Algebraic relations from finite-nuclear-mass effects to test atomic transition rates

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General algebraic relations are derived which provide a stringent test of the accuracy of n-photon electric dipole transition rates when mass-polarization effects are included. They are a generalization of the well-known equivalence of the length, velocity, and acceleration forms of the transition matrix element that follows from gauge invariance. The algebraic relations connect the coefficients in a power series in powers of μ/M for the three gauges, where M is the nuclear mass and μ is the electron reduced mass. These relations also provide a stringent test of the leading infinite-mass term, a quantity that must be calculated with sufficient accuracy for the higher-order terms in powers of μ/M to be correct. As a check, the length-velocity algebraic relations are used to test the accuracy of high-precision calculations for both one-photon ($1s2p\ ^1P - 1s^2\ ^1S$ and $1s2p\ ^3P - 1s2s\ ^3S$) and two-photon ($1s2s\ ^1S - 1s^2\ ^1S$) decay for the heliumlike ions with $Z = 2$–10.

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I. INTRODUCTION

The length, velocity, and acceleration gauges of the dipole matrix element for radiative transition probabilities for atoms and molecules are widely used in comparison as a theoretical check on the accuracy of calculations of quantities, including polarizabilities and decay rates [1]. These gauges can be regarded as particular values of a continuous gauge parameter controlling longitudinal and scalar contributions to the vector potential $\mathbf{A}(\mathbf{r}, t)$ [2]. In the limit of an infinite nuclear mass, the gauges should agree to the extent that the wave functions used are exact. Agreement in the corresponding finite-mass case requires careful treatment of gauge-dependent finite-mass effects. Otherwise, the gauges will disagree due to neglected terms of order μ/M, where M is the nuclear mass and μ is the reduced mass of the electron. The purpose of this paper is to derive algebraic relations which quantify the gauge agreement for any n-photon ($nE1$) finite-mass transition rate and to demonstrate that they are satisfied for heliumlike ions via numerical calculations.

One- and two-photon processes are ubiquitous in atomic physics. One-photon ($E1$) and two-photon ($2E1$) transition rates are used in numerous astrophysical applications (e.g., [3–5]). Resonant rates are important generally in astrophysical emission, and forbidden rates such as the two-photon decay rates are important in the limit of low particle density such as in the characterization of planetary nebulae. The lifetimes of the resonant states are largely determined by the $E1$ decay mechanism [6]. In heliumlike ions, on which we focus in this paper, two-photon decay rates have been calculated more accurately over time, beginning with Göppert-Mayer [7], then Breit and Teller [8] and Dalgarno and Bates [9]. Finite-nuclear-mass effects (hereafter "finite-mass effects") were considered by Fried and Martin [10], Drake [11], and, most recently, Bondy *et al.* [12]. In Ref. [12], algebraic relations were derived to compare decay-rate calculations that include finite-mass effects in the length and velocity gauges to approximately 1 part in 10^8. This method works even for the exotic $\bar{p}^2$-He, where $\mu/M \approx 0.2011$. The present paper generalizes and extends the results of Ref. [12], presenting a full derivation of the resulting algebraic relations for $nE1$ transition rates in heliumlike ions up to approximately 1 part in 10^{12}, and includes the algebraic relationships involving the acceleration gauge.

There has been increasing interest in exotic particles such as muonic, pionic, and even antiprotonic helium, where the electron is replaced by a heavier particle. The Lamb shift in muonic hydrogen was measured by Pohl *et al.* [13], igniting the "proton puzzle," with further measurements by Nebel *et al.* [14]. Theoretical characterization of the muonic Lamb shift was carried out by Pachucki [15]. Posada *et al.* [16] calculated the so-called quantum muon effect in muonic helium and muonic lithium to rigorously study ionization potentials in a physical chemistry application. In one-electron plasma physics, Poszwa *et al.* [17] studied the finite-mass and finite-size effects on muonic hydrogenlike atoms in a Debye plasma. Clearly, exotic few-electron systems play an important role in fundamental physics, and the characterization of finite-mass effects is very important because these effects are much larger than in their electronic counterparts.

In addition to finite-mass corrections of order μ/M, high-precision calculations also require consideration of relativistic corrections of order $(\alpha Z)^2$, where $\alpha \simeq 1/137$ is the fine-structure constant and Z is the nuclear charge. In low-Z heliumlike ions, these effects are of comparable size and are both needed for precise comparison with astrophysical observation and experiment (see, e.g., Drake and Morton [18]), but at lowest order, they can be treated independently. This paper is concerned exclusively with finite-mass effects. Relativistic effects can be found for the one-photon oscillator strengths in Głowacki [19] using relativistic configuration interaction (RCI) wave functions; in transition amplitudes in helium in the work of Johnson *et al.* [20], where eigenfunctions of the no-pair Hamiltonian were used to characterize the role of negative energy states in obtaining gauge agreement; and in the spin-forbidden electric dipole transitions in transition rates in neutral helium by Morton *et al.* [21]. Relativistic effects have been included for the two-photon decay of the $n = 2$ metastable states in heliumlike ions by Drake, who quantitatively estimated them in [11], and by Derevianko and Johnson using an RCI calculation [22].

The balance of this paper is organized as follows. The theory of one- and two-photon transition rates in the framework of Fermi's golden rule is reviewed in Sec. II. In Sec. III, the constitutive relations between the finite- and infinite-mass transition rates in the length, velocity, and acceleration gauges are derived, and the algebraic relations on which the paper is focused are established. General relations, valid for any $nE1$ transition-rate calculation, are given in Sec. III B. Calculations which confirm the length-velocity algebraic relations for the case of one- and two-photon decay in heliumlike ions are described and presented in Sec. IV. A discussion of the results is presented in Sec. V, along with the outlook for future work. The Appendix provides explicit perturbation expressions for the algebraic quantities, with μ/M regarded as a perturbation parameter.

