Relativistic $(Z\alpha)^2$ corrections and leading quantum electrodynamic corrections to the two-photon decay rate of ionic states

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We calculate the relativistic corrections of relative order $(Z\alpha)^2$ to the two-photon decay rate of higher excited S and D states in ionic atomic systems, and we also evaluate the leading radiative corrections of relative order $\alpha(Z\alpha)^2\ln[(Z\alpha)^{-2}]$. We thus complete the theory of the two-photon decay rates up to relative order $\alpha^3\ln(\alpha)$. An approach inspired by nonrelativistic quantum electrodynamics is used. We find that the corrections of relative order $(Z\alpha)^2$ to the two-photon decay are given by the *Zitterbewegung*, by the spin-orbit coupling and by relativistic corrections to the electron mass, and by quadrupole interactions. We show that all corrections are separately gauge invariant with respect to a "hybrid" transformation from velocity to length gauge, where the gauge transformation of the wave function is neglected. The corrections are evaluated for the two-photon decay from 2S, 3S, 3D, and 4S states in one-electron (hydrogenlike) systems, with 1S and 2S final states.

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I. INTRODUCTION

Two-photon decay processes in hydrogenlike ions represent an intriguing physical phenomenon and are the subject of intense research. The metastability of the 2S level, which is limited only by two-photon decay, makes it amenable to high-precision measurements. Interestingly, though, the two-photon decay has never been studied within the so-called $Z\alpha$ expansion beyond the leading order, that is, beyond the order of $\alpha^2(Z\alpha)^6$ for the decay width in units of the electron rest mass (in this paper, we use natural units $\hbar=c=\epsilon_0=1$).

The first study of the two-photon decay rate Γ of the 2S state was carried out by Göppert-Mayer in 1931 [1], and the well-known nonrelativistic result was derived,

$$\tau^{-1}=\Gamma_0=8.229\,352\,Z^6\,s^{-1}=1.309\,742\,Z^6\text{ Hz}. \quad (1)$$

This result has been verified experimentally [2–4].

In the nonrecoil limit, the leading correction terms modifying this result are given by a relativistic correction of relative order $(Z\alpha)^2$ and a radiative correction of relative order $\alpha(Z\alpha)^2\ln[(Z\alpha)^{-2}]$. We can write the following expansion:

$$\Gamma=\Gamma_0\left[1+\gamma_2(Z\alpha)^2+\gamma_3\frac{\alpha}{\pi}(Z\alpha)^2\ln[(Z\alpha)^{-2}]+\dots\right], \quad (2)$$

with coefficients γ_2 and γ_3 to be determined.

The next-higher-order term not included in Eq. (2) is a nonlogarithmic radiative correction of order $\alpha(Z\alpha)^2$. Equation (2) is complete up to order $\alpha^3\ln(\alpha)$.

The coefficient γ_3 is known for the 2S-1S transition [5,6], but it remains unknown for any other two-photon transition in a hydrogenlike ionic system. The coefficient γ_2, which intuitively could be assumed to represent an easy computational task, has not yet been calculated for *any* two-photon transition, to the best of our knowledge. We address both γ_2 and γ_3 in this paper.

The relativistic correction of relative order $(Z\alpha)^2$ actually involves quite a large number of individual contributions: (i) multipole (quadrupole radiation) correction, (ii) relativistic corrections to the electron's transition current, and (iii) relativistic corrections to the Hamiltonian and to the bound-state energies of initial and final states, due to *Zitterbewegung* (zb), relativistic kinetic energy (ke), and spin-orbit coupling. Each one of these contributions entails a computationally demanding sum over virtual states and an integration over the photon energy. We here calculate the corrections one after the other and check gauge invariance all along the way. Finally, we obtain rigorous results for γ_2 and γ_3.

Our approach is inspired by nonrelativistic quantum electrodynamics (NRQED), albeit in a restricted way. In a two-photon decay, the photon energies are bound by the energy difference of the initial and final states and, therefore, the problem of separating the energy scales of the high-energy vertex terms does not arise. However, the interaction Hamiltonian still has to be expanded in the sense of NRQED, and we have the choice between two gauges, which determine the form of the interaction Hamiltonian. Either the "length" (Yennie) or "velocity" (Coulomb) gauge can be chosen. The final result should not depend on the gauge.

In the Appendix of Ref. [7], the gauge invariance of the two-photon decay rate was shown to hold within the fully relativistic formalism, within the class of fully relativistic gauge transformations given by Eq. (A8) of Ref. [7]. The Power-Zienau gauge transformation [8], as given in Eqs. (18) and (19) of Ref. [9], has a nontrivial dependence on the coordinates and allows us to express the QED interaction Hamiltonian exclusively in terms of observable field strengths, which in turn correspond to derivatives of the vector potential. This transformation is most suitable for a nonrelativistic treatment; but due to the nontrivial dependence on the coordinates and due to problems related to the physical interpretation of nongauge-invariant quantities [10–12], a few subtleties arise.

After considerable discussion on this point within the community [10–12], the conclusion has been reached that gauge transformations have to be considered very carefully in bound-state problems. E.g., for the radiative corrections to the two-photon decay rate [5], the results are invariant under a hybrid gauge transformation [11], where the interaction Hamiltonian is gauge transformed, but the gauge transformation of the wave function is neglected, i.e., although a gauge transformation normally entails a local "pointwise" transformation of the wave function, this whole transformation is flatly ignored, and the "usual" Schrödinger eigenstates [13] are used for initial and final states of the process under investigation. We show here that the relativistic corrections to the two-photon decay rate are invariant under such a transformation (the gauge invariance of the leading logarithmic QED corrections was shown in Ref. [5]). In general, properties of atomic states which can be formulated using the adiabatic S-matrix theory are invariant under this kind of hybrid gauge transformation; whereas in time-dependent problems, the choice of gauge has to be taken into account even more carefully [10–12]. In the latter case, the gauge transformation of the wave function cannot be ignored.

When generalizing the results to higher-excited initial and final states, one has to overcome a few subtle difficulties because one has to separate the $3S$-$1S$ double-dipole ($E1E1$) two-photon decay from the cascade $3S$-$2P$-$1S$. The $2P$ state appears both as a virtual state for the two-photon decay process as well as an intermediate state for the cascade process. In the two-photon decay rate, when regarded as differential with respect to the photon energy, the presence of the $2P$ state causes a (quadratic) singularity. Because we are interested in the total decay rate, we have to integrate over this singularity, which is quadratic and thus *a priori* not integrable. Removing the $2P$ state from the sum over virtual intermediate states leads to gauge-dependent results [14–18]. In order to separate the cascade contribution from the two-photon correction for the two-photon decay, one has to use a special integration prescription detailed in Refs. [18–21]; the prescription constitutes a generalization of the principal-value integration to quadratic singularities. Here, we extend the relativistic calculations for two-photon decays to highly excited initial states using this formalism.

We organize the paper as follows. In Sec. II, we explain the theoretical methods used in our approach. In Sec. III, we consider all the corrections separated by their physical origin for the $2S$-$1S$ transition and show explicitly that each contribution is gauge invariant. In Sec. IV, we present numerical results for the $2S$-$1S$ transition and also for transitions from higher-excited states, and we discuss the separation of the cascade contribution from the coherent two-photon correction to the decay rate. Results for the QED radiative corrections of logarithmic order are presented in Sec. V. Conclusions are drawn in Sec. VI. As already mentioned, natural units $\hbar=\epsilon_0=c=1$ are used throughout this paper.

II. THEORETICAL BACKGROUND

The two-photon decay rate is given as the imaginary part of the two-loop self-energy correction [22] which can be derived using NRQED [23]. A detailed derivation of the nonrelativistic two-photon decay rate valid for all transitions, including those involving highly excited states, is contained in previous works [5,18,19,21] and there is no need to reproduce it here.

We recall that in velocity (Coulomb) gauge, the interaction Hamiltonian for the interaction of the electron with the quantized radiation field is given as

$$H_I = -\frac{e}{2m}(\vec{p}\cdot\vec{A}+\vec{A}\cdot\vec{p}) + \frac{e^2\vec{A}^2}{2m}, \tag{3}$$

where $\vec{p}$ is the electron momentum, $\vec{A}$ is the vector potential, and m is the electron mass. This interaction leads to the following expression for the nonrelativistic decay rate:

$$\Gamma^{\xi} = \frac{4\alpha^2}{9\pi m^4}\mathrm{Re}\int_0^{E_i-E_f} d\omega_1\omega_1\omega_2\Bigg(\langle\Phi_f|p^i\frac{1}{H-E_f-\omega_1+i\epsilon}p^j|\Phi_i\rangle + \langle\Phi_f|p^i\frac{1}{H-E_i+\omega_1+i\epsilon}p^j|\Phi_i\rangle\Bigg)^2. \tag{4}$$

Here, "Re" denotes the real part, and the limit $\epsilon\to 0$ is taken after all integrations have been performed. The summation convention is used throughout this paper. The superscript ξ denotes the velocity-gauge form of the expression.

For length (Yennie) gauge, the (leading) interaction Hamiltonian takes the simple form,

$$H_I = -e\vec{E}\cdot\vec{r}. \tag{5}$$

If this Hamiltonian is used, we obtain for the nonrelativistic expression,

$$\Gamma^{\zeta} = \frac{4\alpha^2}{9\pi}\mathrm{Re}\int_0^{E_i-E_f} d\omega_1\omega_1^3\omega_2^3\Bigg(\langle\Phi_f|r^i\frac{1}{H-E_f-\omega_1+i\epsilon}r^j|\Phi_i\rangle + \langle\Phi_f|r^i\frac{1}{H-E_i+\omega_1+i\epsilon}r^j|\Phi_i\rangle\Bigg)^2. \tag{6}$$

Using the relation [10,24]

$$\langle\Phi_f|p^i\frac{1}{H-E_f-\omega_1}p^j|\Phi_i\rangle + \langle\Phi_f|p^i\frac{1}{H-E_i+\omega_1}p^j|\Phi_i\rangle = -m^2\omega_1\omega_2\Bigg(\langle\Phi_f|r^i\frac{1}{H-E_f-\omega_1}r^j|\Phi_i\rangle + \langle\Phi_f|r^i\frac{1}{H-E_i+\omega_1}r^j|\Phi_i\rangle\Bigg), \tag{7}$$

the equivalence of these two expressions can be shown. Note that this is only valid if a complete spectrum is used for the representation of the propagator.

