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Spontaneous two-photon decay rates in hydrogenlike and heliumlike ions

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A theoretical study of the two-photon emission rate from the $1s2s\ ^1S$ state of two-electron ions is presented. High-precision values of the nonrelativistic emission rate for ions with nuclear charge Z up to 36 are obtained by use of correlated variational wave functions of the Hylleraas type. Summations over intermediate states are performed by finite-basis-set methods. The results are used to obtain an accurate extrapolation formula and to study the convergence characteristics of a $1/Z$ expansion for the decay rate. The leading hydrogenic term is calculated to an accuracy which substantially exceeds Klarsfeld's, and the next term is obtained for what is believed to be the first time. Relativistic effects are taken into account by means of a screened hydrogenic approximation. The predicted decay rate for two-electron Kr^{34+} is $(2.993 \pm 0.012) \times 10^{10} \text{ s}^{-1}$, where the error is the uncertainty in the relativistic correction. This lies significantly higher than the value $(2.934 \pm 0.030) \times 10^{10} \text{ s}^{-1}$ recently measured by Marrus *et al.*

I. INTRODUCTION

This paper describes a theoretical study of the two-photon decay rates from the $2s_{1/2}$ and $1s2s\ ^1S_0$ metastable states of the one- and two-electron ions. The primary motivation for the calculations is a recent measurement of the two-photon decay rate in the two-electron ion Kr^{34+} by Marrus *et al.*¹ Their measurement is sufficiently precise to be sensitive to relativistic corrections.

The lifetime of an isolated atom in an excited atomic state is normally determined by the rate at which it decays to a state of lower energy by the emission of a single photon. However, in certain exceptional circumstances, all such single-photon transitions are either strictly forbidden or strongly inhibited by angular momentum and parity-selection rules. Two cases of particularly fundamental importance are the $2s_{1/2}$ state of hydrogen (or hydrogenlike ions) and the $1s2s\ ^1S_0$ state of heliumlike ions. In the former case, the process

$$2s_{1/2} \rightarrow 1s_{1/2} + h\nu \quad (1)$$

can only proceed through relativistic corrections to the magnetic dipole ($M1$) matrix element²⁻⁴ and is therefore slower than an ordinary allowed electric dipole ($E1$) decay rate by a factor of $O(\alpha^6 Z^6)$. In the latter case the process

$$1s2s\ ^1S_0 \rightarrow 1s^2\ ^1S_0 + h\nu \quad (2)$$

is strictly forbidden by the $J=0 \nrightarrow J=0$ selection rule, which follows from the fact that photons have spin 1 and thus transport a quantum of angular momentum.

For the above states the dominant radiative decay mechanism is the simultaneous emission of two $E1$ photons. This arises from a second-order interaction between the atom and the electromagnetic field resulting in the process

$$2s_{1/2} \rightarrow 1s_{1/2} + h\nu_1 + h\nu_2 \quad (3)$$

for hydrogen and

$$1s2s\ ^1S_0 \rightarrow 1s^2\ ^1S_0 + h\nu_1 + h\nu_2 \quad (4)$$

for helium. The two photons are emitted with a continuous distribution of frequencies because conservation of energy only requires that

$$h\nu_1 + h\nu_2 = E(\text{initial}) - E(\text{final}). \quad (5)$$

The theoretical formalism was first worked out by Goeppert-Meyer,⁵ and an early estimate of the two-photon decay rate for hydrogen was obtained by Breit and Teller.⁶ Subsequent nonrelativistic calculations by other authors⁷ culminated in the highly accurate value of Klarsfeld,⁸ who obtained $8.22938Z^6 \text{ s}^{-1}$ for the decay rate of a hydrogenic ion of nuclear charge Z . More recent work^{9,10} offers improvements in the mathematical formalism for expressing the finite summations over intermediate states in terms of hypergeometric functions, but Klarsfeld's result still stands as the most accurate nonrelativistic calculation.

The calculation of two-photon processes in heliumlike ions is much more difficult because of the two-electron nature of the problem. Dalgarno¹¹ obtained the first reliable estimate for helium by explicitly summing over the discrete and continuous oscillator-strength distribution for the intermediate states. His value of 46 s^{-1} for the decay rate compares with 50.85 s^{-1} (length form) and 50.89 s^{-1} (velocity form) obtained by Jacobs¹² in a more sophisticated version of the same calculation. Results in reasonable agreement with these have also been obtained in the time-dependent coupled Hartree-Fock approximation by Victor.¹³

An alternative and very powerful computational method is to replace the infinite summation over bound and continuum intermediate states by a finite summation over a discrete set of states obtained by diagonalizing the Hamiltonian in a finite basis set of the correct symmetry. The method in effect generates a discrete variational representation of the two-electron Coulomb Green's function.

Two photon decay rates have been calculated by this method, with up to 50 Hylleraas-type correlated basis functions, for all the ions from He ($Z=2$) to Ne⁸⁺ ($Z=10$).¹⁴ The result for He (51.3 s^{-1}) is in reasonable agreement with the above values of Jacobs. However, the accuracy is not sufficient to allow a reliable extrapolation to higher values of Z . In fact, if one attempts to fit a simple $1/Z$ expansion to the low- Z calculations of the form

$$\bar{w}(Z) = Z^6 \sum_{n=0}^{\infty} w_n Z^{-n} \quad (6)$$

then the coefficients w_n appear to grow rapidly with increasing n .

The principal aim of the present work is to improve the accuracy of previous nonrelativistic low- Z calculations and extend them to higher values of Z so that a reliable interpolation and extrapolation formula can be extracted. The coefficients w_0 and w_1 in (6) are calculated directly, and the higher-order terms are approximated by an empirical fit to the explicit calculations for ions up to $Z=36$. As a by-product, the finite-basis-set method applied to one-electron ions yields a two-photon decay rate which is substantially more accurate than Klarsfeld's.⁸

The above nonrelativistic calculations provide a firm starting point for the evaluation of relativistic corrections. These have been studied in detail only in the case of one-electron ions. Goldman and Drake¹⁵ used a finite-basis-set method based on the Dirac equation instead of the Schrödinger equation to obtain relativistic two-photon decay rates for hydrogenic ions up to $Z=110$. The calculation includes finite wavelength effects to all orders, and all combinations of multipoles. The results have been confirmed by Parpia and Johnson¹⁶ by an independent method which involves a numerical calculation of the Dirac Coulomb Green's function. The one-electron re-

sults can be used to obtain the exact relativistic corrections to the coefficient w_0 in (1), as discussed in this paper.

