# Perturbation theory for multiphoton ionization without knowledge of the final-state wave function

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We show how the inclusive rate of decay of an atomic system by absorption of any number $N$ of photons can be calculated at $N$th order of perturbation theory without employing the final-state (continuum) wave function. We give a computationally useful formula which involves only the response function for a system perturbed by absorption of $N$ photons. In the case of a two-electron system, the contributions to the inclusive rate from individual channels can be separated using projection operators. [S1050-2947(99)08007-5]

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## I. INTRODUCTION

In this paper we show how the rate for multiphoton decay of an atomic system can be calculated, within the framework of perturbation theory, without employing the final-state (continuum) wave function, a feature which may be particularly useful when systems with two or more electrons are considered. We give a computationally tractable formula for the inclusive rate for $N$-photon decay at $N$th order which involves only the response function for a system perturbed by absorption of $N$ photons. There is no restriction (in principle) on the number of electrons. As a simple test, we provide numerical results for two-photon ionization of hydrogen by circularly polarized light. In the case $N=2$ we demonstrate explicitly the equivalence of the formula presented here to another formula that is directly related to the outgoing photoelectron flux through a large hypersphere. We make use of this equivalance to develop a modified formula, applicable to a two-electron system, for the contributions to the inclusive $N$-photon rate from individual atomic channels; this may facilitate, in particular, the calculation of $N$-photon rates for double escape from a two-electron system.

In reformulating perturbation theory we have in mind two-electron systems and processes in which both electrons actively participate, i.e., either partial breakup accompanied by excitation of the residual one-electron system, or complete breakup. All three interactions — of the electrons with the atomic nucleus and with each other — play a significant role. In view of this, and the fact that the final-state (continuum) wave function is rich in structure, especially if both electrons escape, the task of accurately calculating the decay rate is a challenge. Nevertheless, there is no dearth of interest in the problem [1], and over the past few years significant progress has been made in the treatment of partial breakup with simultaneous excitation by absorption of one [2] or more [3–9] photons, as well as complete breakup [10–15] by one photon, but complete breakup by more than one photon remains an outstanding problem.

The difficulty posed by the final-state wave function can be mitigated significantly by a shift of emphasis to the initial-state channel, which can be realized through the introduction of the $M$-photon response vector [16,4,11]. Let

$$V(t)=FV_+e^{-i\omega t}+FV_-e^{i\omega t} \tag{1}$$

be the interaction of the atomic system with an oscillating monochromatic electric field of amplitude $F$ and frequency $\omega$. If the system is initially in a state with energy $E_0$ represented by $|\phi_0\rangle$, its response to the absorption of $M$ photons is described by

$$|\phi_M\rangle=G_a(E_M+i\eta)V_+|\phi_{M-1}\rangle, \quad M\geqslant 1, \tag{2}$$

where $G_a(E)=(E-H_a)^{-1}$ is the resolvent for the Hamiltonian $H_a$ that governs the unperturbed atomic system, where (we use atomic units hereafter)

$$E_M=E_0+M\omega, \tag{3}$$

and where $\eta$ is positive but infinitesimal. The use of the response function permits the replacement of the exact final-state wave function by its asymptotic form in the matrix element for the transition rate. This is achieved by using $G_a(E_M-i\eta)^\dagger=G_a(E_M+i\eta)$ to shift the resolvent $G_a(E_M-i\eta)$ that is imbedded in the final-state bra to the ket side of the matrix element, where it acts on $V_+|\phi_{M-1}\rangle$ and hence yields the $M$-photon response vector. This simplification is significant because, in contrast to the final-state wave function, which satisfies a *homogeneous* differential equation subject to *standing*-wave asymptotic boundary conditions, the response function satisfies an *inhomogeneous* differential equation,

$$(E_M+i\eta-H_a)|\phi_M\rangle=V_+|\phi_{M-1}\rangle, \tag{4}$$

subject to *outgoing*-wave asymptotic boundary conditions. The boundary conditions on the response function are almost trivial to incorporate — in principle, one has merely to add $i\eta$ to the real energy of the system — since the inhomogeneous term, $V_+|\phi_{M-1}\rangle$, satisfies outgoing-wave boundary conditions (damped by the bound state if $M=1$) and it drives the $M$-photon response function. Moreover, the absence of ingoing waves in the boundary conditions allows the response function to be accurately represented on a set of complex basis functions that have only outgoing-wave character, a basis that in practice guarantees the correct boundary conditions even without the inclusion of $i\eta$.

Going one step further, if the atomic system has only two electrons, the final-state wave function can be eliminated altogether by introducing projection operators that project onto

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the channel subspaces. This device, which is discussed in more detail in Sec. IV, has been used in calculations of cross sections for both double photoionization and electron-impact ionization [17,18]. In this paper we develop further the theory discussed in Ref. [17].

