Asymptotic Expressions for the Average Lifetime of n and (n, ℓ) Hydrogenic Levels

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In this paper, we present the derivation of simple analytical asymptotic expressions for the average lifetimes τ_n and $\tau_{n\ell}$ of hydrogenic levels with principal quantum number n, and principal and azimuthal quantum numbers (n, ℓ), respectively. We first review the calculation of the average level lifetimes based on the calculation of the spontaneous transition probabilities for hydrogenic level transitions, requiring the calculation of the absorption oscillator strengths of those transitions. We then consider the time-consuming exact calculation of the absorption oscillator strengths, their approximate calculation from an asymptotic formula, and briefly review the neglected Gaunt factor of order unity. Finally, we review the derivation of the asymptotic expressions for the average lifetime of hydrogenic levels τ_n and $\tau_{n\ell}$. These simple analytical asymptotic expressions are well-adapted to simplify the analysis of hydrogenic levels and more complex atomic and ionic systems.

1 Introduction

The average lifetimes of atomic and ionic levels are important in the analysis of many fields, such as astrophysical, terrestrial and laboratory applications, the calculation of the spectroscopic properties of non-equilibrium plasmas, and in the study of highly excited states of Rydberg atoms. The calculation of these lifetimes is time-consuming, especially when higher levels are considered. Hydrogenic atoms and ions are the simplest physical systems to analyze and can be used as a basis for the analysis of other more complex cases, such as atoms and ions with a single valence electron. Simple analytic asymptotic expressions are especially desirable for the analysis of the theoretical behavior of such systems.

Bethe and Salpeter [1], in their book *Quantum Mechanics of One- and Two-Electron Atoms* published in 1957, considered this problem and proposed

$$\tau_n \sim n^{4.5}\,, \tag{1}$$

where τ_n is the average lifetime of level n and n is the principal quantum number of the level. In 1979, Millette and Varshni [2] derived the quantum mechanical asymptotic expression

$$\tau_n \sim \frac{n^5}{\ln n}\,. \tag{2}$$

Comparison with the exact value of the lifetimes calculated by the authors showed that the proportionality constant in (2) was approximately equal to $k = 4.3 \times 10^{-11}$ s as seen in Fig. 1, where (1) and (2) are compared by plotting $\tau_n/n^{4.5}$ and $\tau_n \ln n/n^5$ vs. n [2]. Eq. (2) is found to be a much better approximation than (1). In addition, Fig. 1 confirms that (2) is an asymptotic expression, flatlining as $n \to \infty$. In 1982, Omidvar [3] determined the value of the proportionality constant $k = 4.2341 \times 10^{-11}$ s from semiclassical considerations.

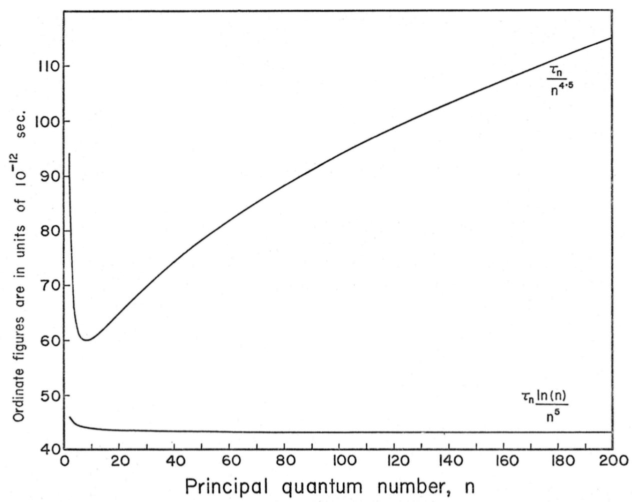

Fig. 1: Comparison of asymptotic τ_n results from Bethe & Salpeter Eq. (1) and Millette & Varshni Eq. (2) [2].