II. THEORY

Although the basic formalism of radiative transition rates is well known, it is valuable to go through the details to ensure that all finite-mass effects are properly included. Following Ref. [12], the discussion of finite-mass effects in light ($Z \leqslant 10$) atoms begins with the nonrelativistic Schrödinger equation,

$$H_{\rm inert}|\psi\rangle = E_{\rm NR}|\psi\rangle, \tag{1}$$

with the Hamiltonian

$$H_{\rm inert} = \frac{\mathbf{P}_{\rm N}^2}{2M} + \sum_{i=1}^{N}\left(\frac{\mathbf{P}_i^2}{2m_{\rm e}} - \frac{Ze^2/4\pi\epsilon_0}{|\mathbf{R}_i - \mathbf{R}_N|} + \sum_{j>i}^{N}\frac{e^2/4\pi\epsilon_0}{|\mathbf{R}_j - \mathbf{R}_i|}\right), \tag{2}$$

where $\mathbf{R}_i$, $\mathbf{R}_N$, $\mathbf{P}_i$, $\mathbf{P}_N$, m_e, and M are the positions, momenta, and masses of the electrons and nucleus, respectively. In center-of-mass (c.m.) coordinates,

$$\mathbf{R}_{\rm cm} = \frac{M\mathbf{R}_{\rm N} + m_{\rm e}\sum\mathbf{R}_i}{M + 2m_{\rm e}}, \tag{3}$$

$$\mathbf{r}_i = \mathbf{R}_i - \mathbf{R}_{\rm N}, \tag{4}$$

$$H_{\rm cm} = \frac{1}{2\mu}\sum_{i=1}^{N}\mathbf{p}_i^2 + \frac{1}{M}\sum_{i=1}^{N}\sum_{j>i}^{N}\mathbf{p}_i\cdot\mathbf{p}_j + \frac{1}{2(M+2m_{\rm e})}\mathbf{P}_{\rm cm}^2 - \sum_{i=1}^{N}\left(\frac{Ze^2/4\pi\epsilon_0}{|\mathbf{r}_i|} + \sum_{j>i}^{N}\frac{e^2/4\pi\epsilon_0}{|\mathbf{r}_j - \mathbf{r}_i|}\right), \tag{5}$$

where $\mu = \frac{m_e M}{m_e + M}$ is the reduced mass. The second term involving the double sum of $\mathbf{p}_i\cdot\mathbf{p}_j$, defines the mass-polarization term, which vanishes in the limit of infinite nuclear mass $M \to \infty$. The third term describes the motion of the c.m. in the inertial frame, and so it can be neglected for an atom in free space.

To treat interactions with the electromagnetic field, we now introduce the interaction Hamiltonian. The vector potential of the electromagnetic field that interacts with the atom is described by

$$\mathbf{A}(\mathbf{R}, t) = A_0(\omega)\hat{\boldsymbol{\epsilon}}\, e^{i\mathbf{k}\cdot\mathbf{R} - i\omega t} + \text{c.c.}, \tag{6}$$

where

$$A_0(\omega) = c\left(\frac{\hbar}{2\epsilon_o\omega\mathcal{V}}\right)^{1/2} \tag{7}$$

corresponds to a photon of frequency ω, wave vector $\mathbf{k}$ ($|\mathbf{k}| = \omega/c$), and polarization $\hat{\boldsymbol{\epsilon}} \perp \mathbf{k}$ normalized to an energy of $\hbar\omega$ in the volume $\mathcal{V}$. This work assumes the long-wavelength and electric dipole approximations, so the factor $e^{i\mathbf{k}\cdot\mathbf{R}}$ in Eq. (6) is replaced by unity so that $\mathbf{A} = A_0\hat{\boldsymbol{\epsilon}}$. In the semiclassical approximation the minimal coupling replacements

$$\mathbf{P}_{\rm N} \to \mathbf{P}_{\rm N} - Ze\mathbf{A}(\mathbf{R}_{\rm N}), \tag{8}$$

$$\mathbf{P}_i \to \mathbf{P}_i + e\mathbf{A}(\mathbf{R}_i) \tag{9}$$

are made in the inertial Hamiltonian given in Eq. (2). The interaction Hamiltonian in the inertial frame is

$$H_{\rm int} = -\frac{Ze}{Mc}\mathbf{P}_{\rm N}\cdot\mathbf{A}(\mathbf{R}_{\rm N}) + \frac{e}{m_e c}\sum_{i=1}^{N}\mathbf{P}_i\cdot\mathbf{A}(\mathbf{R}_i) \tag{10}$$

and will be written in the appropriate c.m. frame in the ensuing equations.

A. One-photon transitions

For the sake of definiteness, we consider the case of spontaneous emission. However, the same algebraic relations apply to the cases of absorption and stimulated emission. Between an initial state $|i\rangle$ and a final state $|f\rangle$, the decay rate is given by Fermi's golden rule,

$$w_{\rm i,f}\,d\Omega = \frac{2\pi}{\hbar}|\langle i|H_{\rm int}|f\rangle|^2\rho(\omega)\,d\Omega, \tag{11}$$

where

$$\rho(\omega) = \frac{\mathcal{V}\omega^2}{(2\pi c)^3\hbar} \tag{12}$$

is the density of states of photons in a volume $\mathcal{V}$ with frequency ω. This can be summed over polarizations and integrated over solid angles $d\Omega$ [23] to give a total decay rate of

$$w_{\rm i,f} = \tfrac{4}{3}\alpha\omega_{\rm i,f}|\langle i|\mathbf{Q}_x|f\rangle|^2, \tag{13}$$

where α is the fine-structure constant, $\omega_{i,f} = (E_i - E_f)/\hbar$, and $x = r$, p, a for the length, velocity, and acceleration forms of the dipole operator. For the velocity form, it follows directly from Eqs. (6) to (12) that

$$\mathbf{Q}_p = -\frac{Z}{Mc}\mathbf{P}_{\rm N} + \frac{1}{m_e c}\sum_{i=1}^{N}\mathbf{P}_i. \tag{14}$$

The length form $\mathbf{Q}_r$ can then be obtained by requiring that the commutation relation

$$[H_{\rm inert}, \mathbf{Q}_r/\hbar\omega_{\rm i,f}] = \mathbf{Q}_p \tag{15}$$

be satisfied, which yields

$$\mathbf{Q}_r = -\frac{i}{c}\omega_{\mathrm{i,f}}\left(Z\mathbf{R}_{\mathrm{N}} - \sum_{i=1}^{N}\mathbf{R}_i\right). \tag{16}$$

The dipole operator in the acceleration form $\mathbf{Q}_a$ can be obtained using the commutation relation

$$[H_{\mathrm{inert}}, \mathbf{Q}_p/\hbar\omega_{\mathrm{i,f}}] = \mathbf{Q}_a, \tag{17}$$

where

$$\mathbf{Q}_a = \frac{iZ}{m_e c\,\omega_{\mathrm{i,f}}}\frac{Zm_e + M}{M}\sum_{i=1}^{N}\frac{(\mathbf{R_i} - \mathbf{R}_{\mathrm{N}})}{|\mathbf{R_i} - \mathbf{R}_{\mathrm{N}}|^3}. \tag{18}$$

Although the numerical tests in this work (as in Ref. [12]) are performed for the length and velocity forms, we present the corresponding acceleration forms throughout the paper and extend the algebraic relations we derive to include this acceleration form.