We adopt the dipole approximation and use the ''velocity'' gauge; thus if $\hat{\boldsymbol{\epsilon}}$ is the unit polarization vector, $V_+ = \hat{\boldsymbol{\epsilon}}\cdot\mathbf{p}/(2\omega)$ and $V_- = \hat{\boldsymbol{\epsilon}}^*\cdot\mathbf{p}/(2\omega)$, where $\mathbf{p}$ is the total canonical momentum operator of the electrons. The rate for $N$-photon decay at $N$th order of perturbation theory is proportional to $F^{2N}$. Factoring out the strength of the field, we write the inclusive rate as $F^{2N}\Gamma_N$. The main results of this paper are as follows. We show that

$$\Gamma_N = -2\,\mathrm{Im}\langle\phi_{N-1}|V_+^\dagger O_N^\dagger G_a(E_N+i\eta)O_N V_+|\phi_{N-1}\rangle, \tag{5}$$

where $O_N$ is in general non-Hermitian and is a product of $N-1$ operators, defined as

$$O_N = \Pi_{M=1}^{N-1}\left(\frac{E_M+i\eta-H_a}{E_M-E_N}\right). \tag{6}$$

Since $O_N$ commutes with $G_a(E)$, we can use Eq. (2) to rewrite Eq. (5) as

$$\Gamma_N = -2\,\mathrm{Im}\langle\phi_{N-1}|V_+^\dagger O_N^\dagger O_N|\phi_N\rangle. \tag{7}$$

Note that $\Gamma_N$ is the sum over all open atomic channels, and that there is no restriction on the number of electrons within the system. If the system contains two electrons, denoted by 1 and 2, we can separate the contributions to the decay rate from individual channels by inserting projection operators that project onto the channel subspaces. Consider the channel in which, after $N$-photon absorption, one of the electrons, say electron 2, escapes while the other electron, i.e., electron 1, remains *bound* in a state of the residual one-electron system characterized by the set of quantum numbers $\alpha$. We introduce the operator $P_{1\alpha}$ which projects onto the subspace in which electron 1 is in state $\alpha$. Since the bound states of a hydrogenic system are known in closed form, $P_{1\alpha}$ can be constructed in closed form. Writing the partial rate for single-electron emission in channel $\alpha$ as $F^{2N}\Gamma_{\alpha,N}$, and denoting by $N_0$ the minimum number of photons which the system must absorb to decay, we show for the case $N=2$ that if $W_{12}$ denotes the interaction between the two electrons

$$\begin{aligned}\Gamma_{\alpha,N} = &-4\,\mathrm{Im}\langle\phi_{N-1}|V_+^\dagger P_{1\alpha}O_N^\dagger O_N|\phi_N\rangle \\ &-2\sum_{M=N_0}^{N}\left(\frac{\omega^{M-N}}{(N-M)!}\right)^2 \\ &\times\langle\phi_M|(V_+^\dagger)^{N-M}[P_{1\alpha},iW_{12}](V_+)^{N-M}|\phi_M\rangle. \end{aligned}\tag{8}$$

We conjecture that Eq. (8) also applies for $N>2$. Note that the commutator $[P_{1\alpha},iW_{12}]$ is Hermitian since $P_{1\alpha}$ is Hermitian and $iW_{12}$ is anti-Hermitian. The rate for double escape is

$$F^{2N}\left(\Gamma_N - \sum_{\alpha,\mathrm{bd}}\Gamma_{\alpha,N}\right),$$

where the sum is over all channels in which one of the electrons remains *bound*.

A few more words about the role of $i\eta$, and the related issue of whether or not $H_a$ is Hermitian, may be helpful. We can treat $H_a$ as Hermitian in a matrix element $\langle b|H_a|a\rangle$ if $\Delta H_a \equiv \langle b|(H_a^\dagger - H_a)|a\rangle$ vanishes, where $\langle b|H_a^\dagger|a\rangle = [\langle a|H_a|b\rangle]^*$. Now $\Delta H_a$ is a volume integral, over $D$ dimensions say, but we can use Green's theorem to write $\Delta H_a$ as an integral over the surface of a $(D-1)$-dimensional hypersphere whose radius, $R$ say, approaches infinity. However, $\eta$ approaches zero, and we have the choice of either (i) letting $\eta$ become zero before letting $R$ become infinite, or (ii) letting $R$ become infinite before letting $\eta$ become zero. In the context of the breakup of a bound system, the functions that represent $|a\rangle$ and $|b\rangle$ in position space vanish exponentially, as $\exp(-\gamma R)$ when $R\to\infty$, where $\gamma$ is positive and either finite (for closed channels) or infinitesimal, proportional to $\eta$ (for open channels). Hence if choice (ii) is made, the integrand of the surface integral vanishes on the hypersurface and $\Delta H_a = 0$. For this choice $H_a$ is Hermitian, but terms in $\eta$ cannot be dropped automatically in an expression that was derived using the Hermiticity of $H_a$; one must first check that all terms that are multiplied by $\eta$ do indeed vanish as $\eta\to 0$, and sometimes they do not. The following example illustrates the point. We can reexpress Eq. (7) for $N=1$ as

$$\Gamma_1 = -2\,\mathrm{Im}\langle\phi_0|V_+^\dagger|\phi_1\rangle \tag{9}$$

$$= -2\,\mathrm{Im}\langle\phi_0|V_+^\dagger G_a^\dagger(E_1+i\eta)(E_1-i\eta-H_a)|\phi_1\rangle \tag{10}$$

$$= -2\,\mathrm{Im}\langle\phi_1|(E_1-i\eta-H_a)|\phi_1\rangle, \tag{11}$$

where we used $G_a(E_1-i\eta)(E_1-i\eta-H_a)=1$ and $G_a(E_1-i\eta)=G_a^\dagger(E_1+i\eta)$ in the second step and Eq. (2) in the third step. Now we can write $-2\,\mathrm{Im}\langle\phi_1|(E_1-H_a)|\phi_1\rangle$ as $i\langle\phi_1|(H_a^\dagger-H_a)|\phi_1\rangle$ which vanishes if we make choice (ii), in which case we arrive at the rather simple looking result