In this paper, we consider the details of the determination of the average lifetime of hydrogenic levels and the derivation of analytical asymptotic expressions for these, and extend the results to the determination of the average lifetime of $\tau_{n\ell}$ levels, where n is the principal and ℓ the azimuthal quantum numbers.

2 Exact calculation of τ_n for hydrogenic levels

The exact quantum mechanical calculation of hydrogenic level lifetimes involves the calculation of the spontaneous transition probability for transitions from those levels.

We consider the spontaneous transition of an electron in an hydrogenic ion from an upper state n to a lower state n'. Within the electric dipole approximation, the Einstein probability coefficient for the transition can be evaluated exactly, and it is given by [4]:

$$A_{n\to n'} = \frac{8\pi^2 e^2}{mc^3}\,\nu_{nn'}^2\,\frac{\omega_{n'}}{\omega_n}\,f_{n'\to n}\,, \tag{3}$$

where ω_n and $\omega_{n'}$ are the statistical weights of levels n and n' respectively, $\nu_{nn'}$ is the frequency of the photon emitted as a result of the transition and $f_{n'\to n}$ is the absorption oscillator strength for the $n' \to n$ transition.

The absorption oscillator strength is given by [4, 5]:

$$\begin{aligned} f_{n'\to n} = \frac{32}{3}\,n^4 n'^2\,\frac{(n-n')^{2n+2n'-4}}{(n+n')^{2n+2n'+3}}\,\times \\ \times\left\{\left[{}_2F_1\left(-n',-n+1;1;-\frac{4nn'}{(n-n')^2}\right)\right]^2 - \right. \\ \left. -\left[{}_2F_1\left(-n'+1,-n;1;-\frac{4nn'}{(n-n')^2}\right)\right]^2\right\} \end{aligned} \tag{4}$$

where

$${}_2F_1\,(a,b;c;x) = \sum_{k=0}^{\infty}\frac{(a)_k\,(b)_k}{(c)_k}\,\frac{x^k}{k!} \tag{5}$$

is the hypergeometric function [6, p, 555] and

$$(a)_k = \Gamma(a+k)/\Gamma(a)\,. \tag{6}$$

If a and b are negative integers, the sum (5) is terminated and the hypergeometric function is then a polynomial. Let $a = -i$ and $b = -j$ where i and j are positive integers and $i \leqslant j$; let $x \geqslant 0$; then (5) becomes

$${}_2F_1\,(-i,-j;1;-x) = \sum_{k=0}^{i}(-1)^k\,\frac{i!}{(i-k)!}\,\frac{j!}{(j-k)!}\,\frac{x^k}{(k!)^2}\,. \tag{7}$$

For large values of n' and n, (7) is difficult to evaluate since it is given by a sum of very large terms which alternate in sign and which tend to cancel one another. The value of the sum is then smaller than the magnitude of these very large terms, and significant loss of accuracy can occur. Furthermore, since the two hypergeometric functions of (4) are very similar, the difference of the square of these functions becomes very small as n' and n increases. An even greater loss of accuracy can then occur. For large values of n', n, and $n - n'$, we thus use the asymptotic formula [4]:

$$f_{n'\to n} = \frac{2^6}{3\sqrt{3}\,\pi}\,\frac{1}{\omega_{n'}}\left(\frac{1}{n'^2}-\frac{1}{n^2}\right)^{-3}\left|\frac{1}{n'^3}\,\frac{1}{n^3}\right| g \tag{8}$$

where $\omega_{n'} = 2n'^2$ is the statistical weight of level n' and g, the Gaunt factor for the $n' \to n$ transition, is of order unity. With $g = 1$, we obtain a value of $f_{20\to 21}$ off by $\sim 25\%$ and a value of $f_{20\to 70}$ off by $\sim 3\%$. The accuracy of (8) can be improved by using a better estimate of the Gaunt factor.