To study mass-polarization effects, $\mathbf{Q}_p$, $\mathbf{Q}_r$, and $\mathbf{Q}_a$ must be transformed to c.m. plus relative coordinates to conform with the Hamiltonian in Eq. (5), with the result

$$\mathbf{Q}_p = \frac{Z_p}{m_e c}\sum_{i=1}^{N}\mathbf{p}_i,$$

$$\mathbf{Q}_r = \frac{i\omega_{\mathrm{i,f}}}{c}Z_r\sum_{i=1}^{N}\mathbf{r}_i,$$

$$\mathbf{Q}_a = \frac{iZ}{m_e c\,\omega_{\mathrm{i,f}}}Z_p\sum_{i=1}^{N}\frac{\mathbf{r}_i}{|\mathbf{r}_i|^3}, \tag{19}$$

where

$$Z_p = \frac{Zm_e + M}{M}, \quad Z_r = \frac{Zm_e + M}{Nm_e + M},$$

and the number of electrons is $N = 2$ for heliumlike atoms. The Z_p and Z_r terms account for the radiation produced by the nucleus as it moves in the c.m. frame. These operators satisfy

$$[H_{\mathrm{cm}}, \mathbf{Q}_r] = \hbar\omega_{\mathrm{i,f}}\mathbf{Q}_p, \quad [H_{\mathrm{cm}}, \mathbf{Q}_p] = \hbar\omega_{\mathrm{i,f}}\mathbf{Q}_a \tag{20}$$

in the c.m. frame. To the extent that the nonrelativistic Schrödinger equation, Eq. (1), is solved exactly, the relation

$$\langle i|\mathbf{Q}_r|f\rangle = \langle i|\mathbf{Q}_p|f\rangle = \langle i|\mathbf{Q}_a|f\rangle \tag{21}$$

is satisfied.

B. Two-photon transitions

According to Fermi's golden rule, the triply differential rate for two-photon decay is

$$dw^{(2\gamma)}d\Omega_1\,d\Omega_2 = \frac{2\pi}{\hbar}\left|U^{(2)}_{\mathrm{i,f}}\right|^2\rho(\omega_1)\rho(\omega_2)d\Omega_1\,d\Omega_2\,dE_1. \tag{22}$$

As in the one-photon case shown in Eq. (12), $\rho(\omega_1)$ and $\rho(\omega_2)$ are the densities of photon states, subject to the energy-conserving condition

$$E_{\mathrm{i}} - E_{\mathrm{f}} = \hbar\omega_1 + \hbar\omega_2. \tag{23}$$

The second-order transitions are described by interaction with the electromagnetic vacuum by [24]

$$U^{(2)}_{\mathrm{i,f}} = -\sum_n\left[\frac{\langle f|H_{\mathrm{int}}(\omega_1)|n\rangle\langle n|H_{\mathrm{int}}(\omega_2)|i\rangle}{E_n - E_{\mathrm{i}} + \hbar\omega_2} + \frac{\langle f|H_{\mathrm{int}}(\omega_2)|n\rangle\langle n|H_{\mathrm{int}}(\omega_1)|i\rangle}{E_n - E_{\mathrm{i}} + \hbar\omega_1}\right]. \tag{24}$$

In the dipole approximation ($\mathbf{A} = A_0\hat{\epsilon}$), together with Eq. (12) for $\rho(\omega)$ and Eq. (7) for A_0, the two-photon decay rate is [12]

$$w^{(2\gamma)} = \frac{1}{2}\int_0^{\Delta}\frac{dw^{(2\gamma)}}{d\omega_1}d\omega_1 = \frac{4\alpha^2\Delta}{3\pi}\int_0^1|Q^{(2\gamma)}(y)|^2dy, \tag{25}$$

with $y = \omega_1/\Delta$ and $\Delta = (E_i - E_f)/\hbar$. The length, velocity, and acceleration forms of this dipole operator $Q^{(2\gamma)}$ are

$$Q^{(2\gamma)}_p(\omega_1,\omega_2) = -(\omega_1\omega_2)^{1/2}\sum_n\langle 1\ {}^1S\,|Q'_{p,z}|n\ {}^1P\rangle\langle n\ {}^1P\,|Q'_{p,z}|2\ {}^1S\rangle\left(\frac{1}{\omega_n - \omega_{\mathrm{i}} + \omega_2} + \frac{1}{\omega_n - \omega_{\mathrm{i}} + \omega_1}\right), \tag{26}$$

$$Q^{(2\gamma)}_r(\omega_1,\omega_2) = -(\omega_1\omega_2)^{1/2}\sum_n\langle 1\ {}^1S\,|Q'_{r,z}|n\ {}^1P\rangle\langle n\ {}^1P\,|Q'_{r,z}|2\ {}^1S\rangle\left(\frac{1}{\omega_n - \omega_{\mathrm{i}} + \omega_2} + \frac{1}{\omega_n - \omega_{\mathrm{i}} + \omega_1}\right), \tag{27}$$

$$Q^{(2\gamma)}_a(\omega_1,\omega_2) = -(\omega_1\omega_2)^{1/2}\sum_n\langle 1\ {}^1S\,|Q'_{a,z}|n\ {}^1P\rangle\langle n\ {}^1P\,|Q'_{a,z}|2\ {}^1S\rangle\left(\frac{1}{\omega_n - \omega_{\mathrm{i}} + \omega_2} + \frac{1}{\omega_n - \omega_{\mathrm{i}} + \omega_1}\right), \tag{28}$$

with

$$\mathbf{Q}'_p = \frac{1}{m_e c}Z_p\sum_{i=1}^{N}\mathbf{p}_i, \tag{29}$$

$$\mathbf{Q}'_r = \frac{i(\omega_1\omega_2)^{1/2}}{c}Z_r\sum_{i=1}^{N}\mathbf{r}_i, \tag{30}$$

$$\mathbf{Q}'_a = \frac{iZ}{m_e c\,(\omega_1\omega_2)^{1/2}}Z_p\sum_{i=1}^{N}\frac{\mathbf{r}_i}{r_i^3}. \tag{31}$$

Comparing Eqs. (29)–(31) with the one-photon version in Eq. (19), we note that the overall frequency ω and Z terms, along with the momentum $\mathbf{p}$ and position $\mathbf{r}$ operators, occur with the same power for the corresponding gauge. The only difference is that the frequency in the prefactor reads $(\omega_1\omega_2)^{1/2}$ for the two-photon dipole operator in the length and acceleration gauges but just $\omega_{\mathrm{i,f}}$ in the corresponding single-photon operator. This correspondence will be used in generalizing the conclusions drawn from one- and two-photon transition rates to the general case of $nE1$ transitions.

