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Radiative lifetime of hydrogenic and quasihydrogenic atoms

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A universal formula for the upper bound of the radiative lifetime of a hydrogenic level is found to be $(3\hbar^3/2m\alpha^3Z^4e^4)n^3(l+\frac{1}{2})^2$. When compared with the exact lifetimes, the expression is found to agree within 10%. For quasihydrogenic atoms and ions, experimental lifetimes are generally found to coincide with the upper bound values.

Quasihydrogenic atoms are Rydberg systems where the optical electron's angular momentum l is sufficiently high for its behavior to be hydrogenic. In such nonpenetrating states, the energy usually deviates from the hydrogenic value by less than 1%, and may readily be calculated by perturbation theory.[1,2] Similar departure from the hydrogenic radiative lifetime has been found to be at the few percent level,[3] which is negligible for the present purpose.

The radiative lifetime of a hydrogenic state can be calculated exactly by summing over the appropriate Einstein A coefficients. However, for applications to astrophysics, plasma physics, and for planning experiments, it is highly desirable to have a simple though approximate closed expression. In this work, the lifetime of quasihydrogenic atoms is found to be given by 93 $n^3(l+\frac{1}{2})^2$ ps. This expression is applicable as long as l is two units or more than the highest orbital angular momenta of the core electrons (with no restriction on the principal quantum number n). It is demonstrated to be usually within the typical experimental error bars of $\pm 10\%$.

For a hydrogenic state specified by n and l, the radiative lifetime has been found to vary as n^3 by Bethe and Salpeter.[4] Without establishing the l dependence, the proportionality constant cannot be found. Restricted to circular orbits where $l=n-1$, an expression with the same constant (93 ps) was obtained[5] both classically and quantum mechanically. Using a semiclassical approach in the general case, Omidvar[6] discovered an l^2 dependence, but it was only asymptotic. In fact, the coefficients varied over more than a factor of 2, depending on n and l. In comparison, the present expression, derived quantum mechanically, varies as $(l+\frac{1}{2})^2$. The constant, derived as an upper bound, is found to yield lifetimes differing from the exact values by only a few percent for all $l \neq 0$. Thus, this universal formula for the radiative lifetime supercedes Omidvar's tables at the present level of experimental accuracy. Indeed, it is found to agree with experimental values in quasihydrogenic systems, which extends from tens of picoseconds to microseconds. Furthermore, the formula is applicable to molecules and exotic atoms.

In a hydrogenic atom of nuclear charge Ze, the electric dipole transition probability $(n,l \rightarrow s,k)$ is given by the Einstein A coefficient.[4]

$$A(n,l \rightarrow s,k) = A_0 Z^4 (n^{-2} - s^{-2})^2 f(n,l \rightarrow s,k)/2 \ , \tag{1}$$

where the basic unit of transition rate is

$$A_0 = m\alpha^3 e^4/\hbar^3 \ . \tag{2}$$

In Eq. (2) m is the reduced mass and α the fine-structure constant. For ordinary atoms, m is practically the mass of the electron, so A_0 has the value of 1.604×10^{10} sec^{-1}.

The oscillator strength f in Eq. (1) is known to have many alternative forms—length, velocity, and acceleration. Since the emission rate is determined by the radiative power, it is more appropriate to choose the velocity-acceleration form.[7]

$$f(n,l \rightarrow s,k) = (2i\hbar/3m)[Z^2e^2(n^{-2}-s^{-2})/2a_0]^{-2} \times \langle n,l|\vec{p}|s,k\rangle^* \cdot \langle s,k|\nabla V|n,l\rangle \ . \tag{3}$$

In Eq. (3), $a_0 = \hbar^2/me^2$ is the Bohr radius, $\vec{p} = -i\hbar\nabla$, and $\nabla V = Ze^2\vec{r}/r^3$. When Eq. (3) is substituted into Eq. (1), the energy factors cancel so that the expression becomes

$$A(n,l \rightarrow s,k) = -(\tfrac{4}{3})A_0 Z a_0^3 \langle n,l|\nabla|s,k\rangle \cdot \langle s,k|\vec{r}/r^3|n,l\rangle \ . \tag{4}$$