$$\Gamma_1 = 2\,\eta\langle\phi_1|\phi_1\rangle. \tag{12}$$

However, $\langle\phi_1|\phi_1\rangle$ is infinite in the limit $\eta\to 0$, such that — see footnote [19] for more details — the right-hand side of Eq. (12), rather than vanishing, approaches $\Gamma_1$. Note that while Eq. (12) is correct, it is not especially useful for the purpose of computation. On the other hand, if choice (i) is made in this example, the right-hand side of Eq. (12) vanishes, but $\langle\phi_1|(H_a^\dagger-H_a)|\phi_1\rangle$ does not vanish. In general, if we make choice (i) the integrand of the surface integral does not vanish on the hypersurface. Nevertheless, as long as the integrand oscillates as $R$ is varied, such that the average value of the surface integral $\Delta H_a$ (averaged over many periods of oscillation) vanishes, we can treat $H_a$ as Hermitian. However, if the integrand does not vanish, and is not oscillatory — which is the case for $\langle\phi_1|(H_a^\dagger-H_a)|\phi_1\rangle$ — we cannot treat $H_a$ as Hermitian.

To summarize, in deciding whether to take the limit $R\to\infty$ or $\eta\to 0$ first, there is no *a priori* reason to prefer one choice over the other, but in general these limits do not commute, and the expression that results from a particular choice may obtain only for that choice. In this paper we make

choice (i), i.e., we let $\eta \to 0$ first, but we often let $i\eta$ remain on display as an important reminder of the asymptotic boundary conditions.

In the next section we derive Eq. (5), and in Sec. III we discuss an application of this formula to the determination of the inclusive rate for two-photon ionization of hydrogen by circularly polarized light. In Sec. IV we derive Eq. (8) for the case $N=2$. We conclude this Introduction by remarking once again that we use the velocity gauge; it is only in this gauge that Eqs. (5), (7), and (8) hold when $N > N_0$.

## II. INCLUSIVE RATE

To prove Eq. (5) we start from Fermi's golden rule generalized to the inclusive rate for $N$-photon absorption:

$$\Gamma_N = 2\pi \sum_\alpha \rho(k_{N\alpha}) \int d\Omega |\langle \psi_\alpha(\mathbf{k}_{N\alpha})|V_+|\phi_{N-1}\rangle|^2, \tag{13}$$

where $|\psi_\alpha(\mathbf{k}_{N\alpha})\rangle$ represents an electron that escapes into the solid angle $d\Omega$ with momentum $\mathbf{k}_{N\alpha}$ leaving the residual ion in a state labeled by $\alpha$. Also, $\rho(k)$ is the density-of-states factor, and the sum over $\alpha$ is over all open channels and may include an integral over some of the continuum states of the residual ion. We have $|\mathbf{k}_{M\alpha}| = k_{M\alpha}$, where

$$k_{M\alpha} = \sqrt{2(E_M - e_\alpha + i\eta)}, \tag{14}$$

with $e_\alpha$ the energy of the residual ion. Now manipulation of the expression on the right-hand side of Eq. (13) can be facilitated by releasing the final-state wave function from the constraint of energy conservation. At first sight it seems possible to do this by merely introducing a $\delta$ function in energy:

$$\Gamma_N = 2\pi \sum_\alpha \int d\Omega\, dE \quad \delta(E_N - e_\alpha - E) \times \rho(k) |\langle \psi_\alpha(\mathbf{k})|V_+|\phi_{N-1}\rangle|^2, \tag{15}$$

where $E = k^2/2$. Unfortunately, unless $N = N_0$ (the minimum number of photons which the system must absorb to decay), this $\delta$ function does not restore energy conservation. The reason is as follows. If $N > L \geq N_0$, the matrix element $\langle \psi_\alpha(\mathbf{k})|V_+|\phi_{N-1}\rangle$ is infinite when $k = k_{L\alpha}$ since, as we see below, the integrand of (the integral representation of) this matrix element has a nonoscillatory component which does not vanish as the photoelectron coordinate tends to infinity; consequently, the non-energy-conserving regions $E \approx E_L - e_\alpha$, where $L = N_0, N_0+1, \ldots, N-1$, contribute to the integral over $E$, despite the presence of $\delta(E_N - e_\alpha - E)$.

To explain this divergence further, we consider the asymptotic boundary condition satisfied by the response function in position space. Let $\mathbf{x}$ be the position vector of the electron that escapes, with $r$ the radial coordinate. We ignore the distortion caused by the Coulomb tail, and the possibility that the residual ion is in a continuum state (these are matters that are only of peripheral concern here). If $M \geq N_0$, we have, for $r \sim \infty$ and *within the velocity gauge* [20],

$$\langle \mathbf{x}|\phi_M\rangle \sim \sum_{L=N_0}^{M} \sum_\alpha \frac{e^{ik_{L\alpha}r}}{r} f_{\alpha ML}, \tag{16}$$

where $f_{\alpha ML}$ is the amplitude (which does not depend on $r$) for real absorption of $L$ photons and virtual absorption of $M-L$ photons, where by ''virtual'' absorption we are referring to the absorption of photons by a *free* electron moving through the radiation field. (At large values of $r$ the photoelectron is more or less free of the force exerted by the residual ion, but the radiation field is still present. A free electron cannot truly absorb photons, i.e., it cannot permanently retain any energy that it absorbs from the radiation field, but it can absorb energy over times much shorter than the cycle time $2\pi/\omega$; this energy is returned to the field before the cycle is complete.) If $L \geq N_0$, we have, at least for the ground state of the residual ion and possibly for some excited states also, $\mathrm{Re}\, k_{L\alpha} > 0$. For such channels the term in $e^{ik_{L\alpha}r}/r$ is not square-integrable (in the limit $\eta \to 0$) since it does not vanish sufficiently rapidly as $r$ increases. Hence $\langle \mathbf{x}|V_+|\phi_M\rangle$ is not square-integrable for $M \geq N_0$. More importantly, the integrand of the matrix element $\langle \psi_\alpha(\mathbf{k})|V_+|\phi_{N-1}\rangle$ has a nonoscillatory component which does not vanish at $r \sim \infty$ when $k = k_{L\alpha}$.