C. Calculations

We begin by rewriting the c.m. Hamiltonian from Eq. (5) in reduced-mass atomic units, given by

$$\boldsymbol{\rho} = \frac{\mu}{m_e}\frac{\mathbf{r}}{a_0}, \quad \tau = \frac{\mu}{m_e}\frac{\alpha c}{a_0}t,$$
$$i\nabla = -\frac{m_e}{\mu}\frac{a_0}{\hbar}\mathbf{p}, \quad \epsilon = \left(\frac{m_e}{\mu}\right)\frac{E}{\alpha^2 m_e c^2}, \tag{32}$$

where a_0 is the Bohr radius and E is the nonrelativistic energy from Eq. (1). With these substitutions, the two-electron Schrödinger equation takes the dimensionless form

$$\left[-\frac{1}{2}(\nabla^2_{\rho_1} + \nabla^2_{\rho_2}) - \frac{\mu}{M}\nabla_{\rho_1}\cdot\nabla_{\rho_2} + V(\rho_1,\rho_2)\right]\Psi = \epsilon\Psi,$$
$$\mathrm{V}(\rho_1,\rho_2) = -\frac{\mathrm{Z}}{\rho_1} - \frac{\mathrm{Z}}{\rho_2} + \frac{1}{|\rho_1-\rho_2|}. \tag{33}$$

Approximate variational solutions are constructed by solving the generalized eigenvalue problem in a double Hylleraas basis set [25] of the form

$$\Psi = c_0\Psi_0 + \sum_{ijk}^{i+j+k\leqslant\Omega}\left[\underbrace{c^{(\mathrm{A})}_{ijk}\varphi_{ijk}(\alpha_\mathrm{A},\beta_\mathrm{A})}_{A\text{ sector}} + \underbrace{c^{(\mathrm{B})}_{ijk}\varphi_{ijk}(\alpha_\mathrm{B},\beta_\mathrm{B})}_{B\text{ sector}}\right]. \tag{34}$$

The individual basis functions have the form

$$\varphi_{ijk}(\alpha,\beta) = r_1^i\, r_2^j\, r_{12}^k\, e^{-\alpha r_1 - \beta r_2}\,\mathcal{Y}^M_{l_1,l_2,L}(\hat{r}_1,\hat{r}_2)$$
$$\pm \text{ exchange}, \tag{35}$$

where $\mathcal{Y}^M_{l_1,l_2,L}(\hat{r}_1,\hat{r}_2)$ are vector-coupled spherical harmonics. The different sectors of the basis functions in Eq. (34) allow for the characterization of both the asymptotic A sector ($r\to\infty$) and short-range B sector ($r\to 0$). The nonlinear parameters α_m and β_m, $m = 1, 2$, are obtained by calculating the four derivatives $\frac{\partial E}{\partial\alpha_m}$ and $\frac{\partial E}{\partial\beta_m}$ analytically and then finding the zeros using Newton's method. $\Omega = (i+j+k)_{\max}$ describes the Pekeris shell defining the number of terms in each basis sector. For the initial and final states in both one- and two-photon decay, an optimized wave function is generated by the aforementioned procedure minimizing the energy of the state in question. A complete set of intermediate states is needed for evaluating two-photon transitions. A pseudospectrum defined by

$$\langle\Psi_n|H|\Psi_m\rangle = \epsilon_n\delta_{n,m}, \quad \langle\Psi_n|\Psi_m\rangle = \delta_{n,m} \tag{36}$$

is generated for this purpose. This pseudospectrum provides a discrete variational representation of all bound and continuum states that is provably complete in the limit $\Omega\to\infty$ [26].

III. FINITE-MASS EFFECTS

It is convenient to express the finite-mass corrections to $w_{x,\infty}$ as the product of three factors: the power of Z_x, which characterizes the radiation emitted by the nucleus moving in the c.m. frame; the power (μ/m_e), a mass-scaling factor analogous to the normal isotope shift; and a power series $F_x(\mu/M)$ that characterizes the mass-polarization correction to the wave functions. The first two are trivial to account for, leaving the remaining focus on the function $F_x(\mu/M)$. We write down these relationships for the case of spontaneous emission but emphasize that the ensuing algebra is the same for other transition rates involving the same number of photons and leads to the same algebraic relationships. For single-photon decay, the three factors enter in the form

$$w_r^{(1\gamma)} = Z_r^2\left(\frac{\mu}{m_e}\right)F_r(\mu/M)w_{r,\infty}^{(1\gamma)}, \tag{37}$$
$$w_p^{(1\gamma)} = Z_p^2\left(\frac{\mu}{m_e}\right)^3F_p(\mu/M)w_{p,\infty}^{(1\gamma)}, \tag{38}$$
$$w_a^{(1\gamma)} = Z_p^2\left(\frac{\mu}{m_e}\right)^3F_a(\mu/M)w_{a,\infty}^{(1\gamma)}. \tag{39}$$

For two-photon decay, they enter in the form

$$w_r^{(2\gamma)} = Z_r^4\left(\frac{\mu}{m_e}\right)F_r(\mu/M)w_{r,\infty}^{(2\gamma)}, \tag{40}$$
$$w_p^{(2\gamma)} = Z_p^4\left(\frac{\mu}{m_e}\right)^5F_p(\mu/M)w_{p,\infty}^{(2\gamma)}, \tag{41}$$
$$w_a^{(2\gamma)} = Z_p^4\left(\frac{\mu}{m_e}\right)^5F_a(\mu/M)w_{a,\infty}^{(2\gamma)}, \tag{42}$$

where $x = r, p, a$ for the length, velocity, and acceleration gauges, respectively. To reiterate, the prefactors of these six equations follow from the definitions of the decay rates in Eqs. (13) and (33) and also from the fact that the calculation is performed in reduced-mass atomic units. The overall powers of (μ/m_e) follow from a factor of (μ/m_e) for each factor of ω or $\mathbf{p}$ in the matrix elements and $(\mu/m_e)^{-1}$ for each factor of $\mathbf{r}$. It is noteworthy that the constitutive relationship between the finite- and infinite-mass decay-rate expressions is identical in the velocity and acceleration cases.

