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A universal formula for the accurate calculation of hydrogenic lifetimes

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Abstract

The quantum mechanical lifetimes of atomic hydrogenic states are shown to follow a universal curve when plotted against a simple function of their quantum numbers n and l. This universal curve is found to agree with a result derived from the correspondence principle. A simple formula which approximates the universal curve can be used to easily calculate lifetimes for all states $n, l \geqslant 1$ to an accuracy of 400 parts per million or better. The formula is especially useful for high-n states, where the full quantum calculation is extremely difficult or even impossible to perform.

The radiative lifetimes of hydrogenic states can be determined by calculating electric dipole matrix elements to all states of lower energy. In the non-relativistic dipole approximation [1, 2] for a hydrogenic atom (with particles of mass M and m and charge Ze and $-ze$), we have

$$\tau_{nl}^{\mathrm{qm}} = \frac{4\tau_0}{\sum\limits_{\substack{n'<n \\ l'=l\pm1 \\ m_l'=m_l,m_l\pm1}} \left(\frac{n^3}{n'^2} - n\right)^3 \left|\langle nlm_l|\frac{\vec{r}}{a}|n'l'm_l'\rangle\right|^2}, \tag{1}$$

where

$$\tau_0 = \frac{3\hbar n^5}{2(zZ)^4\alpha^5\mu c^2}\left(\frac{m+M}{Zm+zM}\right)^2 \tag{2}$$

sets the typical time scale for the lifetimes, and the scale factor $a = \frac{\hbar n^2}{Zz\alpha\mu c}$ makes the terms in the sum independent of Z, z and the reduced mass $\mu = \frac{mM}{M+m}$, and of order unity for $n' \approx n$.

For high-n levels, a large number of dipole matrix elements must be calculated. Even though the hydrogenic wavefunctions are known exactly, the dipole matrix elements are very difficult to calculate for these states. The difficulty arises from the fact that the wavefunctions are extremely oscillatory, causing the negative and positive contributions to cancel, often to hundreds of digits.

For example, the 300*p* to 290*s* electric dipole matrix element, just one of 596 such matrix elements needed to calculate the 300*p* state lifetime, consists of 86 710 terms, each of which needs to be computed to 300 digits of accuracy because of the cancellation between positive and negative terms.

As a result, the calculation of hydrogenic lifetimes is a computationally extremely intensive task for states of high n, usually performed in a symbolic computing environment. The computation becomes prohibitive for plasma simulations where the lifetimes of a vast number of n and l states are required [3].

The goal of the present work is to present a simple, yet accurate formula for these lifetimes. An approximate formula was introduced by Chang [4] who followed up on work by Omidvar [5]:

$$\tau_{nl} \approx \tau_0 \frac{\left(l + \frac{1}{2}\right)^2}{n^2}. \tag{3}$$

For $l \geqslant 1$ states this formula was shown to represent an upper bound to the true lifetimes.

A similar approximation was derived by Marxer and Spruch [6] by considering the evolution of angular momentum in a classically radiating atom:

$$\tau_{nl} \approx \tau_0 \frac{l(l+1)}{n^2}. \tag{4}$$

These authors also introduced a correction for the fact that the magnitude of angular momentum changes by $(\sqrt{l(l+1)} - \sqrt{l(l-1)})\,\hbar$ rather than by $\hbar$. This improved estimate of the lifetime is given by

$$\tau_{nl} \approx \tau_0 \frac{l^2 + l + \frac{l+1}{8l}}{n^2}. \tag{5}$$

Note that the three expressions (3), (4) and (5) can be written in the general form

$$\tau_{nl}^{(0,s)} = \tau_0 \frac{l^2 + l + s}{n^2}, \tag{6}$$

with $s = \frac{1}{4}$, $s = 0$ and $s = \frac{l+1}{8l}$.

