -0.969364797. \quad (20)$$

The corresponding $D(y)$ function now has the form

$$D(y) = \frac{2}{3} \left[\frac{-6.7082(\delta_1 + \delta_2)f_1}{(\delta_1 - y)(\delta_2 + y)} + \frac{(2\frac{\Delta}{\delta E} - \delta_1)(6.7082f_1 - 2.979f_2)}{(\frac{\Delta}{\delta E} - y)(\frac{\Delta}{\delta E} - \delta_1 + y)} \right], \quad (21)$$

$$D(y) \equiv \frac{2}{3} d(y), \quad (22)$$

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where δE is the excitation energy of 1^1s-2^1s transition and $\delta_1 = 1.027829184$, $\delta_2 = 0.027829184$, $f_1 = 0.3945706$, $f_2 = 0.325318348$. It may be noted that eq. (21) reduces to the hydrogen case of eq. (9) by letting $\delta_1 = 1$, $\delta_2 = 0$, $f_1 = f_2 = 1$ and replacing δE by $3/4$ Ryd. Taking into account the spin factor of 2, the transition probability $W(2^1s-1^1s)$ has the form

$$W(2^1s - 1^1s) = (18.415)(\delta E)^5 \int_0^1 d^2(y)y^3(1-y)^3 dy \text{ (in s}^{-1}\text{)}, \quad (23)$$

where $\delta E = 1.43734$ Ryd.

We now define $A(y)$ by

$$W(2^1s - 1^1s) = \frac{1}{2} \int A(y)dy, \quad (24)$$

where $A(y)$ is the photon energy distribution for the 2^1s-1^1s two-photon decay of He. The distribution $A(y)$ will be compared with the known results. Here, y is the fraction of the energy transported by one of the two photons. The factor of $1/2$ is included because only photon pairs are counted.

To evaluate W , the only free parameter is Δ . However, various judicious choices of Δ can be made. For transitions involving a single photon, Δ is usually taken to be the first ionization potential of the atom which yields dipole polarizability with right order of magnitude. A better choice is to choose Δ , so that it reproduces accurately the dipole polarizability of the ground state of the atom. For the two-photon process, we choose Δ so that it reproduces the transition polarizability of the concerned states. In the case of hydrogen, $\alpha_{2s,1s}$ for the $\omega = 0$ case is 8.93923 [21]. Using the formula

$$\alpha_{1s}^{ms}(0) = \frac{1}{3} \langle ms | r^2 | 1s \rangle \left[\frac{1}{\Delta} + \frac{2m^2}{2m^2\Delta + 1 - m^2} \right] \quad (25)$$

we get $\Delta(H) = 0.9522$ Ryd after taking the partial contribution of the intermediate $2p$ state. For He, we simply do the scaling

$$\Delta(\text{He}) = Z_{1s}Z_{2s}\Delta(H), \quad (26)$$

where Z_{1s} and Z_{2s} are the effective charges of the $1s$ and $2s$ orbital in the configuration $1s 2s^1S$. The values of the effective charges are obtained by

$$Z_{1s} = \frac{\langle r^{\text{H}} \rangle_{1s}}{\langle r^{\text{He}} \rangle_{1s}}, \quad (27)$$

$$Z_{2s} = \frac{\langle r^{\text{H}} \rangle_{2s}}{\langle r^{\text{He}} \rangle_{2s}}, \quad (28)$$

where the symbol H represents the hydrogenic values. From our wave function, we get $\langle r^{\text{He}} \rangle_{1s} = 3/4$ and $\langle r^{\text{He}} \rangle_{2s} = 5.3624$, and noting the values of $\langle r^{\text{H}} \rangle_{1s} = 3/2$ and $\langle r^{\text{H}} \rangle_{2s} = 6$, we finally get $\Delta(\text{He}) = 2.131$ Ryd. These values of $\Delta(H)$ and $\Delta(\text{He})$ have been used in the present work to evaluate the two-photon transition probabilities.

3. Results

The decay rate W depends upon the value of Δ . There is no *a priori* way of obtaining Δ . We have evaluated W for two-photon transitions in H and He, using various choices of Δ . The choices are:

- Δ_1 = excitation energy
- Δ_2 = ionization energy of the atom
- Δ_3 = partial closure value (calculated in §2)
- Δ_4 = tuned value that reproduces W
- Δ_5 = mean excitation energy that reproduces the electric dipole polarizability of the ground state of the atom.

The results of transition probabilities for two-photon transition $1s-2s$ in H and 1^1s-2^1s in He are summarized in table 1. As expected, the worst results are for Δ_1 case, because the mean excitation energy must exceed the excitation energy. We also note that W increases with Δ . For H case, the best results are for Δ_2 which corresponds to its ionization energy. The agreement is better than 4%. For He, the partial closure value yields $W = 53.7 \text{ s}^{-1}$, which agrees within 5% with the exact value of 51.3 s^{-1} . For H case, the tuned value is lower than the ionization energy whereas for He, it is higher. The mean excitation energy may exceed ionization energy when the contribution of continuum is significantly more than the discrete intermediate states. As a thumb rule, we should choose Δ_2 or Δ_3 whichever is higher. The Δ_3 value for many atoms may not be known, in that case we suggest that the mean of Δ_2 and Δ_5 be taken for evaluating W for two-photon processes.

In table 2, we give the values of the matrix elements $D_1(\omega)$, $D_2(\omega)$ and $D(\omega)$ for various values of ω (in Ryd) for $1s-2s$ transition in H atom for $\Delta_2 = 1$ Ryd. These are compared with the exact results. We notice excellent agreement between our results and the exact results for the entire range of ω values. The close agreement suggest that the method of using mean excitation energy is quite physical. It mimics the contribution of discrete and continuum intermediate states quite faithfully.