II. THEORY OF TWO-PHOTON EMISSION

The basic theory of two-photon emission is discussed for example by Akhiezer and Berestetskii.¹⁷ For a process such as (3) or (4) only one of the two photon frequencies is independent because of the energy-conserving requirement (5). If the photons are emitted into solid angles $d\Omega_1$ and $d\Omega_2$ with wave vectors $\mathbf{k}_1$ and $\mathbf{k}_2$ ($|\mathbf{k}| = \omega/c$), respectively, then the triply differential emission rate in the energy interval $dE_1 = \hbar d\omega_1$ for photon 1 can be written in the form of Fermi's golden rule,

$$w(\omega_1, \omega_2) d\Omega_1 d\Omega_2 dE_1 = \frac{2\pi}{\hbar} |U_{if}^{(2)}|^2 \rho_f(\omega_1) \rho_f(\omega_2) dE_1 \quad (7)$$

where

$$\rho_f(\omega) = \frac{\mathcal{V} k^2 d\Omega}{(2\pi)^3 \hbar c} \quad (8)$$

is the number of photon states of polarization $\hat{\epsilon}$ per unit energy and solid angle in the arbitrary normalization volume $\mathcal{V}$, and $U_{if}^{(2)}$ is the effective second-order interaction energy with the electromagnetic field. For one-electron ions $U_{if}^{(2)}$ is given in terms of the transverse photon vector potential

$$\mathbf{A}(\omega) = \frac{1}{k} \left[\frac{2\pi\hbar\omega}{\mathcal{V}} \right]^{1/2} \hat{\epsilon} e^{i\mathbf{k}\cdot\mathbf{r}} \quad (9)$$

(normalized to a field energy of the $\hbar\omega$ per unit volume) by¹⁵

$$U_{if}^{(2)} = -\frac{e^2}{\hbar} \sum_n \left[\frac{\langle f | \boldsymbol{\alpha} \cdot \mathbf{A}^*(\omega_1) | n \rangle \langle n | \boldsymbol{\alpha} \cdot \mathbf{A}^*(\omega_2) | i \rangle}{\omega_n - \omega_i + \omega_2} + \frac{\langle f | \boldsymbol{\alpha} \cdot \mathbf{A}^*(\omega_2) | n \rangle \langle n | \boldsymbol{\alpha} \cdot \mathbf{A}^*(\omega_1) | i \rangle}{\omega_n - \omega_i + \omega_1} \right]. \quad (10)$$

Here $\boldsymbol{\alpha}$ is the usual 4×4 Dirac matrix, $|f\rangle$ and $|i\rangle$ denote solutions to the Dirac equation for the final and initial states, respectively, with eigenvalues $E_f = \hbar\omega_f$, etc., and the sum over n includes an integration over both positive and negative frequency continua for all intermediate states.

The general reduction of (10) to reduced matrix elements for a particular combination of multipoles, together with integrations over angles $d\Omega_1, d\Omega_2$ and sums over polarization vectors $\hat{\epsilon}_1, \hat{\epsilon}_2$ is discussed by Goldman and Drake.¹⁵ This paper also addresses the general question of gauge invariance for multiphoton transitions. For the present problem the nonrelativistic electric dipole approximation is simply obtained by making the replacement

$$\boldsymbol{\alpha} \cdot \hat{\epsilon} e^{i\mathbf{k}\cdot\mathbf{r}} \rightarrow \mathbf{p} \cdot \hat{\epsilon} / mc \quad (11)$$

and restricting the sum in (10) to positive frequency states. The singly differential emission rate in this ap-

proximation is then

$$\begin{aligned} \frac{d\bar{w}}{d\omega_1}(\omega_1, \omega_2) &= \hbar \int \int d\Omega_1 d\Omega_2 \sum_{\hat{\epsilon}_1, \hat{\epsilon}_2} w(\omega_1, \omega_2) \\ &= \frac{8\alpha^2}{3\pi} |Q(\omega_1, \omega_2)|^2. \end{aligned} \quad (12)$$

The dimensionless quantity $Q(\omega_1, \omega_2)$ can be expressed in either the velocity (V) or length (L) forms as

$$\begin{aligned} Q_V(\omega_1, \omega_2) &= \frac{-(\omega_1 \omega_2)^{1/2}}{(mc)^2} \sum_n \langle 1s | p_z | np \rangle \langle np | p_z | 2s \rangle \\ &\quad \times \left[\frac{1}{\omega_n - \omega_i + \omega_1} + \frac{1}{\omega_n - \omega_i + \omega_2} \right] \end{aligned} \quad (13)$$

or

$$Q_L(\omega_1, \omega_2) = \frac{(\omega_1 \omega_2)^{3/2}}{c^2} \sum_n \langle 1s | z | np \rangle \langle np | z | 2s \rangle \times \left[\frac{1}{\omega_n - \omega_i + \omega_1} + \frac{1}{\omega_n - \omega_i + \omega_2} \right] \quad (14)$$

where $p_z = (\hbar/i) d/dz$ and m is the electron mass.