To proceed, we observe that

$$(E_M - H_a)|\psi_\alpha(\mathbf{k}_{N\alpha})\rangle = (E_M - E_N)|\psi_\alpha(\mathbf{k}_{N\alpha})\rangle,$$

and hence that

$$O_N|\psi_\alpha(\mathbf{k}_{N\alpha})\rangle = |\psi_\alpha(\mathbf{k}_{N\alpha})\rangle.$$

Therefore, we can replace $|\psi_\alpha(\mathbf{k}_{N\alpha})\rangle$ by $O_N|\psi_\alpha(\mathbf{k}_{N\alpha})\rangle$ in Fermi's golden rule, Eq. (13). The advantage of doing this becomes apparent after first noting that since $(\nabla_{\mathbf{x}}^2 + k^2)\exp(ikr)/r = -4\pi\delta(\mathbf{x})$, and since the kinetic energy operator commutes with $V_+$, the function $\langle \mathbf{x}|O_N V_+|\phi_M\rangle$ is a superposition of square-integrable terms, each of which falls off as $e^{ik_{L\alpha}r}/r^2$ as $r$ increases. Consequently, $\langle \mathbf{x}|O_N V_+|\phi_M\rangle$ is square-integrable; an example, for the case $N=2$, is given in the next section — see Eq. (22). Furthermore, we can treat $O_N$ as Hermitian (in the limit $\eta \to 0$) within the integrand of the matrix element $\langle \psi_\alpha(\mathbf{k}_{N\alpha})|O_N V_+|\phi_{N-1}\rangle$ since, in position space, $\langle \psi_\alpha(\mathbf{k}_{N\alpha})|\mathbf{x}\rangle$ oscillates for large values of $r$ as a standing wave with wave number $k_{N\alpha}$ while $\langle \mathbf{x}|V_+|\phi_{N-1}\rangle$ oscillates as a sum of outgoing waves with the different wave numbers $k_{N_0\alpha}, k_{N_0+1,\alpha}, \ldots, k_{N-1,\alpha}$, so that the product of $\langle \psi_\alpha(\mathbf{k}_{N\alpha})|\mathbf{x}\rangle$ and $\langle \mathbf{x}|V_+|\phi_{N-1}\rangle$ oscillates for large values of $r$. Therefore, $\langle \psi_\alpha(\mathbf{k}_{N\alpha})|V_+|\phi_{N-1}\rangle = \langle \psi_\alpha(\mathbf{k}_{N\alpha})|O_N V_+|\phi_{N-1}\rangle$, and if we make this insertion into Fermi's golden rule before introducing the $\delta$ function, only the energy-conserving region $E \approx E_N$ contributes. Thus in place of Eq. (15) we write

$$\Gamma_N = 2\pi \sum_\alpha \int d\Omega\, dE \quad \delta(E_N - e_\alpha - E)\rho(k) \times \langle \phi_{N-1}|V_+^\dagger O_N^\dagger|\psi_\alpha(\mathbf{k})\rangle \langle \psi_\alpha(\mathbf{k})|O_N V_+|\phi_{N-1}\rangle. \tag{17}$$

We can now use

$$\delta(E_N - H_a) = \sum_\alpha \int d\Omega\, dE \quad \rho(k) \times \delta(E_N - e_\alpha - E)|\psi_\alpha(\mathbf{k})\rangle\langle\psi_\alpha(\mathbf{k})|, \quad (18)$$

where we have omitted bound states since $E_N > 0$, to write

$$\Gamma_N = 2\pi\langle\phi_{N-1}|V_+^\dagger O_N^\dagger \delta(E_N - H_a) O_N V_+|\phi_{N-1}\rangle. \quad (19)$$

Recalling that

$$G_a(E_N + i\eta) = P\frac{1}{E_N - H_a} - i\pi\delta(E_N - H_a), \quad (20)$$

where $P$ implies principal value, we substitute for $\delta(E_N - H_a)$ on the right-hand side of Eq. (19). Noting that the principal part disappears when the imaginary part is taken, we arrive at Eq. (5). To summarize, when $N$ is equal to the minimum number of photons, $N_0$, which the system must absorb to decay, the inclusion of $O_N$ is unnecessary. However, if $O_N$ were omitted in the case $N > N_0$, non-energy-conserving states would play a role and the real absorption of less than $N$ (but $\geqslant N_0$) photons would yield a spurious contribution to $\Gamma_N$.