From the selection rules of an allowed transition, the radiative lifetime is related to the A coefficients by

$$T(n,l) = \left[\sum_{s<n} A(n,l \rightarrow s,l+1) + \sum_{s<n} A(n,l \rightarrow s,l-1)\right]^{-1} \ . \tag{5}$$

Exact values for $T(n,l)$ have been calculated[6] for values of n and l up to 25. The task at hand is to evaluate Eq. (5) analytically by introducing suitable approximations. From Bethe and Salpeter,[4] it is known that the oscillator strengths, and hence the A coefficients, are numerically much smaller when Δn and Δl are in the opposite sense than when they are in the same sense. Furthermore, the A coefficients are positive when $s < n$, but negative when $s > n$. (The sign is derived from the energy factor since the squared dipole matrix element is always positive.)

The first approximation is to neglect all terms in the first sum in Eq. (5), which is valid except in the case of $l=0$ (s states), where all the terms in the second sum vanish. Since all terms in both sums are positive, this approximation results in a lower bound for the denominator or an upper bound for T. The second approximation is to extend the second sum to all values of s including the continuum. Since negative terms are now added to the sum, the result is once more a lower bound for the denominator. Therefore, an upper bound for the radiative lifetime is established,

$$T(n,l) < -3/(4A_0 Z a_0^3 M) \ , \tag{6}$$

where

$$M = \sum_s \langle n,l|\nabla|sl-1\rangle \cdot \langle s,l-1|\vec{r}/r^3|n,l\rangle \ . \tag{7}$$

Applying closure and standard Racah algebra,[8] it is found that

$$M=\frac{l}{2l+1}\left\langle n,l\left|\left(\frac{d}{dr}-\frac{l-1}{r}\right)\frac{1}{r^2}\right|n,l\right\rangle$$

$$=\frac{l}{2l+1}\left\{\left\langle n,l\left|\frac{1}{r^2}\frac{d}{dr}\right|n,l\right\rangle-\left\langle n,l\left|\frac{l+1}{r^3}\right|n,l\right\rangle\right\} . \quad (8)$$

In Eq. (8), the first term is seen to vanish upon integration by parts for $l \neq 0$. The expectation value of r^{-3} in the second term is known analytically,[4] so it is found that

$$M=-[l(l+1)/(2l+1)]Z^3/[n^3\,l(l+\tfrac{1}{2})(l+1)a_0^3] \; . \quad (9)$$

Finally, substituting Eq. (9) into Eq. (6) yields the desired upper bound,

$$T(n,l) < C_0 n^3(l+\tfrac{1}{2})^2/Z^4 \quad (l \neq 0) \; , \quad (10)$$

where $C_0 = 3/(2A_0)$. For an ordinary atom $C_0 = 93.2$ ps, while for an exotic atom, C_0 has to be divided by the reduced mass in electron mass units as is evident from Eq. (2).

The expression in Eq. (10) is now compared with the semiclassical result[6]

$$T(n,l) \sim C_{n,l} n^3\, l^2/Z^4 \quad (n,l >> 1) \; . \quad (11)$$

Apparently they differ only by the replacement of l by $l+\frac{1}{2}$. However, $C_{n,l}$ in Eq. (11) varies with l (and n) approaching a constant only when n and l are much greater than unity, while C_0 in Eq. (10) is independent of n and l. For large values of n and l, Omidvar found an approximate value $C_\infty = 84.7$ (and 87.1) ps, which is consistent with the upper bound value of $C_0 = 93.2$ ps.