In table 3, we present our results for the photon energy distribution for the 2^1s-1^1s two-photon decay of He and compare the results with the accurate values [18]. The distribution is symmetrical about $y = 0.5$ and hence only values up to 0.5 are given. The agreement of our calculations with the accurate values is quite good for the entire range of y values.

Table 1. Transition probabilities for two-photon $1s-2s$ transition in hydrogen and 1^1s-2^1s transition in helium.

Type of Δ	Hydrogen		Helium	
	Value of Δ (Ryd)	W_{1s}^{2s} (s^{-1})	Value of Δ (Ryd)	W_{1s}^{2s} (s^{-1})
Δ_1	3/4	0.0888	1.43734	20.2606
Δ_2	1	8.4975	1.8086	38.9940
Δ_3	0.9522	7.3240	2.131	53.6668
Δ_4	0.988118	8.2260	2.0679	51.3
Δ_5	8/9	5.3918	2.278	58.4864

Table 2. Values of the matrix elements $D_1(\omega)$, $D_2(\omega)$ and $D(\omega)$ (in a.u.) for H-atom for various values of ω for $\Delta = 1.0$ Ryd.

ω (Ryd)	$D_1(\omega)$	$D_2(\omega)$	$D(\omega)$	Exact
0.3750	-17.8885	5.9655	-11.9230	-11.7805
0.5250	-21.2959	6.3301	-14.9657	-14.7319
0.6750	-49.6904	7.7515	-41.9389	-41.1484
0.6875	-58.5443	7.9540	-50.5902	-49.6878
0.7000	-71.8735	8.1765	-63.6971	-62.6595
0.7125	-94.1501	8.4211	-85.7290	-84.5252
0.7250	-138.7905	8.6910	-130.0994	-128.683
0.7375	-272.8762	8.9897	-263.8865	-262.165
0.7475	-1346.1283	9.2520	-1336.8763	-1334.33

Table 3. Photon energy distribution $A(y)$ for the $2^1 s-1^1 s$ two-photon decay of He.

y	$A(y)$ (our results)	Exact
0.000	0.00	0.00
0.025	7.57	7.77
0.050	25.1	25.2
0.075	44.0	43.5
0.100	61.5	59.9
0.125	76.8	74.2
0.150	90.0	86.4
0.175	101.3	96.9
0.200	110	106
0.225	119	113
0.250	126	120
0.275	131	125
0.300	136	130
0.325	140	134
0.350	143	137
0.375	146	140
0.400	148	142
0.425	150	143
0.450	151	145
0.475	152	145
0.500	152	145

In the case of molecules, the transition probability would depend upon the internuclear distances between the atoms. Wave functions in the fixed-nuclei approximation may be taken because the motion of nuclei is much slower than that of the electrons, and nuclei occupy nearly their fixed positions in the molecule when the electronic transition takes place. In the absence of the value of Δ for partial closure, one may take Δ equal to the

average of mean excitation energy which reproduces the exact polarizability of the ground state molecule and the ionization potential of the molecule.

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References

- [1] L Cook, D Olsgard, M Havey and A Sieradzan, *Phys. Rev.* **A47**, 340 (1993)
- [2] R P Meyer, M D Havey and A Beger, XIV ICAP, *Abstracts of contributed papers* (Boulder, CO, 1994) p. 2A-3
- [3] P C Stancil and G E Copeland, *J. Phys.* **B27**, 2801 (1994)
- [4] H Walter, *Laser spectroscopy* edited by H Walter (Springer, Berlin, 1976)
- [5] T W Hansch, S A Lee, R Wallenstein and C Wieman, *Phys. Rev. Lett.* **34**, 307 (1975)
- [6] S A Lee, R Wallenstein and T W Hansch, *Phys. Rev.* **A35**, 1262 (1980)
- [7] A Quattropani, F Bassani and S Carillo, *Phys. Rev.* **A25**, 3079 (1982)
- [8] F Bassani, A Quattropani and J J Forney, *Phys. Rev. Lett.* **39**, 1070 (1977)
- [9] R J Drachman, A K Bhatia and A A Shabazz, *Phys. Rev.* **A42**, 6333 (1990)
- [10] R B Thayyullathil and K J Prasanna, *Phys. Rev.* **A49**, 2432 (1994)
- [11] A Dalgarno and J T Lewis, *Proc. R. Soc. London* **A233**, 70 (1955)
- [12] C J Artura, N Tolk and R Novick, *Astrophys. J.* **157**, L181 (1969)
- [13] A J Duncan, Z A Sheikh, H Kleinpoppen and E Merzbacher, *Selected topics in electron physics* edited by D M Campbell and H Kleinpoppen (New York, Plenum, 1996) pp. 457-70
- [14] A J Duncan, Z A Sheikh and H Kleinpoppen, *J. Phys.* **B30**, 1347 (1997)
- [15] A Dalgarno, *Mon. Not. R. Astron. Soc.* **131**, 311 (1966)
- [16] A Dalgarno and G A Victor, *Proc. Phys. Soc. (London)* **87**, 371 (1966)
- [17] G A Victor, *Proc. Phys. Soc. (London)* **91**, 825 (1967)
- [18] C W F Drake, G A Victor and A Dalgarno, *Phys. Rev.* **180**, 25 (1969)
- [19] J Shapiro and G Breit, *Phys. Rev.* **113**, 179 (1959)
- [20] B H Bransden and C J Joachain, *Physics of atoms and molecules* (Longman Inc., New York, 1983)
- [21] V Chandrasekharan and B Silvi, *J. Phys.* **B14**, 4327 (1981)