For a fully relativistic calculation of the effect, we would have to use the Dirac Hamiltonian H_D in the propagators instead of the Schrödinger Hamiltonian H and also the interaction Hamiltonian and the wave function would have to be changed accordingly. However, as we want to work nonrelativistically, we transform the fully relativistic Dirac Hamiltonian and its interaction Hamiltonian into effective nonrelativistic operators. This can be achieved by using a Foldy-Wouthuysen transformation [25], which identifies the nonrelativistic Hamiltonian as the leading term, and thus leads to a systematic way of expressing the relativistic corrections. Furthermore, it allows us to express the relativistic corrections to the electron's transition current within the $Z\alpha$ expansion.

Alternatively, one can resort to the literature [26], where the corrections to the Schrödinger Hamiltonian have been tabulated. For the noninteracting part, this procedure leads to the well-known corrections to the Schrödinger Hamiltonian H,

$$H \to H + \delta H,$$

$$H = \frac{p^2}{2m} + \frac{Z\alpha}{r},$$

$$\delta H = \frac{\pi Z\alpha}{2m}\delta^3(r) + \frac{\vec{L}\cdot\vec{\sigma}}{4m^2 r^3} - \frac{p^4}{8m^3}. \tag{8}$$

The Darwin term proportional to the Dirac δ originates from the *Zitterbewegung* of the electron. The next term is the spin-orbit coupling, and the last is the correction due to the relativistic kinetic energy. The relativistic corrections to the reference state wave function and to its energy thus read as follows:

$$E \to E + \delta E = E + \langle\Phi|\delta H|\Phi\rangle, \tag{9}$$

$$|\Phi\rangle \to |\Phi\rangle + |\delta\Phi\rangle = |\Phi\rangle + \left(\frac{1}{E-H}\right)'\delta H|\Phi\rangle. \tag{10}$$

The transition current of the electron can be derived by acting with the Foldy-Wouthuysen transformation on a Dirac Hamiltonian, which is coupled to an electromagnetic vector potential. The velocity-gauge result for the interaction Hamiltonian thus is (see Refs. [9,27])

$$H_{\rm int} = -\frac{e\vec{A}\cdot\vec{p}}{m} - \frac{e}{2m}(\vec{\sigma}\times\vec{\nabla})\cdot\vec{A} + \frac{e}{2m^3}(\vec{A}\cdot\vec{p})\vec{p}^2 - \frac{e}{4m^2}(\vec{\sigma}\times\vec{p})\cdot\frac{\partial\vec{A}}{\partial t} - \frac{e}{4m^2}(\vec{\sigma}\times\vec{\nabla}V)\cdot\vec{A} \equiv -e\vec{J}\cdot\vec{A}. \tag{11}$$

We remember that the photon emission is characterized by the creation part of the electromagnetic vector potential operator, which carries a dependence of $\exp(-i\vec{k}\cdot\vec{r})$. The transition current $\vec{J}$ can thus be written as

$$J^i = \frac{p^i}{m} + \delta J^i = \frac{p^i}{m}\left[1 - i\vec{k}\cdot\vec{r} - \frac{1}{2}(\vec{k}\cdot\vec{r})^2\right] - \frac{p^i\vec{p}^2}{2m^3} - \frac{1}{2m^2}\frac{Z\alpha}{r^3}(\vec{r}\times\vec{\sigma})^i - \frac{i}{2m}(\vec{\sigma}\times\vec{k})^i(1 - i\vec{k}\cdot\vec{r}). \tag{12}$$

As we are considering a two-photon effect, contributions from seagull terms also have to be taken into account (here, two photons emerge from the same vertex). Terms proportional to A^2 are included in the seagull Hamiltonian which is given by

$$H_{\rm sea} = \frac{e^2\vec{A}^2}{2m} - \frac{e^2}{2m^3}(\vec{A}\cdot\vec{p})^2 - \frac{e^2}{4m^3}\vec{A}^2\vec{p}^2. \tag{13}$$

Expanding in powers of $(Z\alpha)$ and extracting the photon creation part, we obtain the seagull correction in relative order $(Z\alpha)^2$,

$$\delta S^{ij} = -\frac{1}{2m}(\vec{k}\cdot\vec{r})^2\delta^{ij} - \frac{p^ip^j}{2m^3} - \frac{p^2}{4m^3}\delta^{ij}, \tag{14}$$

written in such a way that it multiplies the (creation part of the) photon fields A^iA^j.

The interaction Hamiltonian in length gauge, including relativistic and multipole corrections, can be obtained by employing two consecutive Power-Zienau transformations [8] after the Foldy-Wouthuysen transformation. This has been shown in Ref. [28]. The interaction Hamiltonian in length gauge thus reads as

$$H_{\rm int} = -e\vec{r}\cdot\vec{E} - \frac{e}{2m}(\vec{L}+\vec{\sigma})\cdot\vec{B} - \frac{e}{2}r^ir^jE^i_{,j} - \frac{e}{6m}(L^ir^j + r^jL^i)B^i_{,j} - \frac{e}{2m}\sigma^ir^jB^i_{,j} - \frac{e}{6}r^ir^jr^kE^i_{,jk} + \frac{e}{4m}\vec{\sigma}(\dot{\vec{E}}\times\vec{r}). \tag{15}$$

Here, the subscript separated by commas denotes the spatial derivatives with respect to the indicated Cartesian coordinates evaluated at the origin [28], which is defined to be the location of the ionic nucleus. This corresponds to a length-gauge transition current

$$I^i \equiv r^i + \delta I^i = r^i\left[1 - \frac{i}{2}\vec{k}\cdot\vec{r} - \frac{1}{6}(\vec{k}\cdot\vec{r})^2\right] + \frac{i\omega}{4m}(\vec{\sigma}\times\vec{r})^i + \frac{1}{2m\omega}(\vec{\sigma}\times\vec{k})^i(1 - i\vec{k}\cdot\vec{r}) + \frac{1}{2m\omega}(\vec{L}\times\vec{k})^i - \frac{i}{6m\omega}\{(\vec{L}\times\vec{k})^i,\vec{k}\cdot\vec{r}\}, \tag{16}$$

where $\{A,B\}=AB+BA$ is the anticommutator, and we examine the emission of a photon with four-vector $(\omega,\vec{k})$. We are now in the position to discuss how the corrections to the decay rate can be determined from the transition currents in the two different gauges. We start with the velocity gauge.

A. Velocity gauge

The nonrelativistic two-photon decay rate in velocity gauge [see Eq. (4)] can be written as

$$\Gamma^{\xi} = \frac{4\alpha^2}{9\pi}\int_0^{E_{\Phi_i}-E_{\Phi_f}} d\omega_1\omega_1\omega_2\xi^2, \tag{17}$$

where the superscript ξ denotes the velocity-gauge expression. Here, due to energy conservation, $\omega_2=E_{\Phi_i}-E_{\Phi_f}-\omega_1$, and

$$\xi = \xi_1 + \xi_2, \tag{18a}$$

$$\xi_1 = \langle\Phi_f|\frac{p^i}{m}\frac{1}{H - E_{\Phi_i} + \omega_1}\frac{p^j}{m}|\Phi_i\rangle, \tag{18b}$$

$$\xi_2 = \langle \Phi_f | \frac{p^i}{m} \frac{1}{H - E_{\Phi_f} - \omega_1} \frac{p^j}{m} | \Phi_i \rangle. \tag{18c}$$

For the gauge invariance of this nonrelativistic expression, see Eq. (7). We only remark that the statement of gauge invariance can be brought into the compact from

$$\xi = -\omega_1 \omega_2 \zeta, \tag{19}$$

where ζ is defined in Eq. (25) below. Here and in the following, we suppress the superscripts ij of the ξ and ζ tensors in order to ensure the compactness of the notation, and we imply that $\xi^2 \equiv \xi^{ij}\xi^{ij}$ (the indices i and j are summed over) and that $\xi\delta\xi \equiv \xi^{ij}\delta\xi^{ij}$. We define $\delta\xi$ to denote the sum of the corrections due to all the previously discussed perturbations (Hamiltonian, energy, and current) and express the first-order relativistic correction $\delta\Gamma$ to the decay rate as (see Ref. [5])

$$\delta\Gamma = 2\frac{4\alpha^2}{9\pi}\int_0^{E_{\Phi_i}-E_{\Phi_f}} d\omega_1 \omega_1 \omega_2 \xi \delta\xi + \frac{4\alpha^2}{9\pi}\delta\omega_{\mathrm{max}}\int_0^{E_{\Phi_i}-E_{\Phi_f}} d\omega_1 \omega_1 \xi^2. \tag{20}$$

The correction $\delta\omega_{\mathrm{max}} = \delta E_{\Phi_i} - \delta E_{\Phi_f}$ is necessary to ensure that the perturbed energy conservation condition is fulfilled,

$$\omega_1 + \omega_2 = E_{\Phi_i} - E_{\Phi_f} + \delta\omega_{\mathrm{max}}, \tag{21a}$$

$$\delta\omega_{\mathrm{max}} = \langle \Phi_i | \delta H | \Phi_i \rangle - \langle \Phi_f | \delta H | \Phi_f \rangle, \tag{21b}$$

so that the frequencies of the two quanta add up to the perturbed transition frequency. However, due to the presence of the seagull terms, further corrections have to be taken into account.