### III. TWO-PHOTON IONIZATION

In this section we specialize to two-photon decay. For computational purposes it is convenient to carry through the operation with $O_2$ in $O_2 V_+|\phi_1\rangle$. We have

$$O_2 V_+|\phi_1\rangle = -(1/\omega)[V_+, H_a]|\phi_1\rangle - (1/\omega)V_+(E_1 - H_a)|\phi_1\rangle. \quad (21)$$

The commutator $[V_+, H_a]$ involves the interaction, $W$ say, of the electrons within the system; we have $[V_+, H_a] = \hat{\boldsymbol{\epsilon}}\cdot(\mathbf{p}W)/(2\omega)$. Using Eq. (4) to replace $(E_1 - H_a)|\phi_1\rangle$ by $V_+|\phi_0\rangle$, we obtain

$$O_2 V_+|\phi_1\rangle = -(1/2\omega^2)\hat{\boldsymbol{\epsilon}}\cdot(\mathbf{p}W)|\phi_1\rangle - (1/\omega)(V_+)^2|\phi_0\rangle. \quad (22)$$

In this last form $O_2 V_+|\phi_1\rangle$ is evidently square-integrable since in position space ($\mathbf{p}W$) and $|\phi_0\rangle$, respectively, fall off as an inverse square and as an exponential of the distance.

We have calculated the rate for two-photon ionization from the ground state of hydrogen, by circularly polarized light, using Eqs. (5) and (22). We used the Dalgarno-Lewis method to determine $|\phi_1\rangle$ and $G_a(E_2 + i\eta)O_2 V_+|\phi_1\rangle$, i.e., we solved the inhomogeneous equations $(E_1 - H_a)|\Psi\rangle = V_+|\phi_0\rangle$ and $(E_2 - H_a)|\Psi\rangle = O_2 V_+|\phi_1\rangle$ subject to outgoing-wave boundary conditions. We expressed these equations on a complex basis consisting of the functions $L_n(2i\kappa r)e^{i\kappa r}Y_{lm}(\hat{\mathbf{x}})$, where $L_n(x)$ is a Laguerre polynomial and $Y_{lm}(\hat{\mathbf{x}})$ is a spherical harmonic. The parameter $\kappa$ was chosen to lie in the upper right quadrant of the complex plane so that the basis simulates outgoing-wave boundary conditions (the inclusion of $i\eta$ is unnecessary). After radial and angular integration, the matrix element on the right-hand side of Eq. (5) becomes a finite double sum of the form

TABLE I. Convergence of the rate for two-photon ionization of H(1$s$) by circularly polarized light of wavelengths $\lambda = 40$ and 70 nm vs the number $n$ of terms in a Padé sum over the radial basis functions used in the calculation. The rate is in atomic units, and has been divided by $F^4$, where $F$ is the amplitude of the electric field. The calculations were performed with a complex basis composed of 30 radial functions (see text), which depend on a complex wave number $\kappa$ chosen so that $|\kappa| = 0.8$ and $\arg\kappa = 75°$ or 60°.

| $n$ | $\lambda = 40$ (nm) $\arg\kappa = 75°$ | $\lambda = 40$ (nm) $\arg\kappa = 60°$ | $\lambda = 70$ (nm) $\arg\kappa = 75°$ | $\lambda = 70$ (nm) $\arg\kappa = 60°$ |
|---|---|---|---|---|
| 1 | 0.08642 | 0.10039 | 0.90376 | 0.51690 |
| 2 | −0.09101 | −0.13874 | −0.50374 | 1.00855 |
| 3 | −0.01774 | −0.02812 | 1.44483 | 0.53818 |
| 4 | 0.03741 | 0.06083 | 1.88777 | 2.32939 |
| 5 | 0.02147 | 0.02616 | 0.96448 | 0.79242 |
| 6 | 0.00510 | 0.00442 | 0.62710 | 0.56809 |
| 7 | 0.00918 | 0.00910 | 0.80332 | 0.87729 |
| 8 | 0.01199 | 0.01032 | 0.72366 | 0.77122 |
| 9 | 0.01398 | 0.00865 | 0.81687 | 0.83169 |
| 10 | 0.01244 | 0.01118 | 0.81641 | 0.79303 |
| 11 | 0.01240 | 0.01275 | 0.80689 | 0.80754 |
| 12 | 0.01265 | 0.01261 | 0.79981 | 0.80091 |
| 13 | 0.01208 | 0.01274 | 0.80366 | 0.80283 |
| 14 | 0.01214 | 0.01256 | 0.80135 | 0.80091 |
| 15 | 0.01212 | 0.01208 | 0.80169 | 0.80213 |
| 16 | 0.01213 | 0.01218 | 0.80170 | 0.80209 |
| 17 | 0.01213 | 0.01212 | 0.80172 | 0.80128 |
| 18 | 0.01216 | 0.01209 | 0.80173 | 0.80168 |
| 19 | 0.01215 | 0.01223 | 0.80173 | 0.80149 |
| 20 | 0.01216 | 0.01212 | 0.80173 | 0.80149 |
| 21 | 0.01216 | 0.01214 | 0.80173 | 0.80151 |
| 22 | 0.01216 | 0.01215 | 0.80175 | 0.80154 |
| 23 | 0.01216 | 0.01215 | 0.80176 | 0.80153 |
| 24 | 0.01216 | 0.01215 | 0.80175 | 0.80155 |
| 25 | 0.01216 | 0.01215 | 0.80176 | 0.80158 |
| 26 | 0.01217 | 0.01216 | 0.80175 | 0.80156 |
| 27 | 0.01216 | 0.01215 | 0.80177 | 0.80158 |
| 28 | 0.01216 | 0.01215 | 0.80174 | 0.80155 |
| 29 | 0.01216 | 0.01215 | 0.80173 | 0.80159 |
| 30 | 0.01216 | 0.01215 | 0.80174 | 0.80154 |

$$\langle\phi_{N-1}|V_+^\dagger O_N^\dagger G_a(E_N + i\eta)O_N V_+|\phi_{N-1}\rangle = \sum_{n=0}^{n_{\max}}\sum_{n'=0}^{n_{\max}} T_{nn'}(\kappa^*, \kappa), \quad (23)$$