3 Approximate calculation of τ_n for hydrogenic levels

Thus, given the difficulty of evaluating exact quantum mechanical absorption oscillator strengths as seen previously, we use the asymptotic formula (8) to evaluate the absorption oscillator strengths when calculating hydrogenic level lifetimes.

Using $\omega_n = 2n^2$ for the atomic levels and

$$\nu_{nn'} = c R_A\left(\frac{1}{n'^2}-\frac{1}{n^2}\right)$$

for atomic species A in (3), we get

$$A_{n\to n'} = 2\pi\alpha^3 c R_A\left(\frac{1}{n'^2}-\frac{1}{n^2}\right)^2\frac{n'^2}{n^2}\,f_{n'\to n}\,, \tag{9}$$

where α is the fine-structure constant, c the speed of light, and R_A the Rydberg constant for atomic species A. In terms of the Rydberg constant R_∞, this expression becomes

$$A_{n\to n'} = 2\pi\alpha^3 c R_\infty \mu Z^4\,\frac{\left(n^2-n'^2\right)^2}{n^6 n'^2}\,f_{n'\to n}\,, \tag{10}$$

where $\mu = M_A/(M_A + m_e)$ is the reduced mass factor for atomic species A where m_e is the mass of the electron, and Z is the effective charge acting on the electron.

Substituting for $f_{n'\to n}$ from (8) with $\omega_{n'} = 2n'^2$ and the Gaunt factor $g \simeq 1$ in (9), we obtain

$$A_{n\to n'} = \frac{64}{3\sqrt{3}}\,\alpha^3 c R_\infty \mu Z^4\left(\frac{1}{n'^2}-\frac{1}{n^2}\right)^{-1}\frac{1}{n'^3}\,\frac{1}{n^5}\,. \tag{11}$$

Defining the constant

$$k_A = \frac{64}{3\sqrt{3}}\,\alpha^3 c R_\infty = 1.5746\times 10^{10}\ \mathrm{s}^{-1}\,, \tag{12}$$

(11) is simplified to

$$A_{n\to n'} = \frac{k_A\,\mu\,Z^4}{n' n^3\,(n^2-n'^2)}\,. \tag{13}$$

The average lifetime τ_n of level n is then calculated from [1]:

$$\tau_n = \left(\sum_{n'=1}^{n-1} A_{n\to n'}\right)^{-1}. \tag{14}$$

3.1 The Gaunt factor

In the derivation of (13), we have set the Gaunt factor of (8), which is of order unity, to $g = 1$. The Gaunt factor expression is essentially equal to the difference between the exact evaluation expression for the oscillator strength given by (4) and the asymptotic formula given by (8). Menzel and Pekeris [4] have investigated the Gaunt factor expressions to allow more accurate approximate values of the oscillator strengths to be calculated.

The accurate calculation of the Gaunt factor is given by

$$g = \pi\sqrt{3}\,\pi\left(\frac{n-n'}{n+n'}\right)^{2n+2n'}\frac{nn'}{n-n'}\,\Delta(n,n')\,, \qquad (15)$$

where $\Delta(n,n')$ is equal to the difference of the hypergeometric functions of (4). As noted previously in §2, for higher level values of n' and n, the exact equations become cumbersome to evaluate.

Menzel and Pekeris [4] have thus applied contour integration and the method of steepest descent to calculate the values of $|\Delta(n,n')|$ in the case when $\frac{n'}{n} \ll 1$. The approximation is then given by

$$g = 1 - \frac{0.1728}{n'^{2/3}}\frac{\left(1+\frac{n'^2}{n^2}\right)}{\left(1-\frac{n'^2}{n^2}\right)^{2/3}} - \frac{0.0496}{n'^{4/3}}\frac{\left(1+\frac{484}{15}\frac{n'^2}{n^2}+\frac{n'^4}{n^4}\right)}{\left(1-\frac{n'^2}{n^2}\right)^{4/3}} + \cdots$$

which tends to 1 as n' and $n \to \infty$.