The algebraic relations studied in this work follow from the coefficients in an expansion of the mass-polarization function $F_x(\mu/M)$ in powers of (μ/M) of the form

$$F_x(\mu/M) = 1 + (\mu/M)C_x + (\mu/M)^2D_x + (\mu/M)^3E_x + \cdots. \tag{43}$$

The mass-polarization term $(\frac{\mu}{M})\boldsymbol{\nabla}_1\cdot\boldsymbol{\nabla}_2$ enters linearly in the Hamiltonian in Eq. (33), and therefore, a uniformly convergent power series in μ/M exists within its radius of convergence. The power series is rapidly convergent for helium and other atomic systems since $\mu/M\sim 10^{-4}$ or smaller, and so only the first few terms are needed. This expansion forms the basis for the algebraic relations discussed in the following section.

A. Algebraic relations

If the wave functions and sums over intermediate states are exact, then for an n-photon transition it should be true that $w_p^{(n\gamma)} = w_r^{(n\gamma)} = w_a^{(n\gamma)}$, or in terms of ratios

$$\frac{w_p^{(n\gamma)}}{w_{p,\infty}^{(n\gamma)}} = \frac{w_r^{(n\gamma)}}{w_{r,\infty}^{(n\gamma)}} = \frac{w_a^{(n\gamma)}}{w_{a,\infty}^{(n\gamma)}}. \tag{44}$$

By expanding the prefactors in the rate equations in powers of μ/M using the relations

$$\mu/m_e = 1 - \mu/M, \tag{45}$$
$$m_e/M = \mu/M + (\mu/M)^2 + (\mu/M)^3 + \ldots \tag{46}$$

and collecting coefficients of equal powers of μ/M up to $(\mu/M)^3$, one can derive algebraic relations connecting the coefficients $C_r, D_r, E_r, \ldots$ in Eq. (43). For one-photon transition rates, the results are

$$\text{Order } (\mu/M): \quad C_p - C_r = -2, \tag{47}$$
$$C_p = C_a,$$
$$\text{Order } (\mu/M)^2: \quad 2C_p + D_p - D_r = -1, \tag{48}$$
$$D_p = D_a,$$
$$\text{Order } (\mu/M)^3: \quad C_p + 2D_p + E_p - E_r = 4, \tag{49}$$
$$E_p = E_a.$$

For two-photon transition rates, the results are

$$\text{Order } (\mu/M): \quad C_p - C_r = -4, \tag{50}$$
$$C_p = C_a,$$
$$\text{Order } (\mu/M)^2: \quad 4C_p + D_p - D_r = -6, \tag{51}$$
$$D_p = D_a,$$
$$\text{Order } (\mu/M)^3: \quad 6C_p + 4D_p + E_p - E_r = 4, \tag{52}$$
$$E_p = E_a.$$

The relationship between the length and velocity coefficients in the above equations is precisely the same as that between length and acceleration, but with the acceleration-form coefficients taking the place of the velocity coefficients. Further, it is seen that the velocity and acceleration coefficients must be equal. The degree to which these equations are satisfied tests how well the length and velocity gauges agree for a given calculation. For example, Ref. [12] demonstrated agreement to 1 part in 10^8 between the length and velocity gauges for the two-photon decay rates of heliumlike ions. In the Appendix, we demonstrate that the aforementioned algebraic relations can be obtained from perturbation theory as well, a topic that will be further explored in a future publication.

B. Generalization to higher-order transitions

The preceding analysis can be extended to the general n-photon transition rate ($nE1$) problem. The constitutive relations between the two gauges can be obtained by accounting for the additional sets of intermediate states needed to accommodate higher-order transitions, leading to extensions of dipole operators given in Eqs. (26) and (27) for the case of two-photon transitions. This involves tracking additional powers of $Z_{p,r}$ and μ/m_e that come from more virtual dipole matrix elements. In the general case, these relationships are

$$w_p^{(n\gamma)} = Z_p^{2n}\left(\frac{\mu}{m_\mathrm{e}}\right)^{2n+1} F_p(\mu/M) w_{p,\infty}^{(n\gamma)}, \tag{53}$$

$$w_r^{(n\gamma)} = Z_r^{2n}\left(\frac{\mu}{m_\mathrm{e}}\right) F_r(\mu/M) w_{r,\infty}^{(n\gamma)}, \tag{54}$$

$$w_a^{(n\gamma)} = Z_p^{2n}\left(\frac{\mu}{m_\mathrm{e}}\right)^{2n+1} F_a(\mu/M) w_{a,\infty}^{(n\gamma)}. \tag{55}$$

In the same fashion as described in Sec. III A, equating the ratios of the finite- and infinite-mass transition rates in the two gauges leads to the generalized algebraic relations mentioned following Eq. (52):

$$\text{Order } (\mu/M): \quad C_p - C_r = -2n, \tag{56}$$
$$C_p = C_a,$$
$$\text{Order } (\mu/M)^2: \quad 2nC_p + D_p - D_r = -n(2n-1), \tag{57}$$
$$D_p = D_a,$$
$$\text{Order } (\mu/M)^3: \quad n(2n-1)C_p + 2nD_p + E_p - E_r = \tfrac{2}{3}n(n+1)(5-2n), \tag{58}$$
$$E_p = E_a,$$

The length-acceleration relations are the same as for the length-velocity cases just presented, provided that the acceleration and velocity coefficients are exchanged. Equations (56)–(58) can be used to compare length and velocity $nE1$ transition rates up to order $(\mu/M)^3$. Equation (58) was not tested in this work or Ref. [12] since we are able to achieve agreement in the finite-mass decay rates between the gauges only to approximately 1 part in 10^9, whereas in helium the third-order corrections are around 1 part in 10^{12}. Extending this set of algebraic relations to higher-order terms in the power series is straightforward and follows the procedure described in this section.