After some algebra, we see that $\delta\xi$ can be expressed as the sum of fifteen terms that account for all the relativistic and multipole perturbations,

$$\delta\xi = \sum_{k=1}^{15} \delta\xi_k. \tag{22}$$

The perturbations of the energies of the initial and final states lead to the following terms:

$$\delta\xi_1 = \langle \Phi_f | \frac{p^i}{m} \left(\frac{1}{H - E_{\Phi_i} + \omega_1} \right)^2 \frac{p^j}{m} | \Phi_i \rangle \langle \Phi_i | \delta H | \Phi_i \rangle, \tag{23a}$$

$$\delta\xi_2 = \langle \Phi_f | \delta H | \Phi_f \rangle \langle \Phi_f | \frac{p^i}{m} \left(\frac{1}{H - E_{\Phi_f} - \omega_1} \right)^2 \frac{p^j}{m} | \Phi_i \rangle. \tag{23b}$$

The perturbations to the initial and final-state wave functions lead to the following four effects:

$$\delta\xi_3 = \langle \Phi_f | \frac{p^i}{m} \frac{1}{H - E_{\Phi_i} + \omega_1} \frac{p^j}{m} \left(\frac{1}{E_{\Phi_i} - H} \right)' \delta H | \Phi_i \rangle, \tag{23c}$$

$$\delta\xi_4 = \langle \Phi_f | \frac{p^i}{m} \frac{1}{H - E_{\Phi_f} - \omega_1} \frac{p^j}{m} \left(\frac{1}{E_{\Phi_i} - H} \right)' \delta H | \Phi_i \rangle, \tag{23d}$$

$$\delta\xi_5 = \langle \Phi_f | \delta H \left(\frac{1}{E_{\Phi_f} - H} \right)' \frac{p^i}{m} \frac{1}{H - E_{\Phi_i} + \omega_1} \frac{p^j}{m} | \Phi_i \rangle, \tag{23e}$$

$$\delta\xi_6 = \langle \Phi_f | \delta H \left(\frac{1}{E_{\Phi_f} - H} \right)' \frac{p^i}{m} \frac{1}{H - E_{\Phi_f} - \omega_1} \frac{p^j}{m} | \Phi_i \rangle. \tag{23f}$$

The perturbation incurred by the Hamiltonian leads to two terms (observe the different denominators),

$$\delta\xi_7 = -\langle \Phi_f | \frac{p^i}{m} \frac{1}{H - E_{\Phi_i} + \omega_1} \delta H \frac{1}{H - E_{\Phi_i} + \omega_1} \frac{p^j}{m} | \Phi_i \rangle, \tag{23g}$$

$$\delta\xi_8 = -\langle \Phi_f | \frac{p^i}{m} \frac{1}{H - E_{\Phi_f} - \omega_1} \delta H \frac{1}{H - E_{\Phi_f} - \omega_1} \frac{p^j}{m} | \Phi_i \rangle. \tag{23h}$$

The correction to the electron's transition current can affect both the initial and the final states, and this gives rise to a total of four terms,

$$\delta\xi_9 = \langle \Phi_f | \frac{p^i}{m} \frac{1}{H - E_{\Phi_i} + \omega_1} \delta J^j | \Phi_i \rangle, \tag{23i}$$

$$\delta\xi_{10} = \langle \Phi_f | \frac{p^i}{m} \frac{1}{H - E_{\Phi_f} - \omega_1} \delta J^j | \Phi_i \rangle, \tag{23j}$$

$$\delta\xi_{11} = \langle \Phi_f | \delta J^i \frac{1}{H - E_{\Phi_i} + \omega_1} \frac{p^j}{m} | \Phi_i \rangle, \tag{23k}$$

$$\delta\xi_{12} = \langle \Phi_f | \delta J^i \frac{1}{H - E_{\Phi_f} - \omega_1} \frac{p^j}{m} | \Phi_i \rangle. \tag{23l}$$

The seagull Hamiltonian acting on the unperturbed wave functions leads to

$$\delta\xi_{13} = -\langle \Phi_f | \delta S^{ij} | \Phi_i \rangle. \tag{23m}$$

The minus sign originates because we have written all matrix elements (second-order perturbations) in the "$1/(H-E)$" form, which corresponds to a negative second-order energy perturbation. In order to be consistent, we have to use the negative higher-order seagull Hamiltonian, which is applied in the first-order perturbation theory. Finally, we have the seagull terms, which were already present in Ref. [5], which account for the emission of two photons from the perturbed initial state or to the perturbed final state. They are given as

$$\delta\xi_{14} = -\frac{1}{m}\langle \Phi_f | \left(\frac{1}{E_{\Phi_i} - H} \right)' \delta H | \Phi_i \rangle \delta^{ij}, \tag{23n}$$

$$\delta\xi_{15} = -\frac{1}{m}\langle\Phi_f|\delta H\left(\frac{1}{E_{\Phi_f}-H}\right)'|\Phi_i\rangle\delta^{ij}, \tag{23o}$$

where we invoke second-order perturbation theory with the leading seagull term $e^2\vec{A}^2/(2m)$. Using a complete basis set of hydrogen eigenfunctions and their orthonormality relations, we can show that

$$\delta\xi_{14} + \delta\xi_{15} = 0. \tag{24}$$

The reason is that both $\delta\xi_{14}$ and $\delta\xi_{15}$ are proportional to the nondiagonal matrix element $\langle\Phi_f|\delta H|\Phi_i\rangle$ but with opposite prefactors.

B. Length gauge

The nonrelativistic length-gauge expression in Eq. (6) can be written as

$$\Gamma^{\zeta} = \frac{4\alpha^2}{9\pi}\int_0^{E_{\Phi_i}-E_{\Phi_f}} d\omega_1\omega_1^3\omega_2^3\zeta^2, \tag{25}$$

where the superscript ζ denotes the length-gauge expression. Here, ω_2 is defined as in Eq. (17), and

$$\zeta = \zeta_1 + \zeta_2, \tag{26a}$$

$$\zeta_1 = \langle\Phi_f|r^i\frac{1}{H-E_{\Phi_i}+\omega_1}r^j|\Phi_i\rangle, \tag{26b}$$

$$\zeta_2 = \langle\Phi_f|r^i\frac{1}{H-E_{\Phi_f}-\omega_1}r^j|\Phi_i\rangle. \tag{26c}$$

Following the same procedure as for the velocity-gauge expression, we can write the first-order correction to the two-photon decay rate in length gauge,

$$\delta\Gamma^{\zeta} = 2\frac{4\alpha^2}{9\pi}\int_0^{E_{\Phi_i}-E_{\Phi_f}} d\omega_1\omega_1^3\omega_2^3\zeta\delta\zeta + 3\frac{4\alpha^2}{9\pi}\delta\omega_{\max}\int_0^{E_{\Phi_i}-E_{\Phi_f}} d\omega_1\omega_1^3\omega_2^2\zeta^2, \tag{27}$$

where again $\delta\zeta$ denotes the sum of all the correction terms incurred by the relativistic perturbations of the Hamiltonian, and of the energies of the initial and final states, and of the length-gauge current. Indeed, in the length gauge, the correction $\delta\zeta$ contains only 12 as opposed to 15 terms,

$$\delta\zeta = \sum_{k=1}^{12}\delta\zeta_k. \tag{28}$$

The energies of the initial and final states are perturbed and this gives rise to the first two correction terms,

$$\delta\zeta_1 = \langle\Phi_f|r^i\left(\frac{1}{H-E_{\Phi_i}+\omega_1}\right)^2 r^j|\Phi_i\rangle\langle\Phi_i|\delta H|\Phi_i\rangle, \tag{29a}$$

$$\delta\zeta_2 = \langle\Phi_f|\delta H|\Phi_f\rangle\langle\Phi_f|r^i\left(\frac{1}{H-E_{\Phi_f}-\omega_1}\right)^2 r^j|\Phi_i\rangle. \tag{29b}$$

In complete analogy to Eqs. (23c)–(23f), the perturbations to the initial and final-state wave functions are accounted for by the following four terms:

$$\delta\zeta_3 = \langle\Phi_f|r^i\frac{1}{H-E_{\Phi_i}+\omega_1}r^j\left(\frac{1}{E_{\Phi_i}-H}\right)'\delta H|\Phi_i\rangle, \tag{29c}$$

$$\delta\zeta_4 = \langle\Phi_f|r^i\frac{1}{H-E_{\Phi_f}-\omega_1}r^j\left(\frac{1}{E_{\Phi_i}-H}\right)'\delta H|\Phi_i\rangle, \tag{29d}$$

$$\delta\zeta_5 = \langle\Phi_f|\delta H\left(\frac{1}{E_{\Phi_f}-H}\right)'r^i\frac{1}{H-E_{\Phi_i}+\omega_1}r^j|\Phi_i\rangle, \tag{29e}$$

$$\delta\zeta_6 = \langle\Phi_f|\delta H\left(\frac{1}{E_{\Phi_f}-H}\right)'r^i\frac{1}{H-E_{\Phi_f}-\omega_1}r^j|\Phi_i\rangle. \tag{29f}$$

Furthermore, the corrections from the perturbed Hamiltonian give rise to two terms,

$$\delta\zeta_7 = -\langle\Phi_f|r^i\frac{1}{H-E_{\Phi_i}+\omega_1}\delta H\frac{1}{H-E_{\Phi_i}+\omega_1}r^j|\Phi_i\rangle, \tag{29g}$$

$$\delta\zeta_8 = -\langle\Phi_f|r^i\frac{1}{H-E_{\Phi_f}-\omega_1}\delta H\frac{1}{H-E_{\Phi_f}-\omega_1}r^j|\Phi_i\rangle. \tag{29h}$$

The length-gauge correction to the current δI gives rise to four more terms,

$$\delta\zeta_9 = \langle\Phi_f|r^i\frac{1}{H-E_{\Phi_i}+\omega_1}\delta I^j|\Phi_i\rangle, \tag{29i}$$

$$\delta\zeta_{10} = \langle\Phi_f|r^i\frac{1}{H-E_{\Phi_f}-\omega_1}\delta I^j|\Phi_i\rangle, \tag{29j}$$

$$\delta\zeta_{11} = \langle\Phi_f|\delta I^i\frac{1}{H-E_{\Phi_i}+\omega_1}r^j|\Phi_i\rangle, \tag{29k}$$

$$\delta\zeta_{12} = \langle\Phi_f|\delta I^i\frac{1}{H-E_{\Phi_f}-\omega_1}r^j|\Phi_i\rangle. \tag{29l}$$

The seagull term is not present in the length gauge. In the next section, we analyze these corrections in the light of gauge invariance. We separate the corrections by their physical origin and show more than the gauge invariance of the final result: namely, we are able to demonstrate that each physically distinguished correction is gauge invariant in itself.