While giving a good approximation, these formulae differ from the exact lifetimes by as much as 10%, as can be seen in figures 1(a)–(c). There the ratios of the quantum-mechanical lifetimes to the approximations $\tau_{nl}^{(0,s)}$ are plotted for all quantum states n and $l \geqslant 1$. These ratios are plotted against

$$\epsilon = \sqrt{1 - \frac{l^2 + l + s}{n^2}}. \tag{7}$$

The choice of the x axis is inspired by the eccentricity of the classical elliptical orbit having energy and angular momentum matching that of the quantum (n, l) state. Using equation (7), equation (6) can be rewritten as

$$\tau_{nl}^{(0,s)} = \tau_0 (1 - \epsilon^2), \tag{8}$$

showing that $\tau_{nl}^{(0,s)} / \tau_0$ is a simple function of ϵ.

Note that s in equation (7) allows for the fact that there are two distinct ways to assign the eccentricity of the classical orbit corresponding to a given state. Semiclassically, one requires $\langle L^2 \rangle = \left(l + \frac{1}{2}\right)^2 \hbar^2 = \hbar^2 \left(l^2 + l + \frac{1}{4}\right)$, and therefore $s = \frac{1}{4}$, to obtain orbits of the correct binding energy. Quantum mechanically, one requires $\langle L^2 \rangle = l(l+1)\hbar^2$, and therefore $s = 0$. Recently, the connection of the semiclassical quantization scheme to quantum mechanics has been investigated [7].

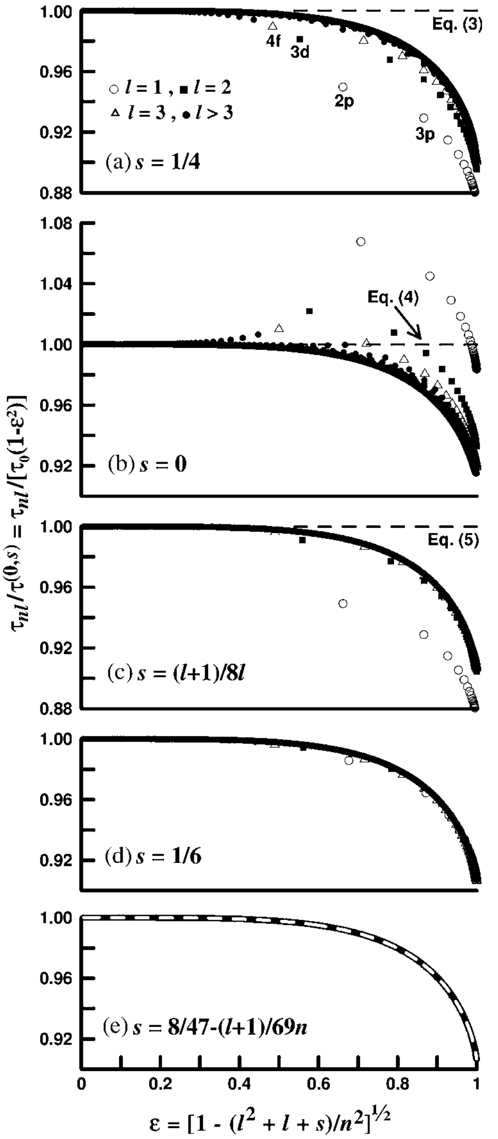

Figure 1. Lifetimes for states $n, l \geqslant 1$ normalized by $\tau^{(0,s)}$ of equation (6), plotted versus $\epsilon = \sqrt{1 - (l^2 + l + s)/n^2}$. Plots (a), (b) and (c) show that the approximations of equations (3)–(5) (black dashed lines) are good to about 10%. Plots (d) and (e) show that all lifetimes approach a universal curve for an appropriate choice of s. The thin dashed white line in (e) is the classical result equation (9) derived from the correspondence principle.

In figure 1(a) we have identified the np series ($l = 1$) by open circles, and likewise the nd ($l = 2$) and nf ($l = 3$) series are marked by squares and open triangles respectively. All higher-l series are marked by solid dots and are so dense that the unresolved points form a solid curve, with a few points that are, upon closer inspection, partially resolved from the curve.

The ratios plotted in figure 1(a) are discrepant from 1.0 by as much as 12%, indicating that equation (3) (the dashed line) gives only an approximate estimate for hydrogenic lifetimes.