For computational purposes it is convenient to express all frequencies in units of $\Delta = \omega_i - \omega_f$. With the definitions

$$y = \omega_1 / \Delta, \quad (15)$$

$$f_n = (\omega_n - \omega_i) / \Delta, \quad (16)$$

then $\omega_2 = (1 - y)\Delta$, and (13) and (14) become

$$Q_V(y) = \frac{-[y(1-y)]^{1/2}}{(mc)^2} \times \sum_n \langle 1s | p_z | np \rangle \langle np | p_z | 2s \rangle \times \left[\frac{1}{f_n + y} + \frac{1}{f_n + 1 - y} \right], \quad (17)$$

$$Q_L(y) = \frac{[y(1-y)]^{3/2} \Delta^2}{c^2} \times \sum_n \langle 1s | z | np \rangle \langle np | z | 2s \rangle \times \left[\frac{1}{f_n + y} + \frac{1}{f_n + 1 - y} \right]. \quad (18)$$

The equivalence of (17) and (18) then easily follows from the sum rule

$$\sum_n \langle 1s | p_z | np \rangle \langle np | p_z | 2s \rangle \left[\frac{1}{f_n} + \frac{1}{f_n + 1} \right] = -(m^2 \Delta / \hbar) \langle 1s | [[H, z], z] | 2s \rangle = 0. \quad (19)$$

Explicitly, the frequency-dependent factor

$$\left[\frac{1}{f_n + y} + \frac{1}{f_n + 1 - y} \right]$$

in (17) can be replaced by

$$\left[\frac{1}{f_n + y} + \frac{1}{f_n + 1 - y} - \frac{1}{f_n} - \frac{1}{f_n + 1} \right] = \frac{-y(1-y)}{f_n(f_n + 1)} \left[\frac{1}{f_n + y} + \frac{1}{f_n + 1 - y} \right]. \quad (20)$$

Equation (18) follows immediately with the use of the well-known identities

$$\frac{\langle 1s | p_z | np \rangle}{f_n + 1} = -im \Delta \langle 1s | z | np \rangle, \quad \frac{\langle np | p_z | 2s \rangle}{f_n} = im \Delta \langle np | z | 2s \rangle. \quad (21)$$

The equivalence of (17) and (18) can also be obtained directly from the gauge invariance of two-photon transitions.¹⁵ Although the above derivation is written for notational clarity for the special case of process (3) the formalism applies to any $J=0 \rightarrow J=0$ two-photon transition. For an N -electron problem one need only sum the operators p_z and z over the electron coordinates and replace the one-electron wave functions by appropriate N -electron wave functions in the matrix elements. Since Q_L and Q_V yield identical results only if the wave functions are exact and the sum over intermediate states is complete, the degree to which they differ provides an indication of the accuracy of the results.

The total two-photon decay rate integrated over frequencies is

$$\bar{\omega} = \frac{1}{2} \int_0^1 \frac{d\bar{\omega}}{d\omega_1} d\omega_1 = \frac{4\alpha^2 \Delta}{3\pi} \int_0^1 |Q(y)|^2 dy. \quad (22)$$

The factor of $\frac{1}{2}$ is included in (22) because the photons are indistinguishable and each pair should only be counted once. A significant advantage of the finite-basis-set methods used here is that the above integration over frequencies can be performed analytically as described in the Appendix.

III. COMPUTATIONAL RESULTS

A. One-electron ions

A calculation of the two-photon decay rate for one-electron ions provides an interesting test of the finite-basis-set method in a case where the accurate values of Klarsfeld⁸ are available for comparison. Since the $1s$ and $2s$ hydrogenic eigenfunctions are known exactly, all that remains is to perform the summation over the intermediate np states (including an integration over the continuum) in (17) and (18). This is accomplished by replacing the actual eigenfunctions $\psi(np)$ by a variationally determined set of discrete pseudostates of the form

$$\tilde{\psi}(np) = \sum_{i=1}^N c_{i,n} r^i e^{-\beta r} \cos \theta, \quad (23)$$

where β is an arbitrary nonlinear adjustable parameter. The linear variational coefficients $c_{i,n}$ are determined from the conditions

$$\langle \tilde{\psi}(np) | \tilde{\psi}(mp) \rangle = \delta_{m,n}, \quad \langle \tilde{\psi}(np) | H | \tilde{\psi}(mp) \rangle = \tilde{E}_n \delta_{m,n},$$

where H is the nonrelativistic Hamiltonian. The result is a set of N linearly independent pseudostates $\tilde{\psi}(np)$ and eigenvalues $\tilde{E}_n$ of the Sturmian type.¹⁸ The completeness of a discrete Sturmian basis set in the limit $N \rightarrow \infty$ is sufficient to guarantee that the results converge to the right answer when the $\tilde{\psi}(np)$ and $\tilde{E}_n$ are used in place of the ac-

tual sum over intermediate states in (17) and (18).

The convergence of the results as N is increased is shown in Table I. Larger basis sets do not yield improved accuracy because, with double-precision arithmetic (about 16 figures), round-off error becomes dominant. The length values appear to converge uniformly from above and the velocity values from below, indicating that they provide a sequence of upper and lower bounds to the exact decay rate. The extrapolated values are obtained from the observation that the ratios of successive differences are nearly constant. The value of β in Eq. (22) affects the rate of convergence, but not the final extrapolated results. The average of the extrapolated values with $\beta=0.5$ is

$$\bar{\omega} = 1.318\,222\,665(2) \times 10^{-3} (Z\alpha)^6 \tau^{-1},$$

where $\tau = a_0/\alpha c$ is the atomic unit of time, and a number in parentheses indicates the uncertainty in the final figure quoted. For comparison, Klarsfeld⁸ obtained

$$\begin{aligned} \bar{\omega} &= \pi^{-1} \left(\frac{2}{9}\right)^4 1.698\,199_4 (Z\alpha)^6 \tau^{-1} \\ &= 1.318\,222_6 \times 10^{-3} (Z\alpha)^6 \tau^{-1} \end{aligned}$$

(the subscript is a notation used by him to denote an uncertain figure). The present value is therefore more accurate by about three significant figures. The numbers in Table I correspond to exactly the values

$$\alpha = 1/137.035\,96 \quad \tau = 2.418\,88 \times 10^{-17} \text{ s}$$

for the fundamental constants.

The above does not include relativistic and finite nuclear-mass corrections. Relativistic corrections are discussed by Goldman and Drake¹⁵ and Parpia and Johnson.¹⁶ The finite nuclear mass contributes a reduced-mass correction factor of $(1-m/M)$. In addition, nuclear motion in the center-of-mass frame introduces a further correction factor^{19,20} which can be obtained as follows. The total dipole moment of an n -electron atom is

$$\begin{aligned} \mathbf{Q} &= Z e \mathbf{r}_N - e \sum_{i=1}^n \mathbf{r}_i \\ &= (Z-n) e \mathbf{r}_N - e \sum_{i=1}^n \boldsymbol{\rho}_i, \end{aligned}$$

TABLE I. Nonrelativistic two-photon decay rates for the $2s$ state of hydrogen (s^{-1}). Finite nuclear-mass corrections are not included. N is the number of powers of r in the basis set and $\beta=0.5$ in Eq. (23).