IV. RESULTS

The algebraic relations given in Sec. III have been tested and verified in numerical calculations involving one- and two-photon decay rates, which, as mentioned previously, give rise to algebraic relationships identical to other transitions involving the same number of photons. The algebraic coefficients, along with the satisfaction of the corresponding algebraic relations, are presented in Tables I and II.

We begin by writing the constitutive relations between the finite- and infinite-mass decay rates in Eqs. (40) and (41) in terms of the expansion parameter μ/M:

$$G_x(\mu/M) = (\mu/M)C_x + (\mu/M)^2 D_x + \cdots, \tag{59}$$

where $G_x(\mu/M)$ is a gauge-dependent function of the finite- and infinite-mass decay rates, the radiation emitted by the nucleus in the c.m. frame, and mass scaling. $G_x(\mu/M)$ differs from the power series $F_x(\mu/M)$ defined in Eqs. (40) and (41) by 1. Next, three values of μ/M were used: μ/M itself, along with $10(\mu/M)$ and $20(\mu/M)$, to establish three equations for Eq. (59). In what follows, the analyses of the one- and two-photon decay cases are treated somewhat differently.

A. One-photon decay

In the case of one-photon decay, this system of three linear equations, a 3×3 system, was explicitly solved in order to include the cubic coefficients E_x of $(\mu/M)^3$ in the mass-polarization power series. This procedure is carried out for successively larger basis sets according to Eq. (34) up to $\Omega = (i+j+k)_{\max} = 17$. These corrections contribute to the extent that the decay rates between the length and velocity gauges agree beyond the $(\mu/M)^2$ order, or better than 1 part in 10^8. The third-order coefficients are not displayed in Table I, nor is the third-order algebraic equation, Eq. (58), tested (the decay rates do not presently agree well enough to warrant

TABLE I. Mass-polarization parameters C_x and D_x from Eq. (43) are shown for the one-photon decay processes in the indicated singlet and triplet He and He-like ions, along with the accompanying algebraic relations, Eqs. (47) and (48). For the triplet transition at the bottom, [†] indicates third-order contributions (E_x terms) are included in the calculation, and [‡] indicates they are omitted.

Ion	C_p	C_r	$C_p - C_r$	D_p	D_r	$2C_p + D_p - D_r$
			$2\,^1P - 1\,^1S$			
^{4}He	−3.572719(1)	−1.57271(3)	−2.00000(3)	8.888(1)	2.73(2)	−0.99(2)
^{7}Li$^+$	−3.299929(3)	−1.299919(7)	−2.00001(1)	6.6723(8)	1.067(4)	−0.995(5)
^{9}Be^{++}	−3.061260(8)	−1.0612(2)	−2.0005(1)	5.3580(3)	0.232(6)	−0.997(6)
^{11}B^{3+}	−2.896567(5)	−0.89655(3)	−2.00002(4)	4.5986(4)	−0.194(5)	−1.000(6)
^{12}C^{4+}	−2.780462(2)	−0.78047(3)	−1.99999(3)	4.1215(2)	−0.439(2)	−0.999(2)
^{14}N^{5+}	−2.6952538(3)	−0.695250(4)	−2.000003(4)	3.800(1)	−0.61(2)	−0.98(2)
^{16}O^{6+}	−2.6304056(1)	−0.630403(2)	−2.000002(2)	3.5687(6)	−0.702(9)	−0.99(1)
^{19}F^{7+}	−2.579540(1)	−0.57953(1)	−2.000006(14)	3.3959(4)	−0.762(1)	−1.001(1)
^{20}Ne^{8+}	−2.5386356(1)	−0.538638(6)	−1.999996(6)	3.2618(8)	−0.812(4)	−1.002(5)
			$2\,^3P - 2\,^3S$			
^{4}He [†]	−7.609183(1)	−5.60918375(4)	−1.999999(1)	12.9523(2)	−1.266053(8)	−1.0000(2)
^{4}He [‡]	−7.609191(1)	−5.60920948(3)	−1.999982(1)	12.9703(1)	−1.206957(4)	−1.0411(1)

such a comparison); however, third-order contributions to lower-order coefficients C_x and D_x are explicitly considered by solving the 3×3 system defined by Eq. (59),

$$\begin{bmatrix} y & y^2 & y^3 \\ 10y & 10y^2 & 10y^3 \\ 20y & 20y^2 & 20y^3 \end{bmatrix} \begin{bmatrix} C_x \\ D_x \\ E_x \end{bmatrix} = \begin{bmatrix} G_x(y) \\ G_x(10y) \\ G_x(20y) \end{bmatrix}, \quad (60)$$

where $y = \mu/M$ and $x = p, r$ for the two gauges. The first- and second-order mass-polarization power-series coefficients that arise in treating one-photon decay in heliumlike ions are presented in Table I. The results are calculated by averaging the largest basis sets, and the standard deviation of these was taken to be the uncertainty. The coefficients of the mass-polarization power series do converge with increasing basis-set sizes, but not in a monotonic fashion as in the decay rates. Thus, the stated results and errors presented in Table II correspond to an average and standard deviation of the calculations from the several largest basis sets. The first- and second-order coefficients in both the length and velocity gauges are presented in Table II, where the coefficients are shown to obey the algebraic relations in Eqs. (50) and (51).

The inclusion of third-order corrections made little difference for the singlet case; a larger difference was observed in the case of triplet decay, where it was necessary to include the E_x coefficients to satisfy the $(\mu/M)^2$ algebraic relation. This point is illustrated in the last two rows of Table I and is a consequence of the Pauli principle: for triplet states, the electron-electron correlation plays a smaller role. Therefore, in the triplet case of one-photon decay, the coefficients (particularly $\{D_x\}$) are sensitive to the $(\mu/M)^3$ contributions.

B. Two-photon decay

In [12], the algebraic relations that are the subject of this paper were derived for the first time and numerically tested for the case of two-photon decay $2\,^1S - 1\,^1S$ in heliumlike ions ($Z = 2 - 10$), along with the heavier μ-He, π-He, and $\bar{p}$-He. These results are reproduced in Table II. Instead of solving the linear system described by Eq. (59), as in the one-photon case, iterative linear regressions are performed on this set of equations to obtain the mass-polarization coefficients C_x and D_x. On the initial iteration, the C_x values are obtained by a linear regression assuming no $(\mu/M)^2$ contributions (i.e., $D_x = 0$). Then, using these C_x values, an updated equation is subject to linear regression to get the D_x coefficients. These updated D_x values are then used for a second regression to find C_x, and the process is repeated once more to update the D_x coefficients.

