

Predictions of the early atomic mean-life theory of Wilhelm Wien

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A recent letter¹ suggested a classical approach to atomic-dipole radiation, in which the mean life is viewed, not as a decaying oscillation of the dipole, but as an amount of stored energy that gradually flows from the near field to the far field. This recalls a picture proposed long ago by Wilhelm Wien who, prior to the advent of modern quantum mechanics, deduced a very close analog to the correct general expression for atomic transition probabilities. Furthermore, using only classical electrodynamics and the Bohr model of the atom, he obtained a specific equation for hydrogenic mean lives, by which

he predicted the H I $3d$ mean life to within 10%. Upon modern re-examination, we find that Wien's lifetime formula is indeed correct within the limits he prescribed, and yields very nearly correct lifetimes for an even larger class of atomic transitions.

Beginning in 1908, Wien²⁻⁴ made a series of measurements that were the first examples of what is today known as beam-gas or beam-foil spectroscopy. In 1919, he attempted³ to obtain a theoretical interpretation for his measured mean lives by assuming that atomic radiation can be described by the classical

expression for energy loss by an accelerated charge, $-dE/dt = 2e^2 a^2 / 3c^3$. He assumed that the radiation arises from the centripetal acceleration of an orbiting charge, but found it necessary to depart from a purely classical picture, because energy loss from the centripetal acceleration would classically introduce a tangential deceleration, and hence a changing frequency. He thus adopted a model in which a quantum of energy becomes available for radiation after an electron passes from one allowed orbit to another, and is radiated from the latter orbit at constant centripetal acceleration.

For simplicity, Wien restricted his considerations to circular orbits, for which $a = \omega^2 r$. In modern notation, this implies consideration of only the highest-angular-momentum state for each principal quantum number, i.e., $l = n - 1$. In hydrogenic level schemes, the l degeneracy and Laporte's rule allow only a single decay branch for these states, with $\Delta n = \Delta l = -1$; hence transition probabilities and inverse mean lives become synonymous.

Wien assumed that the total energy available for the radiation was given by the Planck quantum condition $E = h\omega_R$, and recognized that, in the correspondence limit, the electromagnetic radiation frequency ω_R becomes a harmonic of the electron orbital frequency ω_e , corresponding to the number of orbits jumped. He considered only jumps to neighboring orbits (consistent, in retrospect, with the circular-orbit assumption) and equated the two frequencies, setting $\omega_R = \omega_e = 2\pi c/\lambda$. He then computed the logarithmic time derivative of the energy which, in accordance with his assumptions, contained only constants, and was therefore interpretable as the exponential inverse mean life of the radiation. Thus, Wien obtained

$$\frac{1}{\tau_W} = -\frac{1}{E} \frac{dE}{dt} = \frac{2e^2 \omega^3 r^2}{3\hbar c^3}. \quad (1)$$

If the factor (er) were replaced by $\sqrt{2}$ times the quantum-mechanical dipole matrix element connecting initial and final states, the expression would become identical to the quantum-mechanical transition probability.¹ Lacking such a formalism, Wien substituted for r the radius of the Bohr orbit of the final state, $r = a_0 n_f^2 / \zeta$ (we have generalized Wien's expression to include heavier atoms by considering the jumping electron to move in a central field of charge ζe , corresponding to the net charge of the nucleus and core electrons). Thus, in terms of the (vacuum) radiation wavelength λ and the fine-structure constant $\alpha = e^2 / \hbar c$, Eq. (1) becomes

$$\frac{1}{\tau_W} = \frac{2(2\pi)^3 \alpha c a_0^2 n_f^4}{3 \lambda^3 \zeta^2}. \quad (2)$$

Using modern values for the constants,⁵ we can write this as

$$\tau_W(\text{ns}) = \left[\frac{\lambda(\text{\AA})}{1004.33} \right]^3 \frac{\zeta^2}{n_f^4}. \quad (3)$$

Wien substituted the H_α wavelength into this expression, and obtained a value of 16.6 ns (our more accurate constants yield 17.4 ns), which compared favorably with his measurements and with modern calculations for the $2p-3d$ transition. This agreement is not an isolated success; we see in Table I that Eq. (3) yields lifetimes correct to within 10% for all hydrogenic transitions of the form $1s-2p$, $2p-3d$, $3d-4f$, etc. Furthermore, many transitions in heavier atoms for which configuration mixing is not too severe are also well described in terms of Eq. (3), when the experimental wavelength, partially accounting for screening effects, is used. For example, lifetime predictions for several members of the Li I $2p-3d$ and Na I $3d-4f$ isoelectronic sequences are displayed in Table I. The Li $2p-3d$ mean lives are predicted within 4% for ions from Li I to Ne VII, and the Na I $3d-4f$ mean lives are predicted to within 10% for ions from Na I to Ar VII. Some transitions that do not satisfy the circular-orbit criteria are also well described by the formula, e.g., the He I $2s^3S-2p^3P^o$ isoelectronic sequence has lifetimes predicted to within 4% from Be III to Ne IX. For high excitation energies and highly ionized atoms, transitions tend to become hydrogenic, and Eq. (3) should be expected to predict reliably the transition probabilities between circular orbits.