N	Length form	Velocity form
5	8.230 606 10	8.223 199 20
6	8.229 594 30	8.228 589 99
7	8.229 413 73	8.229 281 49
8	8.229 385 72	8.229 368 63
9	8.229 381 68	8.229 379 53
10	8.229 381 13	8.229 380 86
11	8.229 381 05	8.229 381 00
extrapolated	8.229 381 04	8.229 381 02
Klarsfeld ^a	8.229 38 ₁	

^aReference 8.

where $\mathbf{r}_N$ is the position of the nucleus, $\mathbf{r}_i$ is the position of the i th electron and $\boldsymbol{\rho}_i = \mathbf{r}_i - \mathbf{r}_N$ is the electron position relative to the nucleus. Since

$$(M + nm) \mathbf{r}_N + m \sum_{i=1}^n \boldsymbol{\rho}_i = 0 \quad (24)$$

in the center-of-mass frame, it follows that

$$\mathbf{Q} = -Z_r e \sum_{i=1}^n \boldsymbol{\rho}_i \quad (25)$$

with

$$Z_r = \frac{(Z-n)m}{M+nm} + 1. \quad (26)$$

The quantity $q_{\text{eff}} = -Z_r e$ is the effective radiative charge for the electron. The final result is

$$\begin{aligned} \bar{\omega} &= 8.229\,38 Z^6 Z_r^4 (1-m/M) \\ &\times \frac{[1 + 3.9448(\alpha Z)^2 - 2.040(\alpha Z)^4]}{[1 + 4.6019(\alpha Z)^2]}. \end{aligned} \quad (27)$$

The coefficients of $(\alpha Z)^2$ represent an empirical fit to the direct relativistic calculations with an error of less than $\pm 0.005\%$ in the range $\leq Z \leq 92$.

In summary, the results of this section demonstrate the great power of finite-basis-set methods. Except for matrix diagonalization, all calculations can be done analytically. The matrix-diagonalization step requires a negligible amount of computer time for such small basis sets, and the rest of the calculation is by comparison even faster. All calculations in this and the following sections were done on an IBM PC/AT computer using Microsoft FORTRAN.

B. Two-electron ions

The calculation of two-photon decay rates for two-electron ions closely parallels that of Sec. III A. In analogy with (17) and (18), $Q_L(y)$ is given by

$$\begin{aligned} Q_L(y) &= \frac{[y(1-y)]^{3/2} \Delta^2}{c^2} \sum_n \langle 1s^2 \, ^1S | z_1 + z_2 | n \, ^1P \rangle \\ &\quad \times \langle n \, ^1P | z_1 + z_2 | 1s2s \, ^1S \rangle \\ &\quad \times \left[\frac{1}{f_n + y} + \frac{1}{f_n + 1 - y} \right] \end{aligned} \quad (28)$$

and similarly for $Q_V(y)$. One additional complication is that, in addition to the complete set of $n \, ^1P$ two-electron intermediate states, a variational representation for the initial and final states must also be constructed. All the states were represented in terms of correlated Hylleraas-type functions according to

$$\psi(1s^2 \, ^1S) = (1 + P_{12}) \sum_{\substack{i,j,k \\ (i \geq j)}} c_{i,j,k}^{(1)} r_1^i r_2^j r_{12}^k e^{-Z(r_1 + r_2)}, \quad (29)$$

$$\begin{aligned} \psi(1s2s \, ^1S) &= (1 + P_{12}) \sum_{i,j,k} c_{i,j,k}^{(2)} r_1^i r_2^j r_{12}^k \\ &\quad \times e^{-Z(r_1 + \beta r_2)}, \end{aligned} \quad (30)$$

$$\begin{aligned} \psi(n^1P) = & (1 + P_{12}) \sum_{i,j,k} r_i^i r_2^{1+j} r_{12}^k \cos\theta_2 \\ & \times (d_{i,j,k}^{(n)} e^{-Z(r_1 + \beta r_2)} \\ & + \tilde{d}_{i,j,k}^{(n)} e^{-Z(\beta r_1 + r_2)}), \quad (31) \end{aligned}$$

where $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$ and P_{12} interchanges the coordinates of electrons 1 and 2. All sums over i, j, k start from zero, and include all terms such that $i + j + k \leq \Omega$, where Ω is an integer. The condition $i \leq j$ in (29) is imposed so that basis set members are not duplicated. The second term of (31) ensures that all terms of the form $(z_1 + z_2)\psi(1s2s^1S)$ are included in the 1P basis set, as suggested by the analysis of Dalgarno and Epstein.²¹

Compromises in the choices of nonlinear parameters are obviously necessary in a calculation of this complexity, and the values which optimize the energy are not necessarily the best for two-photon decay rates. The β parameter in (30) and (31) was chosen to be

$$\beta = [-2E(1s2s^1S) - Z^2]^{1/2}/Z \quad (32)$$

so that $\psi(1s2s^1S)$ has the correct asymptotic form. A range of other possibilities for (29)–(31) was tried, but the rate of convergence with basis-set size was not significantly better than with the above choices.

The number of terms (N) in the basis sets for each value of Ω is listed in Table II. N is twice as large for the 1P basis set as for the $1s2s^1S$ basis set because of the doubling of terms in (31). The additional flexibility provided by two exponential factors compensates for the lack of additional powers of r in the basis set, and allows a better representation of doubly excited intermediate states. The basis sets were taken in combinations such that the total number of terms matched as nearly as possible.

The convergence of the results with basis-set size is shown in Table III for the cases $Z=2,3,6$, and in the limit $Z \rightarrow \infty$. The last provides a valuable check on the calculations. The limit is conveniently obtained by setting $Z=1$ and dropping the $1/r_{12}$ term from the Hamiltonian, while all other parts of the calculation remain unchanged. The result, which is just twice the hydrogen atom value in Table I, demonstrates that the hydrogenic part of the problem is reproduced by the basis sets to six-figure accuracy.