Actually, from the exact quantum-mechanical expressions given by Eq. (5), Omidvar has calculated his $C_{n,l}$ for all n and l less than 25. It is of interest to see how close C, defined by

$$C = Z^4 T(n,l)/n^3(l+\tfrac{1}{2})^2 \; , \quad (12)$$

comes to C_0 for various values of n and l when $Z = 1$. In Fig. 1, C is plotted against n for a fixed number of radial nodes in the wave function, given by $n_r = n - l - 1$. For $n_r = 0$ and 1, C rapidly approaches the upper bound C_0 indicated by the arrow. The reasons are that the neglected coefficients $A(n,l \rightarrow s,l+1)$ actually vanish and that the continuum values of $A(n,l \rightarrow s,l-1)$ are very small as indicated by the remark[4] that "circular orbits are difficult to ionize." The solid line for $n_r = 2$ represents a more typical situation and as n_r increases, the more highly elliptical orbits show a larger deviation from C_0. Nevertheless, for all n_r, C approaches (though not reaches) C_0 monotonically as n increases, and even for the lowest values of n, C is only about 10% below its upper limit value. Therefore, Eq. (10) not only gives an upper bound, it also yields an approximate value accurate to 10%.

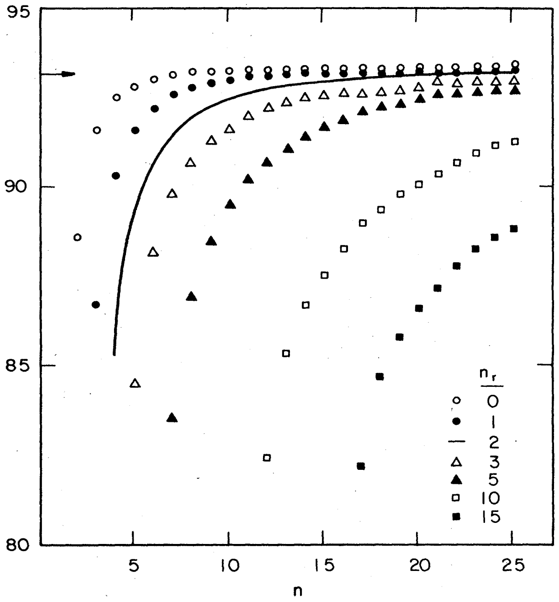

FIG. 1. The constant C given by Eq. (12) for hydrogenic lifetimes. Each curve represents a fixed value of n_r specified in the lower right corner. The arrow indicates the upper bound value of 93.2 ps.

For experimental verification we turn to quasihydrogenic atoms and ions. First the condition for using the hydrogenic formula should be clarified. If the core contains electrons in the state n',l', the transition from n,l to n',l' will be forbidden, or at least disrupted, by the Pauli exclusion principle. Therefore, in the electric dipole process $l-l'$ should be greater than one. For cores with only s electrons, nd states will satisfy this condition, while for cores with p electrons, it requires states with higher l starting with nf. Table I shows recent experimental lifetimes of states in ions[9-22] satisfying the above criterion. When more than one measurement is available, preference is given to the one with the least quoted error or the most recent date. While the lifetimes range over five orders of magnitude, C obtained from Eq. (12) is remarkably constant. Within experimental errors it is usually consistent with and somewhat lower than the upper bound value of 93 ps. Even in the few cases of significant discrepancy, other measurements conforming to the upper limit can often be found. Indeed, Table I suggests that Eq. (10) may be used to discriminate between conflicting data. For example, earlier measurements[23] of the $4f\ ^1F$ and ^3F in O V which yielded lifetimes three times larger than those in Table I were clearly in error.

It is noteworthy to point out that the validity of Eq. (10) is not affected by the presence of an open-shell core as in the cases of O IV and C II in Table I. This is not surprising in view of the fact that in the j-l coupling scheme the line strengths and, hence, A coefficients are hydrogenic when summed over the K (final) quantum number of the lower states.[1] On the other hand, there is considerable evidence that Eq. (10) is not valid unless the aforementioned criterion $l-l' > 1$ is met. Examples are the $np\ ^1P$ series[24] of He I, the nd series[25] of Na I, and the nf series[26] of Rb I, where application of Eq. (12) yields values for C of 26, 160, and 55 ps, respectively. Since the quantum defects of all three series are only a few hundredths, it is evident that replacing n by n^* the effective quantum number does not suffice.