Because of the choice of the x axis, the plot reveals distinct patterns in these discrepancies. The discrepancies are small for $\epsilon \lesssim 0.4$, which corresponds to $l/n \gtrsim 0.9$. For $l > 3$, the discrepancies grow steadily with increasing epsilon and become as large as about 10% for $\epsilon = 1$. The lower-l states show somewhat larger discrepancies that also form distinct patterns, and again show the largest discrepancies at larger values of ϵ (that is, at larger n for each l).

Figures 1(b) and (c) reveal similar patterns: the discrepancies between the quantum-mechanical lifetimes and the estimates of equations (4) and (5) are small at small epsilon, and increase to about 10% for larger epsilon. Again, unresolved high-l lifetimes form a solid curve, and the lower-l states have similar patterns of discrepancies. It should be emphasized that it is only when the lifetimes are plotted against the epsilon defined in equation (7), that the ratios in the plots reveal such patterns. Note that in the top three graphs (figures 1(a)–(c)) the highest-l ratios approach a universal curve which starts at 1.0 for $\epsilon = 0$ and ends at ≈ 0.907 for $\epsilon = 1$.

Close inspection of the top two graphs ($s = 1/4$ and $s = 0$ respectively) shows that each low-l point in figure 1(b) is above the high-l curve by very nearly double the distance that the corresponding point in figure 1(a) is below the curve. The implication is that an s value which is one third of the way between the $s = \frac{1}{4}$ of figure 1(a) and the $s = 0$ of figure 1(b), i.e., $s = \frac{1}{6}$, might move the low-l points very close to the universal curve. This is indeed the case, as can be seen in figure 1(d), where all low-l points are within 0.5% of the high-l curve.

Although $s = \frac{1}{6}$ gives close agreement with the high-l curve, an even better choice is $s = \frac{8}{47} - \frac{l+1}{69n}$ as shown in figure 1(e). Here all points agree with the high-l curve to within 400 parts per million (ppm) for $l = 1$, 300 ppm for $l = 2$ and 150 ppm for $l = 3$. For higher l, the agreement is even better, being <100 ppm for $l > 3$, <10 ppm for $l > 14$, and <1 ppm for $l > 48$.

Figure 1(e) demonstrates the remarkable result that, plotted against the correct function of n and l, the quantum-mechanical radiative lifetimes of all hydrogenic states $n, l \geqslant 1$ lie almost exactly on a universal curve. This pattern of hydrogenic lifetimes has gone unnoticed in the 80 years since the development of quantum mechanics.

Furthermore, this universal curve is given exactly by the correspondence principle (CP). Recently we have used the CP to derive a classical estimate for hydrogenic lifetimes [8]:

$$\tau^{\mathrm{cl}} = \frac{\tau_0}{2\sum_{k=1}^{\infty} k\left(J_k'^2(k\epsilon) + \frac{1-\epsilon^2}{\epsilon^2} J_k^2(k\epsilon)\right)}, \tag{9}$$

where ϵ is the eccentricity, and the Bessel functions arise as a result of the Fourier decomposition of the classical orbit which enters the classical Larmor radiation formula. Equation (9) agrees exactly with the high-l universal curve of figures 1(a)–(d), and with the universal curve for all $n, l \geqslant 1$ of figure 1(e), as shown by the white dashed lines in that plot.

One might be concerned about our having to choose a rather arbitrary value of s to cause quantum mechanics to agree with the classical CP result for the radiative lifetime. We note, however, that similar circumstances arise for other physical quantities. For example, the average of r, the separation of the two charges in a hydrogenic atom, is given in quantum mechanics by [1]

$$\langle r \rangle_{\mathrm{qm}} = a\left(\frac{3}{2} - \frac{l(l+1)}{2n^2}\right), \tag{10}$$

where $a = \frac{\hbar n^2}{\mu z Z \alpha c}$.