In order to investigate how this simple formula can work so well, let us consider the case of a purely hydrogenic transition, and substitute the Rydberg formula for λ into Eq. (2), to obtain

$$\frac{1}{\tau_W} = \frac{2\alpha^4 c \zeta^4}{3a_0} \left[\frac{(n_f + \frac{1}{2})^3}{n_f^2 (n_f + 1)^6} \right]. \quad (4)$$

A reduction of the quantum-mechanical radial-integral formula of Gordon⁶ for the case of hydrogenic transitions between $l = n - 1$ states has been made by Garcia,⁷ who found the transition probability to the single available final state to be

$$\frac{1}{\tau_{QM}} = \frac{2\alpha^4 c \zeta^4}{3a_0} \left[\frac{(n_f + 1)^{2n_f - 2} (n_f)^{2n_f}}{(n_f + \frac{1}{2})^{4n_f + 3}} \right]. \quad (5)$$

TABLE I. Comparison of the predictions of Eq. (3) with presently accepted values.

Atom or ion	Transition	$\lambda(\text{\AA})$	$\tau_W(\text{ns})$	$\tau(\text{ns})^a$
H I	$1s-2p$	1 215.7	1.77	1.60
H I	$2p-3d$	6 562.8	17.4	15.5
H I	$3d-4f$	18 751	80.3	73
H I	$4f-5g$	40 512	256	235
H I	$5g-6h$	74 578	655	608
Li I	$2p-3d$	6 103.6	14.0	14.0
Be II	$2p-3d$	1 512.4	0.85	0.88
B III	$2p-3d$	677.09	0.172	0.176
C IV	$2p-3d$	384.12	0.056	0.056
Na I	$3d-4f$	18 465.3	76.7	71.4
Mg II	$3d-4f$	4 481.2	4.39	4.44
Al III	$3d-4f$	1 935.9	0.80	0.82

^a Values taken from Ref. 8.

TABLE II. Ratio of Wien's formula to the corresponding quantum mechanical formula as a function of principal quantum number.

n_f	τ_W/τ_{QM}
1	1.110
2	1.127
3	1.107
4	1.090
5	1.077
10	1.044
20	1.023
50	1.010
100	1.005

Thus the ratio of Wien's result to that currently accepted is given by

$$\frac{\tau_W}{\tau_{QM}} = \frac{(1+1/n_f)^{2n_f+4}}{(1+1/2n_f)^{4n_f+6}} \quad (6)$$

This expression converges to unity as $(1+1/2n_f)$ for large n_f , hence the bracketed factors in both Eqs. (4) and (5) become $1/n_f^5$ for large n_f , and Wien's formula is correct for hydrogenic circular-orbit transitions, in the correspondence limit. Furthermore, even for low quantum numbers, Eq. (6) is at worst less than 13% greater than unity (ironically the $n_f=2$ transition that Wien used is the worst example). Table II lists the approach of this ratio to the correspondence limit. The validity of the correspondence limit in the vicinity of the ground

state is surprising; Wien questioned why his formula worked so well for H_α , for which $\omega_R/\omega_e=5/9$ rather than unity.

Wien's thorough and methodical experimental work was done in the presence of great technical difficulties. Indeed, many of his lifetime values are clearly spurious, owing to such effects as blending of the degenerate hydrogen lines and in-flight repopulation of the source by radiative cascades and proton recombination (Wien raised the question of multi-exponentiality in his decay curves; in 1927 he described the now-familiar problem of cascades⁴). It is therefore historically interesting and scientifically instructive that he was able to construct a so nearly correct theoretical relationship on the basis of semiclassical considerations, and a single correct lifetime determination.

¹ L. Mandel, J. Opt. Soc. Am. **62**, 1011 (1972).

² A list of references to Wien's work in canal-ray spectroscopy is given in the Preface to *Beam-Foil Spectroscopy*, edited by S. Bashkin (Gordon and Breach, New York, 1968).

³ W. Wien, Ann. Physik **60**, 597 (1919).

⁴ W. Wien, in *Handbuch der Experimentalphysik 14*, edited by W. Wien and F. Harms (Akademische Verlagsgesellschaft, Leipzig, 1927), p. 643.

⁵ B. N. Taylor, W. H. Parker, and D. N. Langenberg, Rev. Mod. Phys. **41**, 375 (1969).

⁶ W. Gordon, Ann. Physik **2**, 1031 (1929).

⁷ J. D. Garcia (private communication).

⁸ W. L. Wiese, M. L. Smith, and B. M. Glennon, *Atomic Transition Probabilities, Vols. I and II*, Natl. Bur. Std. (U.S.) NSRDS-NBS Nos. 4 and 22 (U. S. Government Printing Office, Washington, D. C., 1966 and 1969).