For low values of Z the convergence is determined predominantly by the size of the $1s^2^1S$ basis set and, as has been found previously for eigenvalues,²² the odd- and even- Ω values appear to follow separate convergence paths. For the length form, the even- Ω values appear to

converge from above and the odd- Ω values from below, while for the velocity form they both converge from below but at different rates. This pattern is not altered by changing Ω to $\Omega \pm 1$ for the $1s2s^1S$ and n^1P basis sets. All four cases appear to follow the extrapolation formula

$$\bar{w}_{\text{calc}} = \bar{w}_{\text{exact}} + A/N^2(1s^2^1S) \quad (33)$$

with different values of A in each case, to yield approximately the same value of w_{exact} , as shown by the extrapolated results in Table III. The odd- Ω extrapolations for ions up to $Z=36$ are summarized in Table IV, and the spectral-distribution function $dw(y)/dy$ for helium is given in Table V. Except for the value at $y=0.025$, the present results for dw/dy are slightly larger than those calculated by Jacobs.¹² The integrated decay rate of 51.02 s^{-1} lies between the previous values of Jacobs¹² (50.9 s^{-1}) and of Drake *et al.*¹⁴ (51.3 s^{-1}). The results for $3 \leq Z \leq 10$ are similarly more accurate than the earlier calculations.¹⁴ There are no other theoretical values for $Z > 10$.

C. $1/Z$ expansions

The calculations of Sec. IIIB are sufficient to determine approximate values for the first several coefficients in a $1/Z$ expansion of the form of Eq. (6). However, it is advantageous to calculate directly as many coefficients as possible, and determine the remainder by fitting to the data. To this end w_0 is known to very high accuracy since it is just twice the hydrogenic value given in Table I. Alternatively, it is the value obtained from Eq. (28) if the wave functions are taken to be simple products of unscreened hydrogenic wave functions.

The contributions to w_1 came from inserting the e^2/r_{12} electron-electron interaction as a first-order perturbation to the hydrogenic wave functions and energy differences in (28) and summing over all such insertions acting one at a time. For example, the first-order correction to $1s2s^1S$ is

$$|1s2s^1S\rangle_1 = e^2 \sum_{n,n',l} \frac{|nl n'l^1S\rangle \langle nl n'l^1S| 1/r_{12} |1s2s^1S\rangle}{E_0(1s) + E_0(2s) - E_0(n) - E_0(n')}. \quad (34)$$

Although the sum over l runs from zero to infinity it is not difficult to see that since $z_1 + z_2$ is a sum of one-electron operators only the terms $l=0$ and $l=1$ make nonvanishing contributions to (28). Since

$$r_{12} = r_1 + r_2 - 2r_1 r_2 \cos\theta_{12} \quad (35)$$

TABLE II. Numbers of terms in the basis sets constructed such that $i + j + k \leq \Omega$.

$1s2s^1S$		n^1P		$1s^2^1S$	
Ω	N	Ω	N	Ω	N
5	56	3	40	6	50
6	84	4	70	7	70
7	120	5	112	8	95
				9	125

TABLE III. Convergence study of two-photon decay rates (s^{-1}) for two-electron ions. The even- and odd- Ω $1s^2\ ^1S$ basis sets are denoted by superscripts e and o , respectively.

$N(2\ ^1S)$	$N(n\ ^1P)$	$N(1\ ^1S)$	Length form	Velocity form
$Z=2$				
56	70	50^e	51.124	50.858
84	70	70^o	50.932	50.763
84	112	95^e	51.090	50.969
120	112	125^o	50.992	50.936
	even extrapolation		51.077	51.011
	odd extrapolation		51.020	51.016
$Z=3$				
56	70	50^e	1943.80	1939.02
84	70	70^o	1939.36	1938.39
84	112	95^e	1941.56	1940.11
120	112	125^o	1940.29	1939.87
	even extrapolation		1940.71	1940.52
	odd extrapolation		1940.72	1940.54
$Z=6$				
56	70	50^e	330 396	330 177
84	70	70^o	330 176	330 156
84	112	95^e	330 265	330 216
120	112	125^o	330 220	330 208
	even extrapolation		330 214	330 230
	odd extrapolation		330 240	330 231
$Z \rightarrow \infty$				
56	70	50^e	16.458 82	16.458 35
84	70	70^o	16.458 82	16.458 35
84	112	95^e	16.458 77	16.458 74
120	112	125^o	16.458 76	16.458 74
	exact		16.458 76	$16.458\ 76\ Z^6$

TABLE IV. Results of odd- Ω ($1\ ^1S$) extrapolations for the nonrelativistic two-photon decay rates of two-electron ions ($Z^6\ \text{s}^{-1}$). See Eq. (38) for other Z values not listed in the table.

Z	Length form	Velocity form
2	0.797 18	0.797 12
3	2.662 16	2.661 92
4	4.436 40	4.436 22
5	5.898 46	5.898 24
6	7.078 19	7.078 00
7	8.036 13	8.035 98
8	8.824 10	8.823 98
9	9.481 30	9.481 20
10	10.036 63	10.036 57
14	11.594 63	11.594 62
18	12.547 66	12.547 69
22	13.189 36	13.189 39
26	13.650 45	13.650 52
30	13.997 70	13.997 76
36	14.382 80	14.382 86
∞	16.458 76	16.458 76

TABLE V. Extrapolated spectral-distribution function $d\bar{w}/dy$ (s^{-1}) for the two-photon decay of helium. The parameter y is the fraction of the $1s2s\ ^1S-1s^2\ ^1S$ transition energy transported by one of the two photons.

y	$(d\bar{w}/dy)_L$	$(d\bar{w}/dy)_V$
0.025	7.736	7.733
0.050	25.158	25.150
0.075	43.302	43.291
0.100	59.693	59.680
0.125	73.920	73.906
0.150	86.112	86.098
0.175	96.523	96.509
0.200	105.407	105.393
0.225	112.986	112.973
0.250	119.447	119.435
0.275	124.942	124.932
0.300	129.596	129.587
0.325	133.508	133.500
0.350	136.760	136.753
0.375	139.416	139.410
0.400	141.525	141.520
0.425	143.128	143.124
0.450	144.253	144.249
0.475	144.921	144.917
0.500	145.142	145.138

and by the spherical harmonic addition theorem

$$\cos\theta_{12} = \frac{3}{4\pi} \sum_{m=-1}^1 Y_1^m(\hat{\mathbf{r}}_1) Y_1^m(\hat{\mathbf{r}}_2), \quad (36)$$

a finite basis set containing only the $l=0$ and $l=1$ parts is obtained by retaining only the r_{12}^0 and r_{12}^2 terms in (29) and (30). By a similar argument no higher partial waves contribute at all in first order to the 1P intermediate states (i.e., terms such as $npn'd\ ^1P$) and only the r_{12}^0 part of (31) is needed.