The classical result for the average separation is

$$\langle r \rangle_{\mathrm{cl}} = \tilde{a}\left(1 + \tfrac{1}{2}\epsilon^2\right), \tag{11}$$

where ϵ is the eccentricity, and $\tilde{a}$ the semi-major axis of the elliptical orbit. In order to obtain $\langle r\rangle_{\mathrm{cl}} = \langle r\rangle_{\mathrm{qm}}$, we need $\tilde{a} = a$ and

$$\epsilon = \sqrt{1 - \frac{l^2 + l}{n^2}}. \tag{12}$$

That is, we need $s = 0$. However, to match

$$\langle r^2\rangle_{\mathrm{qm}} = \frac{a^2}{2}\left(5 + \frac{1}{n^2} - \frac{3l(l+1)}{n^2}\right) \tag{13}$$

with

$$\langle r^2\rangle_{\mathrm{cl}} = \tilde{a}^2\left(1 + \tfrac{3}{2}\epsilon^2\right) \tag{14}$$

we need

$$\epsilon = \sqrt{1 - \frac{l^2 + l - \frac{1}{3}}{n^2}}, \tag{15}$$

i.e., $s = -\frac{1}{3}$. Similarly, $\left\langle\frac{1}{r^2}\right\rangle_{\mathrm{qm}} = \left\langle\frac{1}{r^2}\right\rangle_{\mathrm{cl}}$ requires $s = +\frac{1}{4}$.

Other powers of r lead to more complicated expressions. For example, $\langle r^3\rangle_{\mathrm{qm}} = \langle r^3\rangle_{\mathrm{cl}}$ requires

$$s = -\frac{5}{6} + \frac{\frac{l(l+l)}{30} + \frac{5}{72}}{n^2} + O\left(\frac{1}{n^4}\right). \tag{16}$$

Clearly, the assignment of s depends on the physical quantity one wishes to match in the quantum and classical descriptions. From figure 1(e) it is evident that $s = \frac{8}{47} - \frac{(l+1)}{69n}$ provides an excellent match for radiative lifetimes. An even better value of s (for example by expanding in higher powers of $1/n$) might be possible, but seems unnecessary since we have already ignored effects of order $\alpha^2 \approx 100$ ppm by using the non-relativistic electric dipole approximation.

We note that the assignment of an eccentricity in terms of quantum numbers has been investigated extensively in the context of transition matrix elements evaluated in the WKB approximation. In this case the assignment depends on the (n, l) quantum numbers of both the initial and final states and involves an averaging prescription [9–13].

Having expressed the universal curve for radiative lifetimes (figure 1(e)) in terms of the classical result, equation (9), we now revisit the expression for this classical result. It can be separated into

$$\frac{1}{\tau^{\mathrm{cl}}} = R^{+} + R^{-}, \tag{17}$$

where

$$R^{\mp} = \frac{1}{\tau_0}\sum_{k=1}^{\infty} k\left(J_k'(k\epsilon) \pm \sqrt{\frac{1-\epsilon^2}{\epsilon^2}}J_k(k\epsilon)\right)^2 \tag{18}$$

are the rates for increasing/decreasing angular momentum. Thus, the net rate of decrease of angular momentum is

$$\frac{-\langle\dot{L}\rangle}{\hbar} = R^{-} - R^{+} = \frac{4\sqrt{1-\epsilon^2}}{\tau_0\epsilon}\sum_{k=1}^{\infty} kJ_k'(k\epsilon)J_k(k\epsilon), \tag{19}$$

which can be summed analytically to the expression

$$R^{-} - R^{+} = \frac{1}{\tau_0(1-\epsilon^2)}. \tag{20}$$

We can then write

$$\frac{1}{\tau^{\mathrm{cl}}} = (R^- - R^+) + 2R^+ = \frac{1}{\tau_0(1-\epsilon^2)} + 2R^+, \tag{21}$$

where the first term dominates since $R^+ < R^-$ for $\epsilon > 0$. This first term leads to the approximation of equation (8). To find a useful approximation to the full expression, we perform an expansion of this equation:

$$\frac{1}{\tau^{\mathrm{cl}}} = \frac{1 + \sum_{j=2}^{\infty} c_j \epsilon^{2j}}{\tau_0(1-\epsilon^2)}, \tag{22}$$

where the expansion coefficients are analytically determined from the Bessel-function expression to be

$$c_j = \frac{2j+2}{2j+1} a^+_{j+1} + \frac{2j(j+1)^2}{2j+1} a^-_{j+1} + a^+_{j-1} - \frac{4j-1}{2j-1} a^+_j - \frac{2(j-1)j^2}{2j-1} a^-_j, \tag{23}$$

with

$$a^{\pm}_j = \frac{(2j)!}{2^{2j-1}(j!)^2} \sum_{k=1}^{j} (-1)^{j-k} \frac{k^{2j\pm1}}{(j+k)!(j-k)!}. \tag{24}$$