where $n$ and $n'$ are indices of the Laguerre polynomial, with $n_{\max}$ the highest degree included in the basis, and where $T_{nn'}(\kappa^*, \kappa)$ is a function which depends on both $\kappa$ and $\kappa^*$, and is therefore nonanalytic in $\kappa$. The dependence on $\kappa^*$ arises from the complex conjugation of the radial basis functions in the construction of $\langle\phi_{N-1}|(O_N V_+)^\dagger$. In view of the nonanalyticity of the double sum, one may expect it to converge slowly, or perhaps not at all. In fact, when $N = N_0$ $(=2)$ the double sum converges rapidly; but in this case $O_N V_+|\phi_{N-1}\rangle$ represents a closed channel, and its radial part is real, implying that the double sum can be recast in a

form that involves only sums of terms that are analytic in $\kappa$. However, when $N>N_0$, i.e., when $N=2$ and $N_0=1$, the convergence of the double sum is slow; but it can be accelerated by using Padé summation. We evaluated the inner sum, i.e., the sum over $n'$ on the right-hand side of Eq. (23), directly, but we evaluated the outer sum, over $n$, by Padé summation using Wynn's epsilon algorithm [21]. The rate of convergence is illustrated in Table I for calculations done with $n_{\max}=30$, $|\kappa|=0.8$, and $\arg\kappa=75°$ or 60°. (We made no attempt to choose the optimal value of $\kappa$ for rapid convergence.) These results for the two-photon rate are in good agreement (discrepancies of less than 1%) with earlier estimates [22,23] obtained using other methods.

Were we to use the length gauge, in which $V_+=\hat{\boldsymbol{\epsilon}}\cdot\mathbf{x}/2$, the commutator $[V_+,H_a]$ would be $i\hat{\boldsymbol{\epsilon}}\cdot\mathbf{p}/2$, and $[V_+,H_a]|\phi_1\rangle$ would no longer be square-integrable when $N>N_0$. We verified that when $N=N_0$ $(=2)$ the results for the two-photon decay rate are the same in the length and velocity gauges; but when $N>N_0$, i.e., when $N=2$ and $N_0=1$, we were unable to achieve convergence in the length gauge.

## IV. FLUX FORMULA AND PARTIAL RATE

In this section, we verify for the case $N=2$ the formula, Eq. (8), for the partial rate for $N$-photon decay of a two-electron system. We start with an alternative expression [17] for the inclusive $N$-photon decay rate:

$$\Gamma_N=i\sum_{M=N_0}^{N}\sum_{M'=N_0}^{N}\frac{(-\omega)^{M+M'-2N}}{(N-M)!(N-M')!}\times\langle\phi_M|(V_+^\dagger)^{N-M}(H_a-H_a^\dagger)(V_+)^{N-M'}|\phi_{M'}\rangle. \quad (24)$$

Note the absence of $i\eta$, and observe that $H_a$ is not Hermitian in this expression (recall the discussion near the end of the Introduction). Equation (24) relates the rate directly to the outgoing photoelectron flux through a large hypersphere, as follows upon applying Green's theorem to transform from volume to surface integral. While Eq. (24) does not involve the final-state wave function, it is not as useful for computational purposes as Eq. (5); nevertheless, it is formally a useful result.

The path that connects the flux formula Eq. (24) to Eq. (5) provides the way to establish the formula, Eq. (8), for the partial rate. For simplicity, we demonstrate the equivalence of Eqs. (5) and (24) only in the case $N=2$. (We do not restrict the number of electrons.) Putting $N=2$ and $N_0=1$ in Eq. (24) yields four terms:

$$\Gamma_2=\Gamma_{2a}+\Gamma_{2b}+\Gamma_{2c}+\Gamma_{2d}, \quad (25)$$

where

$$\Gamma_{2a}=i\langle\phi_2|(H_a-H_a^\dagger)|\phi_2\rangle, \quad (26)$$

$$\Gamma_{2b}=(i/\omega^2)\langle\phi_1|V_+^\dagger(H_a-H_a^\dagger)V_+|\phi_1\rangle, \quad (27)$$

$$\Gamma_{2c}=-(i/\omega)\langle\phi_1|V_+^\dagger(H_a-H_a^\dagger)|\phi_2\rangle, \quad (28)$$

$$\Gamma_{2d}=\Gamma_{2c}^*. \quad (29)$$

Since $E_2$ is real, we can reexpress $\Gamma_{2a}$ as

$$\Gamma_{2a}=2\,\mathrm{Re}\,i\langle\phi_2|(E_2-H_a)^\dagger|\phi_2\rangle, \quad (30)$$

$$=2\,\mathrm{Re}\,i\langle\phi_1|V_+^\dagger|\phi_2\rangle, \quad (31)$$

$$=2\,\mathrm{Re}\,i\langle\phi_1|V_+^\dagger G_a(E_2)V_+|\phi_1\rangle, \quad (32)$$

where in the second and third steps we used Eqs. (4) and (2). Writing

$$\Gamma_{2b}=2\,\mathrm{Re}(i/\omega^2)\langle\phi_1|V_+^\dagger(E_0-H_a^\dagger)V_+|\phi_1\rangle, \quad (33)$$

we have

$$\Gamma_{2a}+\Gamma_{2b}=2\,\mathrm{Re}(i/\omega^2)\times\langle\phi_1|V_+^\dagger[\omega^2G_a(E_2)+E_0-H_a^\dagger]V_+|\phi_1\rangle. \quad (34)$$