The above considerations suggest the following compact computational scheme as an alternative to performing explicit summations over all first-order perturbations.

(i) Form restricted basis sets such that $i+j+k \leq \Omega$ in (29)–(31) with

$$k = \begin{cases} 0 \text{ or } 2 \text{ for } 1s^2\ ^1S \text{ and } 1s2s\ ^1S \\ 0 \text{ for } n\ ^1P. \end{cases} \quad (37)$$

(ii) Calculate two-photon decay rates for large values of Z , subtract the w_0 contribution, and isolate w_1 by differencing. Calculations of $\bar{w}(Z)$ in this scheme were done for $Z=50, 100$, and 200 , and values of w_1 extracted from the formula

$$w_1 \approx \frac{200}{3} \left[\frac{1}{4} \Delta w(50) - 3 \Delta w(100) + 8 \Delta w(200) \right], \quad (38)$$

where

$$\Delta w(Z) = \bar{w}(Z)/Z^6 - \lim_{Z \rightarrow \infty} \bar{w}(Z)/Z^6. \quad (39)$$

The above combination eliminates the contributions from w_2 and w_3 , and the leading contamination from higher terms is $w_4/100^3$. Provided that w_4 is not excessively large, the quantity $w_4/100^3$ is sufficiently small to allow an accurate estimate of w_1 from Eq. (38). The choice of Z values represents a compromise between making Z as large as possible and keeping Z small enough so that not too many significant figures are lost in calculating differences.

The values of w_1 obtained from (38) with different combinations of restricted basis sets are listed in Table VI. The results have apparently converged to

$$w_1 = -79.633(2) \text{ s}^{-1}.$$

As a check, this value is consistent with, but more accurate than, that obtained by a direct fit to the low- Z data in Table IV.

The final step of this section is to obtain an interpolation and extrapolation formula for the nonrelativistic two-photon decay rates. The following functional form

appears to work extremely well:

$$\bar{w} = w_0(Z - \sigma)^6 \left[1 + \frac{a}{(Z + b)^2} \right] \quad (40)$$

with

$$w_0 = 16.458\,762 \text{ s}^{-1},$$

$$\sigma = w_1/(6w_0) = 0.806\,389,$$

$$a = 1.539,$$

$$b = 2.5.$$

The screening parameter σ is chosen to reproduce exactly the leading two terms in the $1/Z$ expansion of $\bar{w}$. The only adjustable parameters are a and b . The above values fit the direct calculations in Table IV with an error of less than $\pm 0.007\%$ for $Z \geq 10$. (The maximum error for $2 \leq Z \leq 10$ is 0.7% .) Since the differences are a slowly varying function of Z , Eq. (40) provides a reliable interpolation and extrapolation formula for the nonrelativistic decay rates in the high- Z region.

A surprising feature of (40) is that the value $b=2.5$ is so large, indicating that a simple $1/Z$ expansion of the form (6) is not convergent for $Z \leq 2.5$. However, this result is consistent with the earlier observation that the coefficients w_n appear to grow rapidly with increasing n . A power-series expansion of (40) yields

$$\bar{w} = 16.458\,762 Z^6 \left[1 - \frac{4.8383}{Z} + \frac{11.293}{Z^2} - \frac{25.63}{Z^3} + \frac{87.15}{Z^4} + \cdots \right], \quad (41)$$

which is clearly not a useful expansion. Furthermore, the problem is not cured just by taking out a factor of $(Z - \sigma)^6$. This is one case where the “screening approximation” widely used in atomic physics apparently does not improve the convergence characteristics of the remainder.

D. Relativistic corrections

Detailed calculations of relativistic corrections to two-photon decay rates in two-electron ions have not been performed. However, one can estimate the expected magnitude of the effect as follows. Equation (27) is the relativistic decay rate for one-electron ions. Twice this value gives the relativistic correction to the coefficient w_0 in (6).

TABLE VI. Calculation of the first-order correction w_1 to the two-photon decay rate (s^{-1}) of two-electron ions, using restricted basis sets. The restricted basis sets are defined by (37). The last line of the table corresponds to $\Omega(2\ ^1S)=8$, $\Omega(n\ ^1P)=8$, $\Omega(1\ ^1S)=9$, and the other lines to Ω values decreasing in steps of unity.

$N(2\ ^1S)$	$N(n\ ^1P)$	$N(1\ ^1S)$	Length form	Velocity form
21	30	18	−79.668	−79.831
31	42	25	−79.620	−79.635
43	56	32	−79.618	−79.634
57	72	41	−79.632	−79.634

Thus, the relativistic $1/Z$ expansion from (41) is

$$\bar{w}(Z) = 16.548\,762Z^6 \times \left[1 - (\alpha Z)^2 \left[\frac{0.6571 + 2.040(\alpha Z)^2}{1 + 4.6019(\alpha Z)^2} \right] - \frac{4.8383}{Z} [1 + O(\alpha^2 Z^2)] + \cdots \right]. \quad (42)$$

The relativistic corrections of $O(\alpha^2 Z^2)$ for the terms beyond the leading one are not known. However, the total relativistic shift from all terms in (42) can almost certainly be bounded as follows.

(i) Because of electron screening, the shift is likely smaller in magnitude than for a one-electron ion with the same Z .