Thus, we obtain the following expansion for the classical lifetime:

$$\frac{1}{\tau^{\mathrm{cl}}} = \frac{1 + \frac{\epsilon^4}{32} + \frac{5\epsilon^6}{288} + \frac{87\epsilon^8}{8192} + \cdots}{\tau_0(1-\epsilon^2)}. \tag{25}$$

The terms up to and including ϵ^8 form a 100 ppm approximation for τ_{cl} for $\epsilon < 0.6$, but the expansion converges very slowly as ϵ approaches unity.

For large j the Taylor coefficients c_j are approximated very well by

$$c_j = \frac{B_1}{j(j+1)} + \frac{B_2}{j(j+1)(j+2)} + \cdots, \tag{26}$$

which match the Taylor coefficients of the function

$$\frac{B_1(1-\epsilon^2)\ln(1-\epsilon^2)}{\epsilon^2} - \frac{B_2(1-\epsilon^2)^2\ln(1-\epsilon^2)}{\epsilon^4} + \cdots. \tag{27}$$

Combining equation (25) with equation (27) suggests a set of successively-better approximations for the classical lifetime expression with Taylor coefficients with successively-improved matches to the exact coefficients of equation (23) for both large and small values of j. An approximation that is good to within 100 ppm for all $0 \leqslant \epsilon \leqslant 1$ is given by

$$\tau^{\mathrm{cl}} \approx \frac{\tau_0(1-\epsilon^2)}{1 + \frac{19}{88}\left[\left(\frac{1}{\epsilon^2} - 1\right)\ln(1-\epsilon^2) + 1 - \frac{\epsilon^2}{2} - \frac{\epsilon^4}{40}\right]}. \tag{28}$$

Again, since the present calculation is non-relativistic and in the electric dipole approximation, it ignores terms of order $\alpha^2 \approx 100$ ppm, and it is unnecessary to include higher-order corrections to this approximation.

With this approximation we have obtained a simple, yet accurate formula for the radiative lifetime of a hydrogenic state (n, l). One needs only to calculate the value of ϵ according to

$$\epsilon = \sqrt{1 - \frac{l^2 + l + \frac{8}{47} - \frac{(l+1)}{69n}}{n^2}} \tag{29}$$

and insert this into equation (28) with τ_0 from equation (2) $\approx n^5 93.42$ ps for neutral hydrogen. The resulting lifetime estimate is accurate to better than 400 ppm for all $n, l \geqslant 1$, and <300 ppm for $l = 2$, and <200 ppm for $l = 3$. The accuracy is even better for higher l, with $l > 8$ quantum lifetimes all being predicted to better than 100 ppm.

Equations (28) and (29) are applicable to a wide range of hydrogenic and nearly-hydrogenic systems. Hydrogenic systems include neutral hydrogen, hydrogenic ions and exotic atoms such as antihydrogen, positronium and muonium. Nearly-hydrogenic systems include Rydberg states of any atom, molecule or ion, especially high-l (e.g., $l \geqslant 4$) states for which the Rydberg electron is well separated from the ion core due to the centrifugal potential, making the resulting states very hydrogenic. Since hydrogenic and Rydberg systems are common in atomic physics, plasma physics and in astronomy, the simple lifetime expression will be widely applicable.

In summary, we have found a universal curve for hydrogenic lifetimes of states $n, l \geqslant 1$. We have shown that this universal curve agrees with that expected from the correspondence principle. Finally, we have derived a simple, and very accurate approximation for the correspondence principle result, which allows for greatly-simplified calculations of hydrogenic radiative lifetimes.

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