Classical calculation of the lifetimes and branching ratios for radiative decays of hydrogenic atoms

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The correspondence principle for atomic radiation is extended to all hydrogenic states \( n \) and \( l \geq 0 \). Lifetimes and branching ratios are obtained using analytic calculations of the classical radiated spectrum for the elliptical orbit corresponding to a particular quantum state. The polarization of the radiation is used to separate out the angular momentum decreasing and increasing transitions. The lifetimes show excellent agreement with quantum mechanics for all principal quantum numbers \( n \) and \( l \geq 1 \) (e.g., \(<100 \) parts per million for \( l \geq 30 \), \(<0.1\% \) for \( l \geq 9 \), \(<1\% \) for \( l \geq 3 \)). The calculated branching ratios are in reasonable agreement with quantum results for all \( n' \), \( l' \), \( n \), and \( l \geq 1 \).

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Spontaneous radiative decay of even the simplest quantum systems, such as atomic hydrogen, becomes difficult to calculate in quantum mechanics if one is interested in high-\( n \) Rydberg levels. The understanding of radiative cascades in plasmas is of importance in astrophysics as well as in recent laboratory experiments to form antihydrogen [1]. A classical treatment of the problem on the basis of the correspondence principle (CP) is desirable even from this practical point of view. Such an approach will be even more useful when the effects from external fields are to be included.

Heisenberg used the CP in this regard [2] and noticed that the radial quantum transition matrix elements for transitions to neighboring principal quantum number states \( n \rightarrow n-1 \) (and to a lesser extent for \( n \rightarrow n-2 \)) are described accurately by the Fourier coefficients of the Bohr orbit trajectory. Kramers [3] and collaborators worked out a theory of absorption and emission of radiation, and van Vleck [4] formulated the theory of Einstein coefficients and a CP for transition rates. With the development of quantum mechanics, the classical decay model was forgotten, and the usefulness of the classical picture was noted mostly in the context of near-circular orbits [5].

We take the point of view that the CP implies that there should be a complete classical theory that is the analog of the quantum field theoretic problem of a spontaneously radiating atom. This theory consists simply of classical Kepler-Coulomb orbits, as well as the classical Larmor radiated power for the accelerated charges. The rate of radiation is sufficiently slow such that averaging over Keplerian orbits is permissible.

Recently Flannery and Vrinceanu [6] showed that the classical evolution of a given \((n, l)\) Rydberg orbit describes the average properties of the quantum-mechanical cascades. The authors also obtain an estimate of radial matrix elements by multiplying the Fourier coefficients for the initial and final orbits, obtaining good approximations for the quantum-mechanical matrix elements [2] even for large \( \Delta n \). The resulting decay rates are accurate over a significant range of transitions, but fail for large \( \Delta n \) for initial states with \( l/n < 1/3 \).

The purpose of the present paper is to show that a straightforward treatment of the simple problem of a classically radiating elliptical orbit leads to accurate estimates for lifetimes and branching ratios. In particular, we show that these quantities can be deduced from the rate of classical radiation, and from the spectrum and polarization of this radiation. Both the lifetimes and the branching ratios are obtained directly from the classical properties of the initial orbit, without the need to invoke the properties of the final-state orbit. This direct approach yields very accurate lifetimes and branching ratios that are a good approximation of the quantum results for all \( n, l > 0 \).

It is remarkable that this work appears so much later than the original semiclassical and quantum developments. We note, however, that in the context of semiclassical approximations to the Clebsch-Gordan coefficients, there has also been a recent revival of interest in this field [7].

An elliptical orbit is characterized by energy \( E \) and angular momentum \( L \), or alternatively by the semimajor axis

\[
a = -\frac{Ze^2}{2E} = \frac{n^2 \hbar}{\mu Z a c},
\]

and eccentricity

\[
e = \sqrt{1 + \frac{2EL^2}{Z^2 \alpha^2 \mu^2 c^2}},
\]

where \( \mu \) is the electron mass and \( Ze \) is the nuclear charge.

The semiclassical quantization rule \( L^2 = (l + \frac{1}{2}) \hbar^2 \) is used. This quantization of angular momentum is necessary in order to obtain classical orbits whose energies are consistent with the Schrödinger eigenenergies \( E = -\hbar^2 \alpha^2 \mu c^2 / (2n^2) \), and follows from the Einstein-Brillouin-Keller approach. It is also used in the semiclassical wavefunction-based WKB method as postulated by Langer [8]. The connection of this quantization prescription to the quantum result of \( L^2 = l(l+1) \hbar^2 \) was investigated recently [9].

To calculate the spectrum of the classical radiation, it is necessary to decompose the position vector for the elliptical orbit into a Fourier series. For an orbit in the \( xy \) plane and the perihelion aligned with the positive \( x \) axis,
The rate of energy loss is just

\[ \dot{E}_{\text{qm}} = - \sum_{l, l'} \left[ \sum_{\Delta n = 1}^{n/2} r_{\Delta n, l}^{\text{qm}} + \sum_{\Delta n = -1}^{n/2} r_{\Delta n, l}^{\text{qm}} \right] \hbar \omega_{\Delta n, l} \]  

where \( r_{\Delta n, l}^{\text{qm}} \) are the quantum mechanical rate coefficients for angular momentum transitions, and \( \omega_{\Delta n, l} \) is the angular frequency of the transition.

