Theory of double photoionization of a two-electron atom: Circumventing the boundary conditions

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We describe a method for calculating cross sections for double ionization of a two-electron atom (or ion) by one or more photons, and we present results of an application to double ionization of He by one photon. The method does not require the explicit inclusion of the asymptotic boundary conditions for two-electron escape; rather, the contribution from the single ionization channel to the inclusive rate is removed by using the projection operator that projects onto this channel. Energy and angular distributions for double ionization can be obtained by modifying this projection operator.

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I. INTRODUCTION

The theoretical treatment of double ionization of an atomic system by one or more photons is complicated not only by the importance of electron-electron correlation but also by the boundary conditions for two-electron escape. In this paper we describe a method for treating double ionization of a two-electron atom (or ion) without the explicit inclusion of boundary conditions. The interaction of the atom with the radiation field is treated as a perturbation, but within the framework of perturbation theory the method is in principle exact. We present results of an application to double ionization of helium by one photon, along with a comparison to other theoretical and experimental data.

Our method is based on an expression for the total flux passing through a hypersphere of very large radius. In place of asymptotic boundary conditions we invoke projection operators. Thus, double ionization is separated from single ionization by projecting out the bound states of the one-electron ion (or atom) left behind after single ionization. Energy and angular distributions for double ionization can be obtained by modifying this projection operator, as shown below. In the next section we describe the theoretical approach. We begin by considering just one-photon ionization, and then we generalize to multiphoton ionization. In Sec. III we present some results.

II. METHOD

We denote the interaction of the atom with the radiation field as

$$V(t) \equiv V_+ e^{-i\omega t} + V_- e^{i\omega t}, \tag{1}$$

where ω is the frequency and $V_- = V_+^\dagger$. As just noted, we assume that the radiation is sufficiently weak that $V(t)$ can be treated as a perturbation. Let H_a be the Hamiltonian of the bare two-electron atom (or ion), and let E_n and $|\Psi_n\rangle$ be its eigenvalues and eigenvectors, where n is a continuous label when it runs over continuum states. The continuum eigenvectors are normalized on the energy scale. We neglect spin-orbit coupling in the atom. We use atomic units, and we assume that the atom (or ion) is initially in a bound state represented by $|\Psi_0\rangle$, with bound-state energy E_0.

A. One-photon ionization

The rate Γ_1 for the atom to ionize by absorption of one photon is, in lowest order perturbation theory,

$$\Gamma_1 = 2\pi \sum_n |\langle \Psi_n | V_+ | \Psi_0 \rangle|^2 \delta(E_n - E_\omega), \tag{2}$$

where $E_\omega = E_0 + \omega$ and where the sum over n includes an integral over the continuum. The summation becomes implicit if we rewrite Eq. (2) as

$$\Gamma_1 = 2\pi \langle \Psi_0 | V_- \delta(E_\omega - H_a) V_+ | \Psi_0 \rangle. \tag{3}$$

Introducing the resolvent operator $G_a(E)$, defined as

$$G_a(E) = 1/(E - H_a), \tag{4}$$

and noting that, if E is real and if η is positive but infinitesimal, we have

$$\mathrm{Im} G_a(E + i\eta) = -\pi \delta(E - H_a); \tag{5}$$

this enables us to express Eq. (3) in another well-known form:

$$\Gamma_1 = -2\mathrm{Im} \langle \Psi_0 | V_- G_a(E_\omega + i\eta) V_+ | \Psi_0 \rangle. \tag{6}$$

The rate Γ_1 is for *total* ionization, and therefore includes the contributions from both single and double ionization. To extract the rate for double ionization we begin by introducing the factor $G_a(E_\omega + i\eta)(E_\omega + i\eta - H_a)$, which is just unity, to the left of $G_a(E_\omega + i\eta)$ in Eq. (6), and we use

$$G_a(E_\omega + i\eta) = G_a(E_\omega - i\eta) - 2\pi i \delta(E_\omega - H_a) \tag{7}$$

to rewrite Eq. (6) as

$$\Gamma_1 = -2\mathrm{Im} \langle \Phi_1^{(1)} | (E_\omega + i\eta - H_a) | \Phi_1^{(1)} \rangle + 4\pi \langle \Psi_0 | V_- \delta(E_\omega - H_a) V_+ | \Psi_0 \rangle, \tag{8}$$

where

$$|\Phi_1^{(1)}\rangle = G_a(E_\omega + i\eta)V_+|\Psi_0\rangle. \quad (9)$$

It follows from Eqs. (3) and (8) that

$$\Gamma_1 = 2\mathrm{Im}\langle\Phi_1^{(1)}|(E_\omega + i\eta - H_a)|\Phi_1^{(1)}\rangle. \quad (10)$$

At this stage we can drop the infinitesimal term $i\eta$, it being understood that $|\Phi_1^{(1)}\rangle$ satisfies outgoing-wave boundary conditions (appropriate to one or two electrons moving outwards to infinity). Since $2\mathrm{Im}(z) = -i(z - z^*)$, we have, from Eq. (10),

$$\Gamma_1 = i\langle\Phi_1^{(1)}|(H_a - H_a^\dagger)|\Phi_1^{(1)}\rangle. \quad (11)$$

Using Green's theorem in six dimensions, noting that $(H_a - H_a^\dagger) = (T - T^\dagger)$, where T is the total kinetic energy operator for the electrons, we can transform the volume integral on the right-hand side of Eq. (11) to a *surface integral*, which gives the flux passing through a hypersphere of (infinitely) large radius. Hence, when Γ_1 is expressed in the form of either Eqs. (10) or