III. GENERAL PROOF OF GAUGE INVARIANCE

A. Orientation

First of all, let us remember that in all bound-state calculations, we actually use a hybrid gauge transformation [11], where we ignore the gauge transformation of the wave function. The noninteracting relativistic Hamiltonian given in Eq. (8) by definition is gauge invariant. Thus, we only gauge transform the electron's transition current and the photon field operator or, alternatively, we let the interaction Hamiltonian undergo a gauge transformation. We show here that the full gauge invariance is obtained by carefully considering the interplay of the relativistic corrections to the wave function, to the Hamiltonian, and to the energies of the bound states (the initial and the final states).

The whole problem becomes simpler when it is divided into three distinct parts: the first of which is a generalized correction due to the relativistic Hamiltonian, the second of which is a quadrupole correction, and the third is a remaining correction (a further correction to the current), which can be shown to vanish after the use of commutator relations. Gauge invariance can be shown for each of these corrections separately provided some parts of the velocity-gauge correction to the electron's transition current (12) are identified as being generated by the relativistic Hamiltonian (8) and treated together with the correction to the Hamiltonian. Here, the velocity-gauge expression appears to be more complicated. The quadrupole correction by contrast looks a little more involved in the length gauge. Gauge invariance with respect to the velocity gauge can be shown provided we include a part of the seagull term (14) into the velocity-gauge expression for the quadrupole term. It is then relatively easy to show that all remaining terms vanish separately.

In the following, we discuss the general approach to the proof of gauge invariance in some detail. Further aspects are elucidated in Appendixes A and B.

B. Correction to the Hamiltonian

Let us discuss first the general paradigm and start with the corrections induced by the relativistic Hamiltonian (8). The gauge invariance for the leading-order term (the nonrelativistic result) can be traced to the formula (19),

$$\xi = -\omega_1\omega_2\zeta, \tag{30}$$

where ξ represents the velocity-gauge form and ζ represents the length-gauge form.

Both ξ and ζ actually carry superscripts ij, which we suppress here to leave the notation compact, as already discussed. Let us now suppose that the total velocity-gauge correction due to the relativistic Hamiltonian can be expressed as $\delta\xi_H$, and the corresponding length-gauge expression is $\delta\zeta_H$. The precise definition of $\delta\xi_H$ and $\delta\zeta_H$ will be discussed later. We are able to show the following gauge-invariance relation,

$$\delta\xi_H = -\omega_1\omega_2\delta\zeta_H - \delta\omega_{\max}\omega_1\zeta, \tag{31}$$

based on which we can prove the gauge invariance of the entire correction $\delta\Gamma_H$ due to the relativistic Hamiltonian,

$$\begin{aligned}\delta\Gamma_H^{\xi} &= 2\frac{4\alpha^2}{9\pi}\int_0^{E_{\Phi_i}-E_{\Phi_f}} d\omega_1\,\omega_1\omega_2\xi\delta\xi_H \\ &\quad + \frac{4\alpha^2}{9\pi}\delta\omega_{\max}\int_0^{E_{\Phi_i}-E_{\Phi_f}} d\omega_1\,\omega_1\xi^2 \\ &= 2\frac{4\alpha^2}{9\pi}\int_0^{E_{\Phi_i}-E_{\Phi_f}} d\omega_1\,\omega_1\omega_2(-\omega_1\omega_2\zeta)[-\omega_1\omega_2\delta\zeta_H \\ &\quad - \delta\omega_{\max}\omega_1\zeta] + \frac{4\alpha^2}{9\pi}\delta\omega_{\max}\int_0^{E_{\Phi_i}-E_{\Phi_f}} d\omega_1\,\omega_1^3\omega_2^2\zeta^2 \\ &= 2\frac{4\alpha^2}{9\pi}\int_0^{E_{\Phi_i}-E_{\Phi_f}} d\omega_1\,\omega_1^3\omega_2^3\zeta\delta\zeta_H \\ &\quad + 3\frac{4\alpha^2}{9\pi}\delta\omega_{\max}\int_0^{E_{\Phi_i}-E_{\Phi_f}} d\omega_1\,\omega_1^3\omega_2^2\zeta^2 = \delta\Gamma_H^{\zeta}.\end{aligned} \tag{32}$$

Here, again, the superscript ξ denotes the velocity gauge, whereas ζ denotes the length gauge. We are indeed able to show such a relation for all three terms given in Eqs. (8), but only if we include in the definition of $\delta\xi_H$ specific corrections to the electron's transition current. Our gauge-invariance relation can be illustrated as follows. The correction $\delta\xi_H$ contains the wave-function correction in the velocity gauge, the Hamiltonian correction in velocity gauge, the energy correction in velocity gauge, and the seagull term in velocity gauge, as well as the current correction due to the current operator $\delta J_H^i \equiv -i[r^i,\delta H]$. By contrast, $\delta\zeta_H$ equals the sum of the wave-function correction in length gauge, the Hamiltonian correction in length gauge, and the energy correction in length gauge. Note that the term $-\delta\omega_{\max}\omega_1\zeta$ in Eq. (31) is related to the modified energy conservation condition and that $\delta\omega_{\max}$ here is the correction to the transition frequency due to the relativistic Hamiltonian given in Eq. (21b). Using this result, we are able to show that the total correction to the decay rate due to all three terms given in Eqs. (8) is gauge invariant.

The current that we add in the velocity gauge is

$$\begin{aligned}\delta J_H^i &= -i[r^i,\delta H] = -i\left[r^i, -\frac{\vec{p}^4}{8m^3}\right] - i\left[r^i, \frac{\vec{L}\cdot\vec{\sigma}}{4m^2r^3}\right] = -\frac{p^i\vec{p}^2}{2m^3} \\ &\quad - \frac{1}{4m^2}\frac{Z\alpha}{r^3}(\vec{r}\times\vec{\sigma})^i.\end{aligned} \tag{33}$$

The seagull term that we add in velocity gauge is due to a double commutator

$$\begin{aligned}\delta S_H^{ij} &= [[r^i,\delta H],r^j] = \left[\left[r^i, -\frac{p^4}{8m^3}\right], r^j\right] = \left[-i\frac{p^ip^2}{2m^3}, r^j\right] \\ &= -\delta^{ij}\frac{p^2}{2m^3} - \frac{p^jp^i}{m^3}.\end{aligned} \tag{34}$$

This term is part of the seagull Hamiltonian (14). We are now in the position to give the precise definition of $\delta\xi_H$ and $\delta\zeta_H$,

$$\delta\xi_H = \sum_{i=1}^{8} \delta\xi_i + \left. \sum_{i=9}^{12} \delta\xi_i \right|_{\delta J = \delta J_H} + \delta\xi_{13}|_{\delta S = \delta S_H} \qquad (35)$$

and

$$\delta\zeta_H = \sum_{i=1}^{8} \delta\zeta_i. \qquad (36)$$

For further details, see Appendix A.

C. Quadrupole (multipole) correction

The quadrupole correction is not associated with any correction to the bound-state energy or to the Schrödinger Hamiltonian. It can be treated separately and identified with a correction δJ_Q^i to the current in velocity gauge and with a correction δI_Q^i in length gauge. The velocity-gauge current is

$$\delta J_Q^i = \frac{p^i}{m}(-i\vec{k}\cdot\vec{r}) - \frac{1}{2}\frac{p^i}{m}(\vec{k}\cdot\vec{r})^2 \to -\frac{1}{2}\frac{p^i}{m}(\vec{k}\cdot\vec{r})^2. \qquad (37)$$

We can ignore the first term because it vanishes after angular algebra, for the first-order correction to the two-photon decay. This is unlike the $(Z\alpha)^2$ correction to the Lamb shift, where this term contributes as a simultaneous perturbation to both currents because one and the same photon is being emitted. Here, two photons are being emitted, and angular averaging occurs for both of them separately.

The quadrupole current in the length gauge is

$$\begin{aligned}\delta I_Q^i &= r^i\left[-\frac{i}{2}\vec{k}\cdot\vec{r} - \frac{1}{6}(\vec{k}\cdot\vec{r})^2\right] + \frac{1}{2m\omega}(\vec{L}\times\vec{k})^i \\ &\quad - \frac{i}{6m\omega}[(\vec{L}\times\vec{k})^i(\vec{k}\cdot\vec{r}) + (\vec{k}\cdot\vec{r})(\vec{L}\times\vec{k})^i] \\ &\to r^i\left(-\frac{1}{6}(\vec{k}\cdot\vec{r})^2\right) - \frac{i}{6m\omega}[(\vec{L}\times\vec{k})^i(\vec{k}\cdot\vec{r}) \\ &\quad + (\vec{k}\cdot\vec{r})(\vec{L}\times\vec{k})^i], \end{aligned} \qquad (38)$$

where in the last step we have ignored the terms that vanish after angular integration. We find that the quadrupole term is gauge invariant provided we include, in the velocity-gauge expression, the seagull contribution from the term

$$\delta S_Q^{ij} = -\frac{1}{2m}(\vec{k}\cdot\vec{r})^2\delta^{ij}. \qquad (39)$$

Now, the sum of δS_Q^{ij} and δS_H^{ij} is the full higher-order seagull term δS^{ij} given in Eq. (14).