Next we consider the l-averaged lifetime defined by[4]

$$T(n)=\left[\sum_{l=0}^{n-1}(2l+1)/n^2 T(n,l)\right]^{-1} \; . \quad (13)$$

TABLE I. Experimental radiative lifetimes in quasihydrogen ions T is listed in order of decreasing Z and increasing n and l so that the lifetime generally increases. Spectrocsopic terms and configurations are given in cases of possible ambiguity. C is obtained from Eq. (12).

Ion	State	Reference	T (ns)	C (ps)
Ar VIII	$5g$	9	0.063 ± 0.006	102 ± 10
	$6g$		0.115 ± 0.010	108 ± 9
	$6h$		0.143 ± 0.010	89 ± 6
Cl VII	$5g$	10	0.101 ± 0.015	96 ± 14
O VI	$4f$	11	0.051 ± 0.005	84 ± 8
S VI	$4f$	12	0.051 ± 0.002	84 ± 3
Cl VI	$4f\,^3F$	10	0.049 ± 0.004	81 ± 7
S VI	$5g$	12	0.18 ± 0.007	92 ± 5
	$6g$		0.28 ± 0.04	83 ± 12
	$6h$		0.52 ± 0.02	103 ± 4
	$7h$		0.91 ± 0.10	114 ± 13
	$7i$		0.99 ± 0.04	88 ± 4
	$8k$		2.3 ± 0.6	103 ± 27
O V	$4f\,^1F$	11	0.10 ± 0.01	79 ± 8
	$4f\,^3F$		0.11 ± 0.01	88 ± 8
	$5f\,^1F$		0.21 ± 0.02	86 ± 8
	$5f\,^3F$	13	0.22 ± 0.02	99 ± 10
	$5g\,^1G$		0.37 ± 0.04	92 ± 9
	$5g\,^3G$		0.39 ± 0.04	97 ± 10
O IV	$4f\,(2s2p)^2F$	13	0.32 ± 0.03	105 ± 10
	$4f\,(2s2p)^2D$	11	0.23 ± 0.03	75 ± 10
	$4f\,(2s2p)^2G$	13	0.29 ± 0.03	95 ± 10
	$4f\,(2s2p)^4G$		0.24 ± 0.03	78 ± 10
Ti IV	$4f$	14	0.23 ± 0.02	75 ± 7
Ga III	$5g$	15	2.8 ± 0.6	90 ± 19
Li II	$4f\,^3F$	16	5.1 ± 0.4	104 ± 8
C II	$4f\,(2s2p)^4G$	17	4.0 ± 0.2	81 ± 4
Mg II	$4f$	18	3.7 ± 0.4	75 ± 8
He I	$3d\,^1D$	19	15.2 ± 0.5	90 ± 3
	$3d\,^3D$		14.25 ± 0.34	84 ± 2
Li I	$3d$	20	14.9 ± 0.6	88 ± 4
He I	$4d\,^1D$	21	36.4 ± 1.2	91 ± 3
	$4d\,^3D$	19	32.1 ± 1.3	80 ± 3
Li I	$4d$	20	32.7 ± 1.3	81 ± 5
He I	$4f\,^1F$	19	80 ± 6	102 ± 8
	$4f\,^3F$		71.6 ± 3	91 ± 4
He I	$5d\,^1D$		63.5 ± 5.7	81 ± 7
	$5d\,^3D$		57.2 ± 2.3	73 ± 3
Li I	$5d$	16	56 ± 2	72 ± 3
He I	$5f\,^1F$	21	142 ± 20	93 ± 13
Li I	$6d$	20	104.9 ± 5.0	78 ± 4
	$7d$		174.5 ± 10.5	82 ± 5
	$8d$		243 ± 17	76 ± 6
	$9d$		346 ± 31	76 ± 7
	$10d$		487 ± 48	78 ± 8
	$11d$		654 ± 65	79 ± 8
Na I	$13f$	22	2270 ± 400	84 ± 15
	$14f$		2640 ± 450	78 ± 14
	$15f$		3540 ± 500	85 ± 12