We now manipulate the expression in square brackets on the right-hand side of Eq. (34):

$$\omega^2G_a(E_2)+E_0-H_a^\dagger$$
$$=[\omega^2+(E_0-H_a^\dagger)(E_2-H_a)]G_a(E_2) \quad (35)$$
$$=[(E_1-H_a^\dagger)(E_1-H_a)+\omega(H_a-H_a^\dagger)]G_a(E_2) \quad (36)$$
$$=\omega^2O_2^\dagger G_a(E_2)O_2+\omega(H_a-H_a^\dagger)G_a(E_2). \quad (37)$$

It follows that

$$\Gamma_{2a}+\Gamma_{2b}=2\,\mathrm{Re}\,i\langle\phi_1|V_+^\dagger O_2^\dagger G_a(E_2+i\eta)O_2V_+|\phi_1\rangle+2\,\mathrm{Re}(i/\omega)\langle\phi_1|V_+^\dagger(H_a-H_a^\dagger)|\phi_2\rangle. \quad (38)$$

The first term on the right-hand side of Eq. (38) is $\Gamma_2$. Adding $\Gamma_{2c}+\Gamma_{2d}$ results in cancellation of the second term on the right-hand side of Eq. (38), establishing the equivalence of Eqs. (5) and (24) for $N=2$.

The merit of the flux formula is that it depends only on the asymptotic behavior of the electrons on the surface of a large hypersphere. Hence we can immediately write down a formal expression for the partial rate for single-electron emission in channel $\alpha$ from a two-electron system:

$$\Gamma_{\alpha,N}=i\sum_{M=N_0}^{N}\sum_{M'=N_0}^{N}\frac{(-\omega)^{M+M'-2N}}{(N-M)!(N-M')!}\times\langle\phi_M|(V_+^\dagger)^{N-M}P_\alpha(H_a-H_a^\dagger)P_\alpha(V_+)^{N-M'}|\phi_{M'}\rangle, \quad (39)$$

where $P_\alpha$ is [24] the Hermitian projection operator $P_\alpha=P_{1\alpha}+P_{2\alpha}-P_{1\alpha}P_{2\alpha}$ which projects onto the union of subspaces in which electron 1 or 2 is in state $\alpha$. We can drop $P_{1\alpha}P_{2\alpha}$ from $P_\alpha$ on the right-hand side of Eq. (39) since $P_{1\alpha}P_{2\alpha}$ projects onto the subspace in which both electrons are *bound*, a region which does not contribute to the photoelectron flux. We now write

$$H_a\equiv H_{12}+W_{12}, \quad (40)$$

where, recall, $W_{12}$ is the interaction between the electrons and $H_{12}=H_1+H_2$, where $H_1$ and $H_2$ are the Hamiltonians

of the one-electron residual systems created by the departure of electron 1 or 2, respectively. Note that $P_{1\alpha}$ and $P_{2\alpha}$ each commute with $H_1$ and $H_2$, and hence with $H_{12}$. Since $W_{12}$ is Hermitian, we can drop it from $H_a$ on the right-hand side of Eq. (39). We thereby obtain

$$\begin{aligned}\Gamma_{\alpha,N} &= i\sum_{M=N_0}^{N}\sum_{M'=N_0}^{N}\frac{(-\omega)^{M+M'-2N}}{(N-M)!(N-M')!}\\ &\times\langle\phi_M|(V_+^\dagger)^{N-M}(P_{1\alpha}+P_{2\alpha})(H_{12}-H_{12}^\dagger)(P_{1\alpha}+P_{2\alpha})\\ &\times(V_+)^{N-M'}|\phi_{M'}\rangle\\ &= 2\,\mathrm{Re}\,i\sum_{M=N_0}^{N}\frac{\omega^{2M-2N}}{(N-M)!^2}\langle\phi_M|(V_+^\dagger)^{N-M}(P_{1\alpha}+P_{2\alpha})\\ &\times(E_N-H_{12}^\dagger)(P_{1\alpha}+P_{2\alpha})(V_+)^{N-M}|\phi_M\rangle\\ &+ i\sum_{M=N_0}^{N}\sum_{M'\neq M}\frac{(-\omega)^{M+M'-2N}}{(N-M)!(N-M')!}\\ &\times\langle\phi_M|(V_+^\dagger)^{N-M}(P_{1\alpha}+P_{2\alpha})(H_{12}-H_{12}^\dagger)(P_{1\alpha}+P_{2\alpha})\\ &\times(V_+)^{N-M'}|\phi_{M'}\rangle. \qquad (41)\end{aligned}$$

We can commute $(P_{1\alpha}+P_{2\alpha})$ from the left to the right of $(E-H_{12}^\dagger)$, and from the right to the left of $(H_{12}-H_{12}^\dagger)$, on the right-hand side of Eq. (41). This gives $(P_{1\alpha}+P_{2\alpha})^2$ on the right and left, respectively, of $(E-H_{12}^\dagger)$ and $(H_{12}-H_{12}^\dagger)$. Since $P_{1\alpha}^2=P_{1\alpha}$ and $P_{2\alpha}^2=P_{2\alpha}$, we have $(P_{1\alpha}+P_{2\alpha})^2=P_{1\alpha}+P_{2\alpha}+2P_{1\alpha}P_{2\alpha}$. As before, we can drop $P_{1\alpha}P_{2\alpha}$. This yields an expression that is linear in $(P_{1\alpha}+P_{2\alpha})$, and (since the electrons are identical) the separate contributions from $P_{1\alpha}$ and $P_{2\alpha}$ are equal. It follows that