We denote the correction to the quadrupole matrix element in the velocity gauge by $\delta\xi_Q$ (it includes the seagull correction due to δS_Q^{ij}) and use $\delta\zeta_Q$ for the corresponding correction to the matrix element in the length gauge. We are able to show that

$$\begin{aligned}\delta\Gamma_Q^{\xi} &= 2\frac{4\alpha^2}{9\pi}\int_0^{E_{\Phi_i}-E_{\Phi_f}} d\omega_1\omega_1\omega_2\xi\delta\xi_Q \\ &= 2\frac{4\alpha^2}{9\pi}\int_0^{E_{\Phi_i}-E_{\Phi_f}} d\omega_1\omega_1\omega_2(-\omega_1\omega_2\zeta)[-\omega_1\omega_2\delta\zeta_Q] \\ &= 2\frac{4\alpha^2}{9\pi}\int_0^{E_{\Phi_i}-E_{\Phi_f}} d\omega_1\omega_1^3\omega_2^3\zeta\delta\zeta_Q = \delta\Gamma_Q^{\zeta},\end{aligned} \qquad (40)$$

proving the gauge invariance of the quadrupole correction. The precise definition of $\delta\xi_Q$ and $\delta\zeta_Q$ reads as follows:

$$\delta\xi_Q = \left.\sum_{i=9}^{12}\delta\xi_i\right|_{\delta J=\delta J_Q} + \delta\xi_{13}|_{\delta S=\delta S_Q} \qquad (41)$$

and

$$\delta\zeta_Q = \left.\sum_{i=9}^{12}\delta\zeta_i\right|_{\delta I=\delta I_Q}. \qquad (42)$$

Further details are provided in Appendix B.

D. Remaining corrections

We have by now treated the correction due to the entire Hamiltonian (8), the entire seagull term (14), and the quadrupole interaction. The remaining terms are current corrections. In the velocity gauge, these read as

$$\begin{aligned}\delta J_R^i = \delta J^i - \delta J_H^i - \delta J_Q^i &= -\frac{i}{2m}(\vec{\sigma}\times\vec{k})^i(1 - i\vec{k}\cdot\vec{r}) \\ &\quad - \frac{1}{4m^2}\frac{Z\alpha}{r^3}(\vec{r}\times\vec{\sigma})^i.\end{aligned} \qquad (43)$$

Using commutator relations, it is possible to show that

$$\begin{aligned}&\langle\Phi_f|p^i\frac{1}{H - E_{\Phi_i} + \omega}(\vec{\sigma}\times\vec{k})^i|\Phi_i\rangle \\ &\quad + \langle\Phi_f|(\vec{\sigma}\times\vec{k})^j\frac{1}{H - E_{\Phi_i} - \omega}p^j|\Phi_i\rangle = 0.\end{aligned} \qquad (44)$$

This relation is valid for both $\vec{k}=\vec{k}_{1,2}$ if ω is changed according to Eqs. (23i)–(23l), and for arbitrary initial and final states. Thus, the contribution of the first term on the right-hand side of Eq. (43) vanishes. Furthermore, we can replace

$$-\frac{1}{2m}(\vec{\sigma}\times\vec{k})^i(\vec{k}\cdot\vec{r}) \to -\frac{i\omega}{4m^2}(\vec{\sigma}\times\vec{p})^i,$$

$$-\frac{1}{4m^2}\frac{Z\alpha}{r^3}(\vec{r}\times\vec{\sigma})^i \to \frac{i\omega}{4m^2}(\vec{\sigma}\times\vec{p})^i, \qquad (45)$$

when contracted with the photon propagator. This relation is known from Lamb shift calculations (see Ref. [29]). Therefore, the entire contribution from the remaining corrections to the current vanishes in the velocity gauge.

In the length gauge, the remaining corrections to the current are given as

$$\delta I_R^i = \frac{1}{2m\omega}(\vec{\sigma}\times\vec{k})^i(1 - i\vec{k}\cdot\vec{r}) + \frac{i\omega}{4m}(\vec{\sigma}\times\vec{r})^i. \tag{46}$$

The first term vanishes in view of Eq. (44). The remaining terms also do not contribute to the corrections to the decay rate. This follows from the relation

$$\frac{i}{2m\omega}(\vec{\sigma}\times\vec{k})^i(\vec{k}\cdot\vec{r}) \to \frac{i\omega}{4m}(\vec{\sigma}\times\vec{r})^i. \tag{47}$$

for the last two terms of Eq. (46) when contracted with the photon propagator. The precise definition of $\delta\xi_R$ and $\delta\zeta_R$ reads as follows:

$$\delta\xi_R = \left.\sum_{i=9}^{12}\delta\xi_i\right|_{\delta J=\delta J_R} \tag{48}$$

and

$$\delta\zeta_R = \left.\sum_{i=9}^{12}\delta\zeta_i\right|_{\delta I=\delta I_R}. \tag{49}$$

IV. NUMERICAL CALCULATIONS

A. 2S-1S decay

The phenomenologically most important two-photon decay process is the 2S-1S decay. Our gauge-invariant result for the correction to the decay rate due to the relativistic Hamiltonian, as discussed in Sec. III B, reads as

$$\delta\Gamma_H = \Gamma_0[-0.508\,2(Z\alpha)^2]. \tag{50}$$

For the quadrupole correction, the gauge-invariant result is (see Sec. III C)

$$\delta\Gamma_Q = \Gamma_0[-0.155\,5(Z\alpha)^2]. \tag{51}$$

The remaining current corrections vanish, as discussed in Sec. III D,

$$\delta\Gamma_R = 0. \tag{52}$$

The total result for the relativistic correction to the two-photon decay rate thus reads as

$$\delta\Gamma = \delta\Gamma_H + \delta\Gamma_Q + \delta\Gamma_R = \Gamma_0[-0.663\,6(Z\alpha)^2]. \tag{53}$$

It is instructive to break down the corrections to the Hamiltonian further. Namely, according to Eq. (8), we have the *Zitterbewegung* (zb) term,

$$\delta H_{\text{zb}} = \frac{\pi Z\alpha}{2m}\delta^3(\vec{r}), \tag{54}$$

the kinetic energy (ke) term,

$$\delta H_{\text{ke}} = -\frac{p^4}{8m^3}, \tag{55}$$

and the spin-orbit (LS) coupling

TABLE I. Results for the γ_2 coefficient as defined in Eq. (2). This coefficient gives the relativistic corrections to the two-photon decay rate.

	$\lvert\Phi_f\rangle=\lvert 1S_{1/2}\rangle$	$\lvert\Phi_f\rangle=\lvert 2S_{1/2}\rangle$
$\lvert\Phi_i\rangle=\lvert 2S_{1/2}\rangle$	−0.6636	
$\lvert\Phi_i\rangle=\lvert 3S_{1/2}\rangle$	−2.6637	−1.7038
$\lvert\Phi_i\rangle=\lvert 4S_{1/2}\rangle$	−4.5192	−7.8530
$\lvert\Phi_i\rangle=\lvert 3D_{3/2}\rangle$	−2.2978	7.8533
$\lvert\Phi_i\rangle=\lvert 3D_{5/2}\rangle$	−1.0981	−22.2671

$$\delta H_{LS} = \frac{Z\alpha}{4m^2}\frac{\vec{L}\cdot\vec{\sigma}}{r^3}. \tag{56}$$

The corresponding results read, for the 2S-1S decay, as

$$\delta\Gamma_{\text{zb}} = \Gamma_0[-0.757\,7(Z\alpha)^2], \tag{57a}$$

$$\delta\Gamma_{\text{ke}} = \Gamma_0[0.249\,5(Z\alpha)^2], \tag{57b}$$

$$\delta\Gamma_{LS} = 0. \tag{57c}$$

This concludes our discussion of the two-photon decay of the 2S state, and we can now proceed to calculate decays from higher-excited states.

B. Higher-excited states

In principle, one might assume that in order to calculate the relativistic correction to the two-photon decay from higher-excited states, only the initial and final-state wave functions have to be changed accordingly. However, historically the generalization to higher-excited states has proven to be problematic. For higher-excited states, the two-photon transition can take place not only through virtual intermediate states with an equal or higher energy than the initial state but also through cascades via intermediates states with a lower energy. For the 3S initial state, a decay via the cascade 3S-2P-1S is possible. The allowed cascade transitions cause singularities in the propagators. As we are interested in the total decay rate, we integrate over the propagators and thereby also over the singularities. These singularities are quadratic and thus *a priori* not integrable.

Finally, after some discussion [14–19,30], the conclusion has been reached that the two-photon correction to the decay width of the initial state can be obtained using an integration prescription, where the double poles are treated in a manner inspired by quantum electrodynamics, where the photon energy integration contour extends infinitesimally into the complex plane [21,31]. Note that the two-photon correction thus obtained is a further correction that has to be added to the one-photon decay width that is otherwise responsible for the cascade transition. Using this procedure, we were able to determine the relativistic and multipole corrections to the nonrelativistic decay rate for many higher-excited states, which fulfill the same gauge relations as for the 2S-1S transition. Final results are given in Table I.

TABLE II. Results for γ_3 as defined in Eq. (2).

	$\vert\Phi_f\rangle = \vert 1S_{1/2}\rangle$	$\vert\Phi_f\rangle = \vert 2S_{1/2}\rangle$
$\vert\Phi_i\rangle = \vert 2S_{1/2}\rangle$	−2.0203	
$\vert\Phi_i\rangle = \vert 3S_{1/2}\rangle$	9.6521	16.0424
$\vert\Phi_i\rangle = \vert 4S_{1/2}\rangle$	20.7364	61.7499
$\vert\Phi_i\rangle = \vert 3D_{3/2}\rangle$	−5.4681	144.3639
$\vert\Phi_i\rangle = \vert 3D_{5/2}\rangle$	−5.4681	144.3639

V. LEADING LOGARITHMIC QED CORRECTIONS

The *Zitterbewegung* term in the relativistic Hamiltonian, according to Eq. (54), is given as $\delta H_{\rm zb} = \pi Z\alpha\delta^3(\vec{r})/(2m)$. The effective potential that gives the leading QED radiative corrections is

$$\delta H_{\rm rad} = \frac{4\alpha}{3}(Z\alpha)\ln[(Z\alpha)^{-2}]\frac{\delta^3(\vec{r})}{m^2}. \tag{58}$$

This relation implies that the γ_3 coefficient can be obtained as $8\gamma_{2,\rm zb}/3$ where $\gamma_{2,\rm zb}$ is the contribution to γ_2 caused exclusively by the *Zitterbewegung* term. As this contains no spin dependence, the γ_3 coefficient is spin independent. For the $2S$-$1S$ transition, e.g., we have according to Eq. (57a), the relation $\gamma_3 = \frac{8}{3}(-0.757\,7) = -2.020\,5$. Results for other transitions are given in Table II. The γ_3 coefficient becomes numerically rather large for $3D$-$2S$ transitions. Note that the correction is the same for the decay from $3D_{3/2}$ and $3D_{5/2}$ because the potential (58) does not involve any spin-dependent terms.