By analogy, the classical energy loss can be written as

\[ \dot{E}_{\text{cl}} = - \sum_{k=1}^{\infty} \left[ r_{k, l}^{\text{cl}+} + r_{k, l}^{\text{cl}-} \right] \hbar \omega_{k}^{\text{cl}} \]  

where the \( r_{k, l}^{\text{cl}+} \) and \( r_{k, l}^{\text{cl}-} \) are the classical rates for increasing or decreasing angular momentum by \( \hbar \omega_{k}^{\text{cl}} \), where \( \omega_{k}^{\text{cl}} = k \omega \) is the angular frequency of the \( k \)th harmonic.

From Eq. (9), we see that these rates are given by

\[ r_{k, l}^{\text{cl}+} = \frac{\alpha \mu^2}{8 \pi \epsilon_0^2} \left( b_k + c_k \right)^2 \left( \omega_k^{cl} \right)^3. \]  

Since \( c_k \ll b_k \) (with equality when \( \epsilon = 0 \)), \( r_{k, l}^{\text{cl}+} \ll r_{k, l}^{\text{cl}-} \). This shows that the classical rates for angular momentum increasing transitions are lower than those for angular momentum decreasing transitions.

Using the partial rates defined above, the quantum mechanical lifetime is given by

\[ \tau_{\text{qm}} = \left[ \sum_{\Delta n} \left( r_{\Delta n, n+}^{\text{qm}} + r_{\Delta n, n-}^{\text{qm}} \right) \right]^{-1}. \]  

Similarly, the classical estimate of the lifetime is given by

\[ \tau_{\text{cl}} = \left[ \sum_{k=1}^{\infty} \left( r_{k, l}^{\text{cl}+} + r_{k, l}^{\text{cl}-} \right) \right]^{-1}, \]  

which using Eqs. (13) and (5) can be expressed as

\[ \tau_{\text{cl}} = \left[ \frac{4 \alpha \mu^2}{3 n^3 \hbar} \sum_{k=1}^{\infty} k \left( J_k^2(k \epsilon) + \frac{1 - \epsilon^2}{\epsilon^2} J_k(k \epsilon) \right) \right]^{-1}. \]  

This classical estimate is remarkably successful in predicting the actual quantum mechanical lifetime. The contour graph over the plane of initial state quantum numbers \((n, l)\) given in Fig. 1 shows that this estimate is good to 30 parts per million (ppm) for \( l > 55 \), to \(< 100 \) ppm for \( l \geq 30 \), \(< 0.1\% \) for \( l > 9 \), \(< 1\% \) for \( l > 3 \), and \(< 5\% \) for \( l > 1 \). Equation (16) fails for \( l = 0 \) states, for which quantum mechanics forbids the dominant \( l \)-decreasing transitions included in the derivation of that equation. Furthermore, the highly elliptical classical orbits of these \( l = 0 \) states radiate appreciably at very high harmonics of the orbital frequency, and these frequencies would correspond to decays down to energies below those allowed for in quantum mechanics. Figure 1 also shows that Eq. (16) forms an upper bound for the quantum mechanical lifetimes.

An approximation (good to 10% for all \( n, l > 0 \)) to our lifetime expression Eq. (16) is given by

\[ \tau_{\text{cl}}^0 = \frac{3 n^3 \hbar}{2 Z^2 \alpha^2 \mu_0 \epsilon} \left( 1 - \epsilon^2 \right) = \frac{3 n^3 \hbar}{2 Z^2 \alpha^2 \mu_0} \left( l + \frac{1}{2} \right)^2. \]  

This approximation has been discussed in detail in Ref. [12], and has been used [13] to explain many experimental data. The formula was derived in Ref. [12] from the rate of change of angular momentum. To compare to that derivation, we note that, by the definition of \( r_{k, l}^{\text{cl}+} \), the rate of decrease of angular momentum is
FIG. 1. Relative error between the classical lifetime as calculated from the Fourier spectrum and the quantum lifetimes as a function of the \( n \) and \( l \) quantum numbers in parts per million.

\[
-\langle \dot{L} \rangle = \hbar \sum_{k=1}^{\infty} (r_{k,-}^{cl} - r_{k,+}^{cl}).
\]

Using Eqs. (13) and (5), this expression can be summed analytically to get

\[
-\langle \dot{L} \rangle = \left( \frac{2a\hbar}{3c^2} \right) \frac{2}{1 - e^{-2}} = \frac{\hbar}{\tau_{qm}^0},
\]

in exact agreement with the expression for \( \langle \dot{L} \rangle \) obtained directly from averaging the equations of motion \([11,12]\). Note that whereas \( -r_{k,+}^{cl} \) appears in Eq. (18), \( +r_{k,-}^{cl} \) appears in Eq. (15), causing the estimate of \( 1/\tau_{qm}^0 \) from Ref. [12] to miss two times the \( l \)-increasing rate. Because this \( l \)-increasing rate is small (<5% of the \( l \)-decreasing rate), Eq. (17) is a reasonable approximation and forms an upper bound \([13]\) to the lifetimes. Our use of the polarization of the emitted radiation to separate out \( \Delta l = +1 \) and \( \Delta l = -1 \) rates allows us to include the \( l \)-increasing rate with the correct sign and leads to the high accuracy of Eq. (16).