4 Derivation of the τ_n asymptotic expression

The average lifetime τ_n of level n is calculated by substituting (13) into (14):

$$\tau_n^{-1} = \sum_{n'=1}^{n-1}\frac{k_A\,\mu\,Z^4}{n'n^3\,(n^2-n'^2)}\,, \qquad (16)$$

where the constant k_A is given by (12). Common factors are taken out of (16) and rearranged to obtain

$$\tau_n^{-1} = \frac{k_A\,\mu\,Z^4}{n^5}\sum_{n'=1}^{n-1}\frac{1}{n'}\frac{n^2}{(n-n')(n+n')}\,. \qquad (17)$$

Using partial fractions expansion, (17) becomes

$$\tau_n^{-1} = \frac{k_A\,\mu\,Z^4}{n^5}\sum_{n'=1}^{n-1}\left[\frac{1}{n'}+\frac{1}{2}\frac{1}{n-n'}-\frac{1}{2}\frac{1}{n+n'}\right]. \qquad (18)$$

In the asymptotic case as $n \to \infty$, the individual sums are given by [6]:

$$\begin{aligned}
&\sum_{n'=1}^{n-1}\frac{1}{n'} \sim (\ln n+\gamma) - \frac{1}{2n} - \frac{1}{12n^2} + \cdots\,,\\
&\sum_{n'=1}^{n-1}\frac{1}{2}\frac{1}{n-n'} \sim \frac{1}{2}(\ln n+\gamma) - \frac{1}{4n} - \frac{1}{24n^2} + \cdots\,, \qquad (19)\\
&\sum_{n'=1}^{n-1}\frac{1}{2}\frac{1}{n+n'} \sim \frac{1}{2}\ln 2 - \frac{3}{8n} + \frac{1}{32n^2} - \cdots\,,
\end{aligned}$$

where $\gamma = 0.57721...$ is Euler's constant. Substituting the individual sums (19) into (18), we obtain

$$\tau_n^{-1} \sim \frac{k_A\,\mu\,Z^4}{n^5}\left[\frac{3}{2}(\ln n+\gamma) - \frac{1}{2}\ln 2 - \frac{3}{8}\frac{1}{n} - O\left(\frac{1}{n^2}\right)\right]. \qquad (20)$$

n	τ_n (sec) (exact)	τ_n (sec) Eq. (22)	Percent difference
2	2.128×10^{-9}	1.955×10^{-9}	8.9
50	3.460×10^{-3}	3.382×10^{-3}	2.3
100	9.374×10^{-2}	9.194×10^{-2}	2.0
150	6.533×10^{-1}	6.417×10^{-1}	1.8
200	2.601	2.557	1.7

Table 1: Comparison of exact values of τ_n calculated by Millette and Varshni (unpublished) and asymptotic values of τ_n calculated from Eq. (22).

The zeroth order term $\frac{3}{2}\gamma - \frac{1}{2}\ln 2 = 0.5192$ and in the asymptotic limit, can be dropped along with terms of order $1/n$ and above to obtain

$$\tau_n^{-1} \sim \frac{3}{2}\,k_A\,\mu\,Z^4\,\frac{\ln n}{n^5}\,\mathrm{s}^{-1}\,. \qquad (21)$$

Using the value of the constant k_A from (12), we obtain the following asymptotic expression for the average lifetime τ_n of level n:

$$\tau_n \sim \frac{4.234\times10^{-11}}{\mu\,Z^4}\,\frac{n^5}{\ln n}\,\mathrm{s}\,. \qquad (22)$$

In Table 1, we compare the exact values of τ_n calculated by Millette and Varshni (unpublished) with the asymptotic values calculated from (22).