VI. CONCLUSIONS

The precise treatment of the two-photon decay width in ionic hydrogenlike bound systems with low nuclear charge numbers demands an evaluation of the relativistic and multipole correction of relative order $(Z\alpha)^2$, which is the leading correction to the classic result [1]. The leading logarithmic QED correction of relative order $\alpha(Z\alpha)^2\ln[(Z\alpha)^{-2}]$ also needs to be determined. These corrections can be parametrized according to Eq. (2) in terms of two coefficients γ_2 and γ_3, which are given in Tables I and II.

Of particular interest is the result

$$\gamma_2(2S\text{-}1S) = -0.663\,6 \tag{59}$$

for the $2S$-$1S$ decay. This result [see Eq. (53)] is the sum of a correction due to the relativistic Hamiltonian [Eq. (50)] and a correction due to the quadrupole term [Eq. (51)]. We also generalize our approach to the two-photon decay from higher-excited states (Tables I and II). As usual in quantum electrodynamic calculations, the magnitude of the correction terms grows with the principal quantum number. The decay from D states is also treated, and it is worthwhile noting that the spin-independent logarithmic correction terms of relative order $Z\alpha^2\ln(Z\alpha)$ turn out to be large in magnitude (see Table II). Finally, as shown in Appendix C below, a comparison of our results to those of a nonperturbative (in $Z\alpha$) calculation for the $3S$-$1S$ decay (Ref. [20]) reveals that the term of relative order $(Z\alpha)^2$ can account for the bulk of the relativistic correction up to some rather high nuclear charge numbers ($Z \lesssim 40$).

With our NRQED-inspired approach, we can uniquely identify the physical origin of the $(Z\alpha)^2$-correction terms to the two-photon decay width, as discussed in Secs. III B–III D, and give their values separately. It is sometimes worthwhile to use the effective nonrelativistic treatment of NRQED because it may yield information, which could not be obtained by a fully relativistic treatment, regarding the breakdown of the corrections. Furthermore, the calculation of the full spectrum of the propagator can be greatly simplified using lattice methods [32], increasing the speed as well as the numerical stability of the evaluation, which is especially important in the domain of low nuclear charge numbers.

Another aspect is that the proof of the gauge invariance, as carried out in full detail in Appendixes A and B, turns out to be a surprisingly lengthy calculation. We stress once more that the gauge invariance is shown to hold even if we ignore the gauge transformation of the wave function, in the sense of the hybrid gauge transformation developed in Refs. [11,12].

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APPENDIX A: GAUGE INVARIANCE OF THE HAMILTONIAN CORRECTION

We give further details regarding the gauge invariance of the seagull term. Useful general relations are $p^i = im[H-E+\omega, r^i]$ and $\omega_2 = E_{\Phi_i} - E_{\Phi_f} - \omega_1$. The term $\delta\xi_1$ can be transformed to

$$\begin{aligned}\delta\xi_1 &= \langle\Phi_f|\frac{p^i}{m}\left(\frac{1}{H-E_{\Phi_i}+\omega_1}\right)^2\frac{p^j}{m}|\Phi_i\rangle\langle\Phi_i|\delta H|\Phi_i\rangle \\ &= -\omega_1\omega_2\langle\Phi_f|r^i\left(\frac{1}{H-E_{\Phi_i}+\omega_1}\right)^2 r^j|\Phi_i\rangle\langle\Phi_i|\delta H|\Phi_i\rangle \\ &\quad + (\omega_2-\omega_1)\langle\Phi_f|r^i\frac{1}{H-E_{\Phi_i}+\omega_1}r^j|\Phi_i\rangle\langle\Phi_i|\delta H|\Phi_i\rangle \\ &\quad + \langle\Phi_f|r^i r^j|\Phi_i\rangle\langle\Phi_i|\delta H|\Phi_i\rangle.\end{aligned} \tag{A1}$$

An analogous relation also holds for $\delta\xi_2$,

$$\begin{aligned}\delta\xi_2 &= \langle\Phi_f|\frac{p^i}{m}\left(\frac{1}{H-E_{\Phi_f}-\omega_1}\right)^2\frac{p^j}{m}|\Phi_i\rangle\langle\Phi_f|\delta H|\Phi_f\rangle \\ &= -\omega_1\omega_2\langle\Phi_f|r^i\left(\frac{1}{H-E_{\Phi_f}-\omega_1}\right)^2 r^j|\Phi_i\rangle\langle\Phi_f|\delta H|\Phi_f\rangle + (\omega_1-\omega_2)\langle\Phi_f|r^i\frac{1}{H-E_{\Phi_f}-\omega_1}r^j|\Phi_i\rangle\langle\Phi_f|\delta H|\Phi_f\rangle \\ &\quad + \langle\Phi_f|r^i r^j|\Phi_i\rangle\langle\Phi_f|\delta H|\Phi_f\rangle. \end{aligned} \tag{A2}$$

These relations are equal to those found in Ref. [5] for a radiative correction potential. The relations for the correction to the wave functions are altered because we are considering a different Hamiltonian. Thus, $\delta\xi_3$ gives

$$\begin{aligned}\delta\xi_3 &= \langle\Phi_f|\frac{p^i}{m}\frac{1}{H-E_{\Phi_i}+\omega_1}\frac{p^j}{m}\left(\frac{1}{E_{\Phi_i}-H}\right)'\delta H|\Phi_i\rangle \\ &= -\omega_1\omega_2\langle\Phi_f|r^i\frac{1}{H-E_{\Phi_i}+\omega_1}r^j\left(\frac{1}{E_{\Phi_i}-H}\right)'\delta H|\Phi_i\rangle \\ &\quad -\omega_2\langle\Phi_f|r^i\frac{1}{H-E_{\Phi_i}+\omega_1}r^j|\Phi_i\rangle\langle\Phi_i|\delta H|\Phi_i\rangle + \underbrace{\langle\Phi_f|r^i(H-E_{\Phi_i}+\omega_2)r^j\left(\frac{1}{E_{\Phi_i}-H}\right)'\delta H|\Phi_i\rangle}_{\equiv T_3} \\ &\quad -\langle\Phi_f|r^i r^j|\Phi_i\rangle\langle\Phi_i|\delta H|\Phi_i\rangle + \langle\Phi_f|r^i r^j\delta H|\Phi_i\rangle + \omega_2\langle\Phi_f|r^i\frac{1}{H-E_{\Phi_i}+\omega_1}r^j\delta H|\Phi_i\rangle. \end{aligned} \tag{A3}$$

For $\delta\xi_4$, this yields

$$\begin{aligned}\delta\xi_4 &= \langle\Phi_f|\frac{p^i}{m}\frac{1}{H-E_{\Phi_f}-\omega_1}\frac{p^j}{m}\left(\frac{1}{E_{\Phi_i}-H}\right)'\delta H|\Phi_i\rangle \\ &= -\omega_1\omega_2\langle\Phi_f|r^i\frac{1}{H-E_{\Phi_f}-\omega_1}r^j\left(\frac{1}{E_{\Phi_i}-H}\right)'\delta H|\Phi_i\rangle \\ &\quad -\omega_1\langle\Phi_f|r^i\frac{1}{H-E_{\Phi_f}-\omega_1}r^j|\Phi_i\rangle\langle\Phi_i|\delta H|\Phi_i\rangle + \underbrace{\langle\Phi_f|r^i(H-E_{\Phi_f}-\omega_2)r^j\left(\frac{1}{E_{\Phi_i}-H}\right)'\delta H|\Phi_i\rangle}_{\equiv T_4} \\ &\quad -\langle\Phi_f|r^i r^j|\Phi_i\rangle\langle\Phi_i|\delta H|\Phi_i\rangle + \langle\Phi_f|r^i r^j\delta H|\Phi_i\rangle + \omega_1\langle\Phi_f|r^i\frac{1}{H-E_{\Phi_f}-\omega_1}r^j\delta H|\Phi_i\rangle. \end{aligned} \tag{A4}$$

For the correction $\delta\xi_5$ to the final-state wave function, we get

$$\begin{aligned}\delta\xi_5 &= \langle\Phi_f|\delta H\left(\frac{1}{E_{\Phi_f}-H}\right)'\frac{p^i}{m}\frac{1}{H-E_{\Phi_i}+\omega_1}\frac{p^j}{m}|\Phi_i\rangle \\ &= -\omega_1\omega_2\langle\Phi_f|\delta H\left(\frac{1}{E_{\Phi_f}-H}\right)'r^i\frac{1}{H-E_{\Phi_i}+\omega_1}r^j|\Phi_i\rangle \\ &\quad +\omega_1\langle\Phi_f|r^i\frac{1}{H-E_{\Phi_i}+\omega_1}r^j|\Phi_i\rangle\langle\Phi_f|\delta H|\Phi_f\rangle + \underbrace{\langle\Phi_f|\delta H\left(\frac{1}{E_{\Phi_f}-H}\right)'r^i(H-E_{\Phi_f}-\omega_1)r^j|\Phi_i\rangle}_{\equiv T_5} \\ &\quad -\langle\Phi_f|\delta H|\Phi_f\rangle\langle\Phi_f|r^i r^j|\Phi_i\rangle + \langle\Phi_f|\delta H r^i r^j|\Phi_i\rangle - \omega_1\langle\Phi_f|\delta H r^i\frac{1}{H-E_{\Phi_i}+\omega_1}r^j|\Phi_i\rangle, \end{aligned} \tag{A5}$$

and for $\delta\xi_6$

$$\delta\xi_6 = \langle\Phi_f|\delta H\left(\frac{1}{E_{\Phi_f}-H}\right)'\frac{p^i}{m}\frac{1}{H-E_{\Phi_f}-\omega_1}\frac{p^j}{m}|\Phi_i\rangle$$
$$= -\omega_1\omega_2\langle\Phi_f|\delta H\left(\frac{1}{E_{\Phi_f}-H}\right)' r^i\frac{1}{H-E_{\Phi_f}-\omega_1}r^j|\Phi_i\rangle$$
$$+\omega_2\langle\Phi_f|\delta H|\Phi_f\rangle\langle\Phi_f|r^i\frac{1}{H-E_{\Phi_f}-\omega_1}r^j|\Phi_i\rangle + \underbrace{\langle\Phi_f|\delta H\left(\frac{1}{E_{\Phi_f}-H}\right)' r^i(H-E_{\Phi_i}+\omega_1)r^j|\Phi_i\rangle}_{\equiv T_6}$$
$$-\langle\Phi_f|\delta H|\Phi_f\rangle\langle\Phi_f|r^ir^j|\Phi_i\rangle + \langle\Phi_f|\delta H r^ir^j|\Phi_i\rangle - \omega_2\langle\Phi_f|\delta H r^i\frac{1}{H-E_{\Phi_f}-\omega_1}r^j|\Phi_i\rangle. \tag{A6}$$