We expect that our very accurate expression for hydrogenic lifetimes for states of high \( n \) and \( l \), for which the calculation of exact quantum results is computationally very difficult will lead to more accurate simulations of radiative phenomena.

The quantum-mechanical branching ratio for a state \((n,l)\) to a state \((n-\Delta n, l \pm 1)\) is given by

\[
b_{\Delta n, \pm}^{qm} = \sum_{\Delta n} \frac{r_{\Delta n, \pm}^{qm}}{\sum_{\Delta n} (r_{\Delta n, +}^{qm} + r_{\Delta n, -}^{qm})} = r_{\Delta n, \pm}^{qm}. \tag{20}
\]

These are plotted for \( n=30, l=18, \Delta l=\pm 1 \) in Fig. 2. The classical analogs, \( r_{\Delta n, \pm}^{cl} \), are plotted as squares in the figure. For \( k=1 \) there is reasonable agreement with \( r_{\Delta n, \pm}^{qm} \) (as pointed out by Heisenberg), but the approximation becomes poorer for larger \( k \). The problem for higher \( k \) is that the classical radiation occurs at equally spaced frequency intervals, whereas the quantum-mechanical radiation occurs at increasingly spaced frequency intervals. If we correct for this discrepancy and compare the total branching ratio per unit of frequency, the classical results show much better agreement with the quantum rates. This correction can best be done by noting that

\[
\omega_{\Delta n}^{qm} = \frac{E_n - E_{n-\Delta n}}{\hbar} = k_{\Delta n} \omega,
\]

where \( k_{\Delta n} \) is the (noninteger) effective harmonic index and is given by

\[
k_{\Delta n} = \frac{n}{2} [ (1 - \Delta n/n)^{-2} - 1 ]. \tag{22}
\]

The density of classical frequencies \( k_\omega \) is larger than the quantum density of radiated frequencies by a factor of

\[
\frac{dk_{\Delta n}}{d\Delta n} = (1 - \Delta n/n)^{-3}. \tag{23}
\]

Therefore, a classical estimate of the \( \Delta n \) transition rate is given by

\[
R_{\Delta n, \pm}^{cl} = k_{\Delta n, \pm}^{cl} (1 - \Delta n/n)^{-3}. \tag{24}
\]

The fact that \( k_{\Delta n} \) is not necessarily an integer is not a problem, since
As expected, the method of Ref. [6] fails for this example of low $l/n$. Our classical estimates are excellent at small frequencies $f$, somewhat small at intermediate $f$, and somewhat too high at large $f$.

For the much smaller $\Delta l = +1$ branching ratios shown in Fig. 3(b), our classical calculations do well in the most relevant part of the spectrum. For higher $f$ our data again somewhat overestimate the branching ratios, while the model of Ref. [6] again shows a significant drop.

From Fig. 3 it can be seen that all of the branching ratios for this initial state agree with our classical estimate to an absolute accuracy of 0.25%. A better figure of merit is the difference between the classical estimate and the quantum branching ratio divided by the quantum branching ratio for the state. It can be seen from the figure that for all $\Delta n$, the discrepancies between the classical estimates and the quantum calculations are less than 10% of the maximum branching ratio, with the majority showing much better agreement than this. For higher-$l$ initial states, the agreement becomes even better, scaling approximately as $1/l$. Even for lower-$l$ initial states, the discrepancy between our classical estimates and the quantum branching ratio is less than 35% for all branching ratios from any initial state $(n, l > 0)$ to any final state $(n', l')$, with the vast majority being estimated by the classical formula to within a few percent of the maximum branching ratio.

In summary, we have presented an extension of the correspondence principle for radiative transitions based on solving the problem of a radiating hydrogenic Bohr atom in classical electrodynamics. It is shown that the radiative lifetimes agree extremely well with the quantum results. The branching ratios also agree reasonably well, which means that the model should work for cascade models of Rydberg transitions. The lifetimes and branching ratios are presented as simple expressions involving Bessel functions, and are therefore easily computed.

Although this paper considered only hydrogenic atoms, the results are also relevant to highly excited (Rydberg) states of any atom or molecule, since these are well approximated by hydrogenic states. Inclusion of a polarizable core and a charge distribution in the center of the classical orbit may allow the result to be extended to include the most important nonhydrogenic features and thus also describe lower excitation states.

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