TABLE II. Mass-polarization parameters C_x and D_x from Eq. (43) are shown for two-photon decay in He and He-like ions, along with the accompanying algebraic relations, Eqs. (50) and (51), for the metastable singlet transition indicated. This table is reproduced from Ref. [12].

Ion	C_p	C_r	$C_p - C_r$	D_p	D_r	$4C_p + D_p - D_r$
			$2\,^1S - 1\,^1S$			
^{4}He	−5.2333588(30)	−1.23336(8)	−4.0000(8)	16.4344(10)	1.607(26)	−6.106(27)
^{7}Li$^+$	−5.385078(8)	−1.385078(12)	−4.000000(17)	17.124(27)	1.95(32)	−6.37(35)
^{9}Be^{++}	−5.487355(9)	−1.4871(5)	−4.0002(5)	17.799(7)	1.74(35)	−5.89(36)
^{11}B^{3+}	−5.557584(1)	−1.5575(1)	−4.00008(13)	18.3518(12)	2.09(12)	−5.97(12)
^{12}C^{4+}	−5.6094000(16)	−1.60943(13)	−3.99996(13)	18.8227(18)	2.47(14)	−6.08(14)
^{14}N^{5+}	−5.64973214(24)	−1.649718(24)	−4.000014(24)	19.24196(29)	2.661(28)	−6.018(28)
^{16}O^{6+}	−5.68233816(7)	−1.682327(12)	−4.000010(12)	19.61265(9)	2.903(16)	−6.020(16)
^{19}F^{7+}	−5.7094498(5)	−1.70942(6)	−4.000025(61)	19.9487(8)	3.099(99)	−5.99(10)
^{20}Ne^{8+}	−5.73247255(30)	−1.73249(3)	−3.99998(3)	20.2487(10)	3.40(10)	−6.08(10)

This procedure is carried out for successively larger basis sets according to Eq. (34) up to $\Omega = (i + j + k)_{\max} = 17$. The slight disagreement in the $(\mu/M)^2$ relation for $Z = 2$ and 3 indicates that the rates between the gauges do not quite agree to order $(\mu/M)^2$. This is because $\mu/M \propto 1/Z$ and $Z = 2$ and 3 are the largest μ/M values considered.

V. CONCLUSIONS AND DISCUSSION

This paper has both derived and numerically tested general algebraic relations that quantify the agreement between the length and velocity gauges for the general n-photon ($nE1$) finite-mass transition-rate equations and tested them for heliumlike ions. The corresponding relationships between the length or velocity and acceleration gauges have also been derived. These relations are built on the postulate, initially put forward in Ref. [12], that the mass-polarization component of the finite-mass effect can be treated with a power series in μ/M. Equations (53)–(55) provide constitutive relations that can be used to account for finite-mass effects for $nE1$ transition rates. The prefactors in these equations can be used to convert infinite-mass transition rates calculated in any theoretical or computational framework to the corresponding finite-mass rates. Equations (56)–(58) are the corresponding algebraic relationships that test for gauge agreement to ensure that mass-polarization effects are included correctly to a desired order in μ/M. These relations place tight constraints on theoretical calculations of finite-mass effects in $nE1$ transition processes, as demonstrated in the case of the spontaneous emission of heliumlike ions. They also test the leading infinite-mass term since an error here would carry through to the higher-order terms in μ/M.

Another approach to obtaining the coefficients $F_x(\mu/M)$ contained in Eqs. (53)–(55) is to treat the mass-polarization term, $\nabla_{\rho_1} \cdot \nabla_{\rho_2}$, in Eq. (33) perturbatively in the parameter μ/M. This would provide a more direct, but also more computationally intensive, method for calculating the coefficients $C_x, D_x, E_x, \ldots$ of the successive powers of μ/M. This will be explored in a future publication, but it is worth noting that the coefficients C_x and D_x, already calculated in Tables I and II, satisfy the given algebraic relations up to order $(\mu/M)^2 \approx 10^{-8}$. A further improvement could be a more judicious selection of values for μ/M used to demonstrate numerically the algebraic relations. Currently, the actual μ/M value is used, along with both 10 and 20 times this value; however, there is nothing particular about these choices, and there is no need to use μ/M itself. Exploring the space of possibilities here would likely lead to a more convincing demonstration of the algebraic relations.

The formalism developed here for treating the mass-polarization component of the finite-mass effect in the calculation of $nE1$ transition rates in heliumlike ions could be extended to other atomic processes. The form of the resulting algebraic relations would be different from those presented here for other $nE1$ processes, depending on the form of the quantity being calculated; however, they would still serve as a theoretical check between calculations in the velocity and length gauges and would be derived in the same way as presented here and in Ref. [12]. In calculations of stimulated emission, absorption, and photoionization [27,28], the same algebraic relations would apply as for spontaneous emission, but the numerical values of the C_x, D_x, etc., coefficients would be different. One possible application would be to the study of Feshbach resonances [27]. For precision QED calculations [28,29] to be compared with experiments, finite-mass effects are needed, and the method in this paper provides a systematic method for their inclusion. In the particular problem of two-photon decay, accurate comparison with experimental results [30] requires a correct relativistic treatment. This was done previously in Refs. [11,22], but a future publication of ours will add relativistic effects to the finite-mass effects discussed in this paper by a highly accurate perturbation calculation.