However, the corrections to the wave functions lead to some remainder terms, which have to be analyzed separately. They can be transformed to give

$$T_3+T_4 = \frac{1}{m}\langle\Phi_f|\left(\frac{1}{E_{\Phi_i}-H}\right)'\delta H|\Phi_i\rangle\delta^{ij} + \langle\Phi_f|r^ir^j|\Phi_i\rangle\langle\Phi_i|\delta H|\Phi_i\rangle - \langle\Phi_f|r^ir^j\delta H|\Phi_i\rangle, \tag{A7}$$

$$T_5+T_6 = \frac{1}{m}\langle\Phi_f|\delta H\left(\frac{1}{E_{\Phi_f}-H}\right)'|\Phi_i\rangle\delta^{ij} + \langle\Phi_f|\delta H|\Phi_f\rangle\langle\Phi_f|r^ir^j|\Phi_i\rangle - \langle\Phi_f|\delta H r^ir^j|\Phi_i\rangle. \tag{A8}$$

We observe the seagull terms $\delta\xi_{14}$ and $\delta\xi_{15}$ emerge and cancel, explicitly. The other terms on the right-hand side will be treated separately, later. The term $\delta\xi_7$ arising from the correction of the Hamiltonian can be brought into length-gauge form in the following way:

$$\delta\xi_7 = -\langle\Phi_f|\frac{p^i}{m}\frac{1}{H-E_{\Phi_i}+\omega_1}\delta H\frac{1}{H-E_{\Phi_i}+\omega_1}\frac{p^j}{m}|\Phi_i\rangle = \omega_1\omega_2\langle\Phi_f|r^i\frac{1}{H-E_{\Phi_i}+\omega_1}\delta H\frac{1}{H-E_{\Phi_i}+\omega_1}r^j|\Phi_i\rangle,$$
$$-\omega_2\langle\Phi_f|r^i\frac{1}{H-E_{\Phi_i}+\omega_1}\delta H r^j|\Phi_i\rangle + \omega_1\langle\Phi_f|r^i\delta H\frac{1}{H-E_{\Phi_i}+\omega_1}r^j|\Phi_i\rangle - \langle\Phi_f|r^i\delta H r^j|\Phi_i\rangle. \tag{A9}$$

Finally, for $\delta\xi_8$ we have

$$\delta\xi_8 = -\langle\Phi_f|\frac{p^i}{m}\frac{1}{H-E_{\Phi_f}-\omega_1}\delta H\frac{1}{H-E_{\Phi_f}-\omega_1}\frac{p^j}{m}|\Phi_i\rangle$$
$$= \omega_1\omega_2\langle\Phi_f|r^i\frac{1}{H-E_{\Phi_f}-\omega_1}\delta H\frac{1}{H-E_{\Phi_f}-\omega_1}r^j|\Phi_i\rangle$$
$$-\omega_1\langle\Phi_f|r^i\frac{1}{H-E_{\Phi_f}-\omega_1}\delta H r^j|\Phi_i\rangle + \omega_2\langle\Phi_f|r^i\delta H\frac{1}{H-E_{\Phi_f}-\omega_1}r^j|\Phi_i\rangle - \langle\Phi_f|r^i\delta H r^j|\Phi_i\rangle. \tag{A10}$$

Our intermediate result thus reads as follows:

$$\sum_{i=1}^{8}\delta\xi_i = -\omega_1\omega_2\sum_{i=1}^{8}\delta\zeta_i - \delta\omega_{\max}\omega_1\zeta + \omega_2\langle\Phi_f|r^i\frac{1}{H-E_{\Phi_i}+\omega_1}[r^j,\delta H]|\Phi_i\rangle + \omega_1\langle\Phi_f|r^i\frac{1}{H-E_{\Phi_f}-\omega_1}[r^j,\delta H]|\Phi_i\rangle$$
$$+\omega_2\langle\Phi_f|[r^i,\delta H]\frac{1}{H-E_{\Phi_i}+\omega_1}r^j|\Phi_i\rangle + \omega_1\langle\Phi_f|[r^i,\delta H]\frac{1}{H-E_{\Phi_f}-\omega_1}r^j|\Phi_i\rangle - \langle\Phi_f|[[r^i,\delta H],r^j]|\Phi_i\rangle, \tag{A11}$$

where $\delta\omega_{\max}$ is defined in Eq. (21b). Fortunately, we can rewrite the terms with the $[r^j,\delta H]$ commutators further,

$$\omega_1\langle\Phi_f|[r^i,\delta H]\frac{1}{H-E_{\Phi_i}+\omega_1}r^j|\Phi_i\rangle + \omega_2\langle\Phi_f|[r^i,\delta H]\frac{1}{H-E_{\Phi_f}-\omega_1}r^j|\Phi_i\rangle$$
$$+\omega_2\langle\Phi_f|r^i\frac{1}{H-E_{\Phi_i}+\omega_1}[r^j,\delta H]|\Phi_i\rangle + \omega_1\langle\Phi_f|r^i\frac{1}{H-E_{\Phi_f}-\omega_1}[r^j,\delta H]|\Phi_i\rangle$$
$$= -\langle\Phi_f|\delta J_H\frac{1}{H-E_{\Phi_i}+\omega_1}\frac{p^j}{m}|\Phi_i\rangle - \langle\Phi_f|\delta J_H\frac{1}{H-E_{\Phi_f}-\omega_1}\frac{p^j}{m}|\Phi_i\rangle - \langle\Phi_f|\frac{p^i}{m}\frac{1}{H-E_{\Phi_i}+\omega_1}\delta J_H|\Phi_i\rangle$$
$$-\langle\Phi_f|\frac{p^i}{m}\frac{1}{H-E_{\Phi_f}-\omega_1}\delta J_H|\Phi_i\rangle + 2\langle\Phi_f|[[r^i,\delta H],r^j]|\Phi_i\rangle,$$
$$= -\sum_{i=9}^{12}\delta\xi_i\Bigg|_{\delta J=\delta J_H} + 2\langle\Phi_f|[[r^i,\delta H],r^j]|\Phi_i\rangle. \tag{A12}$$

The current $J_H = -i[r^i,\delta H]$ is defined in Eq. (33). Combining Eqs. (A11) and (A12), we obtain the relation

$$\sum_{i=1}^{8}\delta\xi_i + \sum_{i=9}^{12}\delta\xi_i\Bigg|_{\delta J=\delta J_H} = -\omega_1\omega_2\sum_{i=1}^{8}\delta\zeta_i - \delta\omega_{\max}\omega_1\zeta - \delta\xi_{13}|_{\delta S=\delta S_H}. \tag{A13}$$

With the definitions (35) and (36), this leads directly to our gauge-invariance relation (31).

APPENDIX B: GAUGE INVARIANCE OF THE QUADRUPOLE CORRECTION

For the proof of gauge invariance of the quadrupole correction, it is more convenient to start from the length-gauge expression. As the quadrupole term is a correction to the transition current, only the terms $\delta\zeta_{9,\ldots,12}$ are relevant. The length-gauge transition current δI is [see Eq. (38)]

$$\delta I_Q^i = r^i\left[-\frac{1}{6}(\vec{k}\cdot\vec{r})^2\right] + \frac{1}{6m\omega}[(\vec{L}\times\vec{k})^i(-i\vec{k}\cdot\vec{r}) + (-i\vec{k}\cdot\vec{r})(\vec{L}\times\vec{k})^i]. \tag{B1}$$

It is helpful to rewrite the second part of the transition current as

$$(\vec{L}\times\vec{k})^i(-i\vec{k}\cdot\vec{r}) + (-i\vec{k}\cdot\vec{r})(\vec{L}\times\vec{k})^i = (\vec{k}\cdot\vec{r})p^i(-i\vec{k}\cdot\vec{r}) - r^i(\vec{k}\cdot\vec{p})(-i\vec{k}\cdot\vec{r}) + (-i\vec{k}\cdot\vec{r})(\vec{k}\cdot\vec{r})p^i - (-i\vec{k}\cdot\vec{r})r^i(\vec{k}\cdot\vec{p}). \tag{B2}$$

Using this and the general relations from Appendix A, we can transform the first term $\delta\zeta_9$ to give

$$-\omega_1\omega_2\delta\zeta_9 = \omega_2\frac{1}{6}\langle\Phi_f|r^i\frac{1}{H-E_{\Phi_i}+\omega_1}\left\{\omega_1(\vec{k}_1\cdot\vec{r})^2r^j + \frac{i}{m}[(\vec{L}\times\vec{k}_1)^j(\vec{k}_1\cdot\vec{r}) + (\vec{k}_1\cdot\vec{r})(\vec{L}\times\vec{k}_1)^j]\right\}|\Phi_i\rangle$$
$$= \langle\Phi_f|\frac{p^i}{m}\frac{1}{H-E_{\Phi_i}+\omega_1}\left[-\frac{1}{2}(\vec{k}_1\cdot\vec{r})\right]\frac{p^j}{m}|\Phi_i\rangle - \frac{1}{6}\omega_1\langle\Phi_f|r^i(\vec{k}_1\cdot\vec{r})^2r^j|\Phi_i\rangle$$
$$+\frac{i}{6}\langle\Phi_f|\frac{p^i}{m}(\vec{k}_1\cdot\vec{r})^2r^j|\Phi_i\rangle - \left(\frac{i}{6}k_1^lk_1^m\right)\langle\Phi_f|r^ir^l\frac{p^j}{m}r^m - r^ir^j\frac{p^l}{m}r^m + r^ir^mr^l\frac{p^j}{m} - r^ir^mr^j\frac{p^l}{m}|\Phi_i\rangle. \tag{B3}$$