Substituting Eq. (10) into (13), it is seen that

$$T(n) < C_0(n^5/2Z^4)\left\{\sum_{l=0}^{n-1}(l+\tfrac{1}{2})^{-1}\right\}^{-1} , \tag{14}$$

where the small A coefficient for $l=0$ is neglected. As is Omidvar's work, the sum in Eq. (14) can be obtained analytically in the limit of large n, i.e.,

$$\sum_{l=1}^{n=1}(l+\tfrac{1}{2})^{-1} = \lim_{n\to\infty}[(2n-1)+\gamma+\ln 2-2] , \tag{15}$$

where γ is Euler's constant. For a finite value of n, the left-hand side (LHS) exceeds the right-hand side (RHS). Therefore, when Eq. (15) is substituted into Eq. (14), the upper bound no longer holds. Instead, the lifetime is approximately given by

$$T(n) \approx C_0(n^5/2Z^4)[\ln(2n-1)-0.365]^{-1} . \tag{16}$$

Clearly Eq. (16) supports Omidvar's asymptotic $n^5/\ln n$ law. Once more, Eq. (16) may be compared with the semiclassical expression:[6]

$$T^{\mathrm{sc}}(n) \approx C_\infty(n^5/2Z^4)[\ln(1.4136n)]^{-1} . \tag{17}$$

Obviously they differ only in the constant and in the details of the logarithm factor. In Table II, T and T^{sc} are compared with the exact lifetime for n ranging up to 25. Evidently T always lies between the T^{sc} and the exact value and never deviates from the latter by more than a few percent. These considerations suggest that the radiative lifetimes of radio recombination lines[27] such as the H 66α and the H 166α will be accurately predicted by Eq. (16). As seen in Table II, the latter just exceeds one second.

Another useful application in astrophysics is to the recently identified infrared emission lines from the solar chromosphere.[2] The lifetimes for these Rydberg states centered on $n=7$ and $l=6$ in Mg I and Si I are trivially given by Eq. (10). They should facilitate the disentangling of the cascading processes and the modeling of the solar atmosphere. Similarly, lifetimes for the intermediate range ($2 < n < 10$) radiative cascades in muonic and in other exotic atoms[28] can be predicted to the required accuracy.

TABLE II. Hydrogenic l-averaged lifetimes T and T^{sc} are given by Eqs. (16) and (17), respectively. The number in parenthesis is the power of 10. All lifetimes are in nanoseconds.

n	$T^{(\mathrm{exact})}$ (ns)	T (ns)	T^{sc} (ns)
2	2.13(0)	2.03(0)	1.31(0)
3	1.00(1)	9.17(0)	7.12(0)
4	3.31(1)	3.01(1)	2.50(1)
5	8.65(1)	7.94(1)	6.77(1)
10	1.91(3)	1.81(3)	1.60(3)
15	1.23(4)	1.18(4)	1.06(4)
20	4.66(4)	4.51(4)	4.06(4)
25	1.32(5)	1.29(5)	1.16(5)
66	· · ·	1.29(7)	1.17(7)
166	· · ·	1.08(9)	0.98(9)

Finally, Eq. (10) is also applicable to certain molecular Rydberg states. So far the only direct lifetime measurements[29] appear to be for the $n=3$ levels in para-H_2. For the 13 reported $3d$ levels, they range from 11.1 to 15.6 ns with a varying accuracy of a few percent. The corresponding values of C are from 71 to 96 ps, generally conforming to the upper limit value of 93 ps in spite of considerable mixing with the $3s$ level whose hydrogenic lifetime is an order of magnitude larger. For less penetrating states such as the $4f$ and the $5g$ levels,[30] our universal formula is expected to predict the radiative lifetime even more accurately.

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