(ii) Since relativistic effects come primarily from the region near the nucleus, the shift is probably larger in magnitude than for a one-electron ion with nuclear charge $Z - \sigma$. The relativistic shift is therefore calculated to be the one-electron shift from (27) evaluated at an effective nuclear charge $\tilde{Z}$ such that $Z - \sigma < \tilde{Z} < Z$. Using (40) for the nonrelativistic part, the final result is

$$\bar{w} = 16.458\,762$$

$$\times \left[(Z - 0.806\,389)^6 \left[1 + \frac{1.539}{(Z + 2.5)^2} \right] - \tilde{Z}^6 (\alpha \tilde{Z})^2 \left[\frac{0.6571 + 2.040(\alpha \tilde{Z})^2}{1 + 4.6019(\alpha \tilde{Z})^2} \right] \right] s^{-1} \quad (43)$$

in the high- Z region. For $Z < 10$, the first term of (43) should be replaced by the more accurate nonrelativistic values listed in Table IV.

Table VII gives the relativistically corrected two-photon decay rates for ions up to $Z=92$. The values listed correspond to the average of the unscreened ($\tilde{Z}=Z$) and fully screened ($\tilde{Z}=Z-\sigma$) relativistic corrections in (43), and the error is the difference between the average and the two extremes. As examples, the individual contributions for a few special cases are given in Table VIII. As can be seen from Table VII, the decay rate (in units of $Z^6 \text{ s}^{-1}$) reaches a maximum around $Z=42$ because it is suppressed by the electron-electron interaction at the low- Z end, and by relativistic effects at the high- Z end. The tabulated values do not include the finite nuclear-mass correction factors of $(1 - m/M)$ and Z_r^4 given by Eq. (26) with $n=2$.

TABLE VII. Two-photon decay rates of two-electron ions including estimated relativistic corrections ($Z^6 \text{ s}^{-1}$).

Z	$\bar{w}$	Z	$\bar{w}$
2	0.7960(11)	26	13.319(41)
3	2.6592(24)	27	13.389(43)
4	4.4309(38)	28	13.451(44)
5	5.8895(54)	29	13.507(46)
6	7.0645(71)	30	13.556(47)
7	8.1067(88)	32	13.639(50)
8	8.798(11)	34	13.703(53)
9	9.447(12)	36	13.750(56)
10	9.993(14)	38	13.783(59)
11	10.458(16)	40	13.803(62)
12	10.857(17)	42	13.811(65)
13	11.203(19)	45	13.805(69)
14	11.504(21)	50	13.751(75)
15	11.769(23)	54	13.674(81)
16	12.002(24)	56	13.626(83)
17	12.209(26)	60	13.512(88)
18	12.393(28)	65	13.340(94)
19	12.557(30)	70	13.14(10)
20	12.704(31)	74	12.96(11)
21	12.836(33)	80	12.65(11)
22	12.954(35)	82	12.54(12)
23	13.060(36)	85	12.37(12)
24	13.156(38)	90	12.07(12)
25	13.242(39)	92	11.94(13)

IV. DISCUSSION

The comparison between theory and experiment up to 1980 for two-photon decay rates in one-electron ions is contained in the paper of Goldman and Drake.¹⁵ The measurements summarized there for ions from He^+ to Ar^{17+} are in agreement with theory, but the experimental uncertainties of $\pm 7\%$ or larger do not allow a test of relativistic effects. Since then the accuracy for Ar^{17+} has been improved by Gould and Marrus.²³ They obtained a decay rate of $(2.868 \pm 0.030) \times 10^8 \text{ s}^{-1}$, in comparison with the theoretical value of $2.8590 \times 10^8 \text{ s}^{-1}$. The theoretical value comes from a nonrelativistic rate of $2.7990 \times 10^8 \text{ s}^{-1}$, a relativistic correction of $-0.0308 \times 10^8 \text{ s}^{-1}$ and an $M1$ contribution of $0.0908 \times 10^8 \text{ s}^{-1}$.²⁴ The experiment is therefore sensitive to the $M1$ contribution, but not to the relativistic correction. In another recent experiment Perrie *et al.*²⁵ have carefully measured the polarization correlation of the two photons emitted by deuterium $2s_{1/2}$. The results are in agreement with quantum-mechanical

TABLE VIII. Examples of the contributions to the total two-photon decay rates of two-electron ions listed in Table VII (s^{-1}). $\bar{w}_{\text{NR}}$ is the nonrelativistic value, and Δw is the relativistic correction for no screening ($\sigma=0$) and complete screening ($\sigma=0.806$).

Z	$\bar{w}_{\text{NR}}$	$\Delta w (\sigma=0)$	$\Delta w (\sigma=0.806)$	Total
10	1.0036×10^7	-5.71×10^4	-2.92×10^4	$(9.993 \pm 0.014) \times 10^7$
18	4.2676×10^8	-6.19×10^6	-4.30×10^6	$(4.215 \pm 0.010) \times 10^8$
36	3.1308×10^{10}	-1.50×10^9	-1.25×10^9	$(2.993 \pm 0.012) \times 10^{10}$
54	3.7305×10^{11}	-3.60×10^{10}	-3.20×10^{10}	$(3.391 \pm 0.020) \times 10^{11}$
92	9.4680×10^{12}	-2.31×10^{12}	-2.15×10^{12}	$(7.238 \pm 0.077) \times 10^{12}$

TABLE IX. Comparison of theory and experiment for the two-photon decay rates of two-electron ions (s^{-1}).

Ion	Theory	Experiment
He	50.943 ± 0.073	50 ± 2.5^a
Ar ¹⁶⁺	$(4.215 \pm 0.010) \times 10^8$	$(4.31 \pm 0.34) \times 10^8^b$
Kr ³⁴⁺	$(2.993 \pm 0.012) \times 10^{10}$	$(2.934 \pm 0.030) \times 10^{10}^c$

^aVan Dyck *et al.*, Ref. 27.^bGould and Marrus, Ref. 23.^cMarrus *et al.*, Ref. 1.

predictions but violate Bell's inequality by nearly two standard deviations. The experiment therefore helps to rule out local hidden-variable theories as an alternative to quantum mechanics.