For $\delta\zeta_{10}$, we obtain in an analogous manner

$$-\omega_1\omega_2\delta\zeta_{10} = \omega_1\frac{1}{6}\langle\Phi_f|r^i\frac{1}{H-E_{\Phi_f}-\omega_1}\left\{\omega_2(\vec{k}_2\cdot\vec{r})^2r^j + \frac{i}{m}[(\vec{L}\times\vec{k}_2)^j(\vec{k}_2\cdot\vec{r}) + (\vec{k}_2\cdot\vec{r})(\vec{L}\times\vec{k}_2)^j]\right\}|\Phi_i\rangle$$
$$= \langle\Phi_f|\frac{p^i}{m}\frac{1}{H-E_{\Phi_f}-\omega_1}\left[-\frac{1}{2}(\vec{k}_2\cdot\vec{r})\right]\frac{p^j}{m}|\Phi_i\rangle - \frac{1}{6}\omega_2\langle\Phi_f|r^i(\vec{k}_2\cdot\vec{r})^2r^j|\Phi_i\rangle$$
$$+\frac{i}{6}\langle\Phi_f|\frac{p^i}{m}(\vec{k}_2\cdot\vec{r})^2r^j|\Phi_i\rangle - \left(\frac{i}{6}k_2^lk_2^m\right)\langle\Phi_f|r^ir^l\frac{p^j}{m}r^m - r^ir^j\frac{p^l}{m}r^m + r^ir^mr^l\frac{p^j}{m} - r^ir^mr^j\frac{p^l}{m}|\Phi_i\rangle. \tag{B4}$$

For the correction $\delta\zeta_{11}$ with the current acting on the left side, this yields

$$-\omega_1\omega_2\delta\zeta_{11} = \omega_1\frac{1}{6}\langle\Phi_f|\left\{\omega_2(\vec{k}_2\cdot\vec{r})^2 r^i + \frac{i}{m}[(\vec{L}\times\vec{k}_2)^i(\vec{k}_2\cdot\vec{r}) + (\vec{k}_2\cdot\vec{r})(\vec{L}\times\vec{k}_2)^i]\right\}\frac{1}{H-E_{\Phi_i}+\omega_1}r^j|\Phi_i\rangle$$
$$= \langle\Phi_f|\frac{p^i}{m}\left[-\frac{1}{2}(\vec{k}_2\cdot\vec{r})\right]\frac{1}{H-E_{\Phi_i}+\omega_1}\frac{p^j}{m}|\Phi_i\rangle + \frac{1}{6}\omega_2\langle\Phi_f|r^i(\vec{k}_2\cdot\vec{r})^2 r^j|\Phi_i\rangle$$
$$-\frac{i}{6}\langle\Phi_f|r^i(\vec{k}_2\cdot\vec{r})^2\frac{p^j}{m}|\Phi_i\rangle + \left(\frac{i}{6}k_2^l k_2^m\right)\langle\Phi_f|r^l\frac{p^i}{m}r^m r^j - r^i\frac{p^l}{m}r^m r^j + r^m r^l\frac{p^i}{m}r^j - r^m r^i\frac{p^l}{m}r^j|\Phi_i\rangle, \quad \text{(B5)}$$

and finally for $\delta\zeta_{12}$,

$$-\omega_1\omega_2\delta\zeta_{12} = \omega_2\frac{1}{6}\langle\Phi_f|\left\{\omega_1(\vec{k}_1\cdot\vec{r})^2 r^i + \frac{i}{m}[(\vec{L}\times\vec{k}_1)^i(\vec{k}_1\cdot\vec{r}) + (\vec{k}_1\cdot\vec{r})(\vec{L}\times\vec{k}_1)^i]\right\}\frac{1}{H-E_{\Phi_f}-\omega_1}r^j|\Phi_i\rangle$$
$$= \langle\Phi_f|\frac{p^i}{m}\left[-\frac{1}{2}(\vec{k}_1\cdot\vec{r})\right]\frac{1}{H-E_{\Phi_f}-\omega_1}\frac{p^j}{m}|\Phi_i\rangle + \frac{1}{6}\omega_1\langle\Phi_f|r^i(\vec{k}_1\cdot\vec{r})^2 r^j|\Phi_i\rangle$$
$$-\frac{i}{6}\langle\Phi_f|r^i(\vec{k}_1\cdot\vec{r})^2\frac{p^j}{m}|\Phi_i\rangle + \left(\frac{i}{6}k_1^l k_1^m\right)\langle\Phi_f|r^l\frac{p^i}{m}r^m r^j - r^i\frac{p^l}{m}r^m r^j + r^m r^l\frac{p^i}{m}r^j - r^m r^i\frac{p^l}{m}r^j|\Phi_i\rangle. \quad \text{(B6)}$$

Combining these results, we get

$$-\omega_1\omega_2\sum_{i=9}^{12}\delta\zeta\Bigg|_{\delta I=\delta I_Q} = \sum_{i=9}^{12}\delta\xi\Bigg|_{\delta J=\delta J_Q} - \left(\frac{i}{6}k_1^l k_1^m\right)\langle\Phi_f|r^i r^l\frac{p^j}{m}r^m - r^i r^j\frac{p^l}{m}r^m + r^i r^m r^l\frac{p^j}{m} - r^i r^m r^j\frac{p^l}{m} - \frac{p^i}{m}r^l r^m r^j|\Phi_i\rangle$$
$$-\left(\frac{i}{6}k_2^l k_2^m\right)\langle\Phi_f|r^i r^l\frac{p^j}{m}r^m - r^i r^j\frac{p^l}{m}r^m + r^i r^m r^l\frac{p^j}{m} - r^i r^m r^j\frac{p^l}{m} - \frac{p^i}{m}r^l r^m r^j|\Phi_i\rangle$$
$$+\left(\frac{i}{6}k_2^l k_2^m\right)\langle\Phi_f|r^l\frac{p^i}{m}r^m r^j - r^i\frac{p^l}{m}r^m r^j + r^m r^l\frac{p^i}{m}r^j - r^m r^i\frac{p^l}{m}r^j - r^i r^l r^m\frac{p^j}{m}|\Phi_i\rangle$$
$$+\left(\frac{i}{6}k_1^l k_1^m\right)\langle\Phi_f|r^l\frac{p^i}{m}r^m r^j - r^i\frac{p^l}{m}r^m r^j + r^m r^l\frac{p^i}{m}r^j - r^m r^i\frac{p^l}{m}r^j - r^i r^l r^m\frac{p^j}{m}|\Phi_i\rangle. \quad \text{(B7)}$$

In order to simplify the resulting expression, we now commute the momentum operators in the remainder terms to the right side of the position operators,

$$-\omega_1\omega_2\sum_{i=9}^{12}\delta\zeta\Bigg|_{\delta I=\delta I_Q} = \sum_{i=9}^{12}\delta\xi\Bigg|_{\delta J=\delta J_Q} + \langle\Phi_f|\frac{1}{2m}\delta^{ij}(\vec{k}_1\cdot\vec{r})^2|\Phi_i\rangle + \langle\Phi_f|\frac{1}{2m}\delta^{ij}(\vec{k}_2\cdot\vec{r})^2|\Phi_i\rangle. \quad \text{(B8)}$$

The last two terms can be identified as the negative of the quadrupole contribution to the higher-order seagull term as given in Eq. (39) summed over the two-photon momenta k_1 and k_2. Finally, this leads to the equality

$$-\omega_1\omega_2\sum_{i=9}^{12}\delta\zeta\Bigg|_{\delta I=\delta I_Q} = \sum_{i=9}^{12}\delta\xi\Bigg|_{\delta J=\delta J_Q} + \delta\xi_{13}|_{\delta S=\delta S_Q}, \quad \text{(B9)}$$

which verifies the gauge-invariance relation given in Eq. (40).

APPENDIX C: COMPARISON OF ANALYTIC AND NUMERICAL RESULTS

We would like to compare our results for the analytic coefficients listed in Tables I and II to numerical data obtained for 2S-1S (see Ref. [7]) and 3S-1S (see Ref. [20]). The authors of Ref. [7] obtained a fit to a convenient functional form in $Z\alpha$, leading to an approximate formula valid across the whole range of nuclear charge numbers Z [see Ref. [7] and also Eq. (4.16) of Ref. [33]],

$$\Gamma \approx \Gamma_0\frac{1+3.944\,8(Z\alpha)^2 - 2.040(Z\alpha)^4}{1+4.601\,9(Z\alpha)^2}. \quad \text{(C1)}$$

Upon re-expansion in $Z\alpha$, one may thus hope to obtain an estimate for the correction of relative order $(Z\alpha)^2$. Indeed, the estimate thus obtained $\gamma_2 \approx -0.657\,1$ is in fair agreement with the precise result (59), which reads as $\gamma_2 = -0.663\,6$.

For the 3S-1S decay, we compare to a fully relativistic calculation carried out in Ref. [20], where the relativistic effects have been calculated for different values of Z. When using our results for γ_2, one can determine the corrected decay rate for different values of Z. For $Z=40$, our analytic results augmented by the relativistic correction of relative order $(Z\alpha)^2$ lead to a result of $\Gamma \approx 1.61(Z=40)^6$ rad/s to be compared with the result $\Gamma = 1.60(Z=40)^6$ rad/s from Ref. [20] for the $E1E1$ two-photon decay rate.

In general, there is quite a subtle interplay of the fully relativistic calculations with the Dirac-Coulomb propagator, which have meanwhile been done for a number of QED and other problems and the $Z\alpha$-expansion approach. Numerically, more accurate results can be obtained with the former, and these are relevant especially for highly charged ions, but the physical origin of the relativistic corrections is much more transparent within the $Z\alpha$ expansion. Furthermore, the analytic calculations allow for a systematic expansion in powers of α and $Z\alpha$, as demonstrated in Eq. (2).

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