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APPENDIX: EXAMPLE DERIVATION OF MASS POLARIZATION COEFFICIENTS USING PERTURBATION THEORY

This Appendix demonstrates that perturbation theory can be used to obtain the algebraic relations that are the subject of this paper. According to Rayleigh-Schrödinger perturbation theory, since the mass-polarization term enters the Schrödinger equation linearly, its coefficient μ/M can be regarded as a perturbation parameter. Rayleigh-Schrödinger perturbation theory then generates a power-series expansion in powers of μ/M for the wave functions and energies that is uniformly convergent within the radius of convergence. For transition rates, the coefficients correspond to those extracted numerically in the present work. As an example, we consider explicitly the relationship for the first-order mass-polarization coefficients between the length and velocity forms of single-photon transitions, given in Eq. (47) as

$$C_p - C_r = -2.$$

The single-photon decay rate, given in Eq. (13), is

$$w_{\mathrm{i,f}} = \tfrac{4}{3}\alpha\omega_{\mathrm{i,f}}|\langle i|\mathbf{Q}_x|f\rangle|^2.$$

We will work in center-of-mass coordinates, using reduced-mass atomic units, given in Eq. (32), such that the length and velocity operators are $\boldsymbol{\rho} \equiv \boldsymbol{\rho_1} + \boldsymbol{\rho_2}$ and $\boldsymbol{\nabla} \equiv \boldsymbol{\nabla_1} + \boldsymbol{\nabla_2}$, respectively. The condition that the length and velocity gauge should be equal with all finite-mass effects included is

$$Z_p^2\left(\frac{\mu}{m_{\mathrm{e}}}\right)^3 \Delta E|\langle i|\boldsymbol{\nabla}|f\rangle|^2 = Z_r^2\left(\frac{\mu}{m_{\mathrm{e}}}\right)\Delta E^3|\langle i|\boldsymbol{\rho}|f\rangle|^2,$$

$$|\langle i|\boldsymbol{\nabla}|f\rangle|^2 = \left(\frac{Z_r}{Z_p}\right)^2\left(\frac{\mu}{m_{\mathrm{e}}}\right)^{-2}\Delta E^2\ |\langle i|\boldsymbol{\rho}|f\rangle|^2, \tag{A1}$$

where we have used $\omega_{\text{i,f}} = \Delta E_{\text{i,f}} \equiv \Delta E$ in atomic units and all finite-mass dependence besides mass polarization has been factored out. In what follows, the expansions in Eqs. (45) and (46) are utilized to give

$$\left(\frac{Z_r}{Z_p}\right)^2\left(\frac{\mu}{m_e}\right)^{-2} = 1 - 2\mu/M + \cdots .$$

The fundamental perturbation equations

$$\left(H_0 + \frac{\mu}{M}\nabla_{\rho_1}\cdot\nabla_{\rho_2}\right)\left(|\Psi\rangle^{(0)} + \frac{\mu}{M}|\Psi\rangle^{(1)} + \cdots\right) = \left(\Delta E^{(0)} + \frac{\mu}{M}\Delta E^{(1)} + \cdots\right)\left(|\Psi\rangle^{(0)} + \frac{\mu}{M}|\Psi\rangle^{(1)} + \cdots\right)$$

can then be solved to write ΔE and the squared dipole matrix elements $|\langle i|\boldsymbol{\rho}|f\rangle|^2$ and $|\langle i|\nabla|f\rangle|^2$ as expansions in μ/M. These are

$$\begin{aligned}(\Delta E)^2 &= \left[\Delta E^{(0)} + \frac{\mu}{M}\Delta E^{(1)} + \cdots\right]^2\\ &= [\Delta E^{(0)}]^2 + 2\frac{\mu}{M}[\Delta E^{(1)}]^2 + \cdots ,\\ |\langle i|\nabla|f\rangle|^2 &= \left[\langle i|\nabla|f\rangle^{(0)} + \frac{\mu}{M}\langle i|\nabla|f\rangle^{(1)} + \cdots\right]^2\\ &= |\langle i|\nabla|f\rangle^{(0)}|^2 + 2\frac{\mu}{M}|\langle i|\nabla|f\rangle^{(1)}|^2 + \ldots ,\\ |\langle i|\boldsymbol{\rho}|f\rangle|^2 &= \left[\langle i|\boldsymbol{\rho}|f\rangle^{(0)} + \frac{\mu}{M}\langle i|\boldsymbol{\rho}|f\rangle^{(1)} + \cdots\right]^2\\ &= |\langle i|\boldsymbol{\rho}|f\rangle^{(0)}|^2 + 2\frac{\mu}{M}|\langle i|\boldsymbol{\rho}|f\rangle^{(1)}|^2 + \cdots .\end{aligned}$$

The first-order dipole matrix element terms $\langle i|\nabla|f\rangle^{(1)}$ and $\langle i|\boldsymbol{\rho}|f\rangle^{(1)}$ both contain two terms, arising from first-order corrections to both the initial- and final-state wave functions. Finally, putting these expansions back into Eq. (A1) gives

$$\begin{aligned}(1 - 2\mu/M + \cdots)&\left[(\Delta E^{(0)})^2 + 2\frac{\mu}{M}(\Delta E^{(1)})^2 + \cdots\right]\\ &\times\left[(R^{(0)})^2 + 2\frac{\mu}{M}(R^{(1)})^2 + \ldots\right]\\ &= (P^{(0)})^2 + 2\frac{\mu}{M}(P^{(1)})^2 + \cdots ,\end{aligned}$$

where the perturbation coefficients for the length and velocity dipole matrix elements are written in a slightly abbreviated notation using $R^{(n)} \equiv |\langle i|\boldsymbol{\rho}|f\rangle^{(n)}|$ and $P^{(n)} \equiv |\langle i|\nabla|f\rangle^{(n)}|$, respectively. Solving these perturbation equations yields

$$(\Delta E^{(0)}R^{(0)})^2 = (P^{(0)})^2$$

in zeroth order, successfully recovering the commutator identity. In first order, we obtain

$$(\Delta E^{(1)}R^{(0)})^2 + (\Delta E^{(0)}R^{(1)})^2 - (\Delta E^{(0)}R^{(1)})^2 = (P^{(1)})^2.$$

Rearranging and using the zeroth-order identity give

$$2\left(\frac{P^{(1)}}{P^{(0)}}\right)^2 - 2\frac{(\Delta E^{(1)}R^{(0)})^2 + (\Delta E^{(0)}R^{(1)})^2}{(\Delta E^{(0)}R^{(0)})^2} = -2.$$

By identifying

$$C_p \equiv 2\left(\frac{P^{(1)}}{P^{(0)}}\right)^2, \tag{A2}$$

$$C_r \equiv 2\frac{(\Delta E^{(1)}R^{(0)})^2 + (\Delta E^{(0)}R^{(1)})^2}{(\Delta E^{(0)}R^{(0)})^2}, \tag{A3}$$

we have derived explicit perturbation expressions for C_p and C_r and recovered the desired algebraic relation in Eq. (47) connecting the first-order length and velocity mass-polarization coefficients that arise in transition rates in single-photon transitions.

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