For two-electron ions direct measurements of the two-photon decay rate have been made only for the cases He, Ar¹⁶⁺, and Kr³⁴⁺ as summarized in Table IX.²⁶ The He result, though of low accuracy, is important because it verifies the strong suppression of the two-photon decay rate for low Z due to the electron-electron Coulomb interaction. However, the recent measurement for Kr³⁴ is of primary interest for the present work. The experimental value lies more than 1.5 standard deviations below theory, even when one takes the downward relativistic shift to be that for an unscreened hydrogenic ion of the same $Z=36$. This extreme case corresponds to the lower limit of the theoretical uncertainty in Table IX; i.e., the value $2.981 \times 10^{10} s^{-1}$ quoted by Marrus *et al.*¹ To put the matter another way, one must assume an effective nuclear charge in the range $36.5 \leq Z \leq 38.0$ in calculating the relativistic shift in order to reproduce the experimental range of values. Since a large negative screening of the nuclear charge does not seem likely, the experimental value appears to lie significantly lower than theory.

The discrepancy could be caused by an accidental cancellation of contributions to the one-electron relativistic shift which does not also occur in the two-electron case, making the two-electron shift larger than expected. It could also be caused, for example, by a larger than expected cascade contribution to the measured decay rate. There is clearly a need for more detailed calculations of relativistic corrections in the two-electron case.

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APPENDIX: ANALYTIC INTEGRATION OVER FREQUENCIES

Since the infinite sums and integrals over intermediate states in (17) and (18) are represented entirely in terms of finite basis sets, the integration over y in (21) can be performed analytically. The problem is in principle straight-forward but the derivation is quite lengthy. In addition, care must be taken to avoid severe numerical cancellation. The integration formulas are therefore recorded here for future use.

The integral in (21) is

$$I = \int_0^1 |Q(y)|^2 dy = \sum_{n=1}^N \sum_{n'=1}^N D_{n,n'}^{(K)} I_{n,n'}^{(K)}, \quad (A1)$$

$$D_{n,n'}^{(K)} = \begin{cases} (mc)^{-4} (p_z)_{1s,np} (p_z)_{np,2s} (p_z)_{2s,n'p} (p_z)_{n'p,1s} & (V \text{ form}) \\ (\Delta/c)^4 (z)_{1s,np} (z)_{np,2s} (z)_{2s,n'p} (z)_{n'p,1s} & (L \text{ form}) \end{cases}$$

and

$$I_{n,n'}^{(K)} = \int_0^1 [y(1-y)]^K \left[\frac{1}{f_n + y} + \frac{1}{f_{n'} + 1 - y} \right] \times \left[\frac{1}{f_{n'} + y} + \frac{1}{f_n + 1 - y} \right] dy \quad (A2)$$

with $K=1$ for the velocity (V) form and $K=3$ for the length (L) form. For brevity put $f_n = f$, $f_{n'} = f'$, and define $g = f(f+1)$. The integral for $K=1$ is then

$$I_{n,n'}^{(1)} = \frac{2}{g-g'} \left[g(2f'+1) \ln \left[\frac{f+1}{f} \right] - g'(2f+1) \ln \left[\frac{f'+1}{f'} \right] \right] \quad (A3)$$

for $f' \neq f$ and

$$I_{n,n}^{(1)} = 2 \left[-1 + \left[\frac{2g+1}{2f+1} \right] \ln \left[\frac{f+1}{f} \right] \right] \quad (A4)$$

for $f' = f$. These formulas can be used as they stand. For the length form the integral is

$$I_{n,n'}^{(3)} = \frac{2}{g-g'} \left[g^3(2f'+1) \ln \left[\frac{f+1}{f} \right] - g'^3(2f+1) \ln \left[\frac{f'+1}{f'} \right] \right] + (2f+1)(2f'+1)(1/6 - g - g') \quad (A5)$$

for $f' \neq f$, and

$$I_{n,n}^{(3)} = 2g^2 \left[-1 + \left[\frac{10g+3}{2f+1} \right] \ln \left[\frac{f+1}{f} \right] \right] \quad (\text{A6})$$

for $f'=f$. These formulas cannot be used as they stand because of severe numerical cancellation. In fact, for large f (A5) and (A6) contain terms proportional to f^6 , while the original integral (A2) is only proportional to f^{-2} . The problem can be circumvented by expanding

$$\ln \left[\frac{f+1}{f} \right] = \frac{2}{2f+1} \left[1 + \frac{1}{3(2f+1)^2} + \frac{1}{5(2f+1)^4} + \cdots \right] \quad (\text{A7})$$

and subtracting out explicitly the leading terms. With the additional definitions

$$\begin{aligned} \ln^{(3)} \left[\frac{f+1}{f} \right] &= \ln \left[\frac{f+1}{f} \right] - \frac{2}{2f+1} \left[1 + \frac{1}{3(2f+1)^2} + \frac{1}{5(2f+1)^4} \right] \\ &= \sum_{j=3}^{\infty} \frac{2}{(2j+1)(2f+1)^{2j+1}} \quad (\text{for large } f) \end{aligned} \quad (\text{A8})$$

and $p=(2f+1)^2$, the final results are

$$I_{n,n'}^{(3)} = \frac{2}{g-g'} \left[g^3(2f'+1) \ln^{(3)} \left[\frac{f+1}{f} \right] - g'^3(2f+1) \ln^{(3)} \left[\frac{f'+1}{f'} \right] \right] + \frac{1}{5(pp')^{1/2}} \left[\frac{3}{4} - \frac{(p'+p)}{3pp'} + \frac{(p'^3-p^3)}{4p^2p'^2(p'-p)} \right] \quad (\text{A9})$$

for $f'=f$, and

$$I_{n,n}^{(3)} = 2g^2 \left[\frac{10g+3}{2f+1} \right] \ln^{(3)} \left[\frac{f+1}{f} \right] + \frac{1}{20p} \left[\frac{1}{2} + \frac{7}{3p} + \frac{1}{2p^2} \right] \quad (\text{A10})$$

for $f'=f$. These formulas are now proportional to f^{-2} for large f , as they should be. All the results have been checked numerically.

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