$$\begin{aligned}\Gamma_{\alpha,N} &= 4\,\mathrm{Re}\,i\sum_{M=N_0}^{N}\frac{\omega^{2M-2N}}{(N-M)!^2}\langle\phi_M|(V_+^\dagger)^{N-M}(E_N-H_{12}^\dagger)\\ &\times P_{1\alpha}(V_+)^{N-M}|\phi_M\rangle\\ &+ 2i\sum_{M=N_0}^{N}\sum_{M'\neq M}\frac{(-\omega)^{M+M'-2N}}{(N-M)!(N-M')!}\\ &\times\langle\phi_M|(V_+^\dagger)^{N-M}P_{1\alpha}(H_{12}-H_{12}^\dagger)(V_+)^{N-M'}|\phi_{M'}\rangle\\ &= 4\,\mathrm{Re}\,i\sum_{M=N_0}^{N}\frac{(\omega)^{2M-2N}}{(N-M)!^2}\langle\phi_M|(V_+^\dagger)^{N-M}[(E_N-H_a^\dagger)\\ &+ W_{12}]P_{1\alpha}(V_+)^{N-M}|\phi_M\rangle\\ &+ 2i\sum_{M=N_0}^{N}\sum_{M'\neq M}\frac{(-\omega)^{M+M'-2N}}{(N-M)!(N-M')!}\\ &\times\langle\phi_M|(V_+^\dagger)^{N-M}P_{1\alpha}(H_a-H_a^\dagger)(V_+)^{N-M'}|\phi_{M'}\rangle, \qquad (42)\end{aligned}$$

where in the last step we reinserted $W_{12}$ in $H_a$. Note that $2\,\mathrm{Re}\,i\langle\chi|W_{12}P_{1\alpha}|\chi\rangle$ can be rewritten as $-i\langle\chi|[P_{1\alpha},W_{12}]|\chi\rangle$.

Putting $N=2$ and $N_0=1$ in Eq. (42) gives

$$\Gamma_{\alpha,2}=\Gamma_{\alpha,2a}+\Gamma_{\alpha,2b}+\Gamma_{\alpha,2c}+\Gamma_{\alpha,2d}, \qquad (43)$$

where

$$\begin{aligned}\Gamma_{\alpha,2a} &= 4\,\mathrm{Re}\,i\langle\phi_2|(E_2-H_a)^\dagger P_{1\alpha}|\phi_2\rangle\\ &- 2i\langle\phi_2|[P_{1\alpha},W_{12}]|\phi_2\rangle, \qquad (44)\end{aligned}$$

$$\begin{aligned}\Gamma_{\alpha,2b} &= 4\,\mathrm{Re}(i/\omega^2)\langle\phi_1|V_+^\dagger(E_0-H_a^\dagger)P_{1\alpha}V_+|\phi_1\rangle-(2i/\omega^2)\\ &\times\langle\phi_1|V_+^\dagger[P_{1\alpha},W_{12}]V_+|\phi_1\rangle, \qquad (45)\end{aligned}$$

$$\Gamma_{\alpha,2c}=-(2i/\omega)\langle\phi_1|V_+^\dagger P_{1\alpha}(H_a-H_a^\dagger)|\phi_2\rangle, \qquad (46)$$

$$\Gamma_{\alpha,2d}=\Gamma_{2c}^*. \qquad (47)$$

We now retrace the steps leading from Eq. (25) to Eq. (38), and find

$$\begin{aligned}\Gamma_{\alpha,2a}+\Gamma_{\alpha,2b} &= 4\,\mathrm{Re}\,i\langle\phi_1|V_+^\dagger P_{1\alpha}O_2^\dagger G_a(E_2+i\eta)O_2V_+|\phi_1\rangle\\ &+ 4\,\mathrm{Re}(i/\omega)\langle\phi_1|V_+^\dagger P_{1\alpha}(H_a-H_a^\dagger)|\phi_2\rangle\\ &- 2i\langle\phi_2|[P_{1\alpha},W_{12}]|\phi_2\rangle-(2i/\omega^2)\\ &\times\langle\phi_1|V_+^\dagger[P_{1\alpha},W_{12}]V_+|\phi_1\rangle. \qquad (48)\end{aligned}$$

Adding $\Gamma_{2c}+\Gamma_{2d}$ yields Eq. (8) for $N=2$.

## ACKNOWLEDGMENT

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$$\Gamma_1 = 4\pi \sum_\alpha k_{1\alpha}|f_\alpha|^2.$$

Now consider the right-hand side of Eq. (12). Writing $\langle \phi_1|\phi_1\rangle$ as a volume integral, we need only be concerned with the divergent part of the integral since the finite part vanishes after multiplication by $\eta$. The divergent part comes from the nonoscillating part of the integrand in the region of large $r$, and noting that $\mathrm{Im}\, ik_{1\alpha} = \eta/k_{1\alpha}$ we have

$$\langle \phi_1|\phi_1\rangle \sim \int d\Omega \int^\infty r^2\, dr \sum_\alpha \exp(-2\eta r/k_{1\alpha})|f_\alpha|^2/r^2.$$

The integration over solid angle gives $4\pi$ and performing the integration over $r$ yields $\langle \phi_1|\phi_1\rangle \sim (2\pi/\eta)\Sigma_\alpha k_{1\alpha}|f_\alpha|^2$, thereby confirming Eq. (12).
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