5 Derivation of the $\tau_{n\ell}$ asymptotic expression

As specified by Bethe and Salpeter [1, p. 269], the lifetime of an excited level specified by the principal and azimuthal quantum numbers n and ℓ respectively, denoted by $\tau_{n\ell}$, is related to the average lifetime τ_n of level n by:

$$\tau_n = \left(\sum_{\ell=0}^{n-1}\frac{2\ell+1}{n^2}\,\frac{1}{\tau_{n\ell}}\right)^{-1}. \qquad (23)$$

In the limit as $n \to \infty$, we have the asymptotic relation

$$\frac{4.234\times10^{-11}}{\mu\,Z^4}\,\frac{n^5}{\ln n} \sim \left(\sum_{\ell=0}^{n-1}\frac{2\ell+1}{n^2}\,\frac{1}{\tau_{n\ell}}\right)^{-1}. \qquad (24)$$

Asymptotically, $\tau_{n\ell}$ behaves as [1]

$$\tau_{n\ell} \sim f(\ell)\,n^3\,, \qquad (25)$$

where $f(\ell)$ denotes a function of ℓ. Substituting for $\tau_{n\ell}$ in (24), we obtain

$$\sum_{\ell=0}^{n-1}\frac{2\ell+1}{f(\ell)} \sim \frac{\mu\,Z^4}{4.234\times10^{-11}}\,\ln n\,, \qquad (26)$$

Asymptotically, one has the relation [6]

$$\gamma = \lim_{n\to\infty}\left(\sum_{m=1}^{n}\frac{1}{m} - \ln n\right), \qquad (27)$$

where $\gamma = 0.57721...$ is Euler's constant. Rewriting (27) as

$$\lim_{n\to\infty} \ln n = \lim_{n\to\infty} \sum_{\ell=0}^{n-1} \frac{1}{\ell+1} - \gamma\,, \qquad (28)$$

and substituting (28) in (26), we obtain

$$\sum_{\ell=0}^{n-1} \frac{2\ell+1}{f(\ell)} \sim \frac{\mu Z^4}{4.234\times 10^{-11}} \sum_{\ell=0}^{n-1} \frac{1}{\ell+1}\,, \qquad (29)$$

where Euler's constant has been dropped in keeping with the nature of the asymptotic approximation. Equating each term of the summations and solving for $f(\ell)$, we obtain

$$f(\ell) = \frac{4.234\times 10^{-11}}{\mu Z^4} (\ell+1)(2\ell+1)\,, \qquad (30)$$

and hence from (25), the asymptotic expression over n for $\tau_{n\ell}$, in the limit as $n \to \infty$, is given by

$$\tau_{n\ell} \sim \frac{8.468\times 10^{-11}}{\mu Z^4} \left(\ell + \tfrac{1}{2}\right)\left(\ell+1\right) n^3 \text{ s}\,, \qquad (31)$$

In the limit of both $n \to \infty$ and $\ell \to \infty$, we obtain the asymptotic expression over n and ℓ for $\tau_{n\ell}$

$$\tau_{n\ell} \sim \frac{8.468\times 10^{-11}}{\mu Z^4}\, \ell^2 n^3 \text{ s}\,. \qquad (32)$$

6 Discussion and conclusion

In this paper, we have derived analytical asymptotic expressions for the average lifetimes τ_n and $\tau_{n\ell}$ of hydrogenic levels with principal quantum number n, and principal and azimuthal quantum numbers (n, ℓ), respectively.

We first reviewed the calculation of the average level lifetimes based on the calculation of the spontaneous transition probabilities for hydrogenic level transitions, which further require the calculation of the absorption oscillator strengths of those transitions. We then considered the time-consuming exact calculation of the absorption oscillator strengths, their approximate calculation from an asymptotic formula, and briefly reviewed the neglected Gaunt factor of order unity where the complexity is hidden.

Finally, we considered the derivation of the asymptotic expressions for the average lifetime of hydrogenic levels τ_n and $\tau_{n\ell}$. These provide simple analytical asymptotic expressions that are well-adapted to simplify the analysis of hydrogenic levels and more complex atomic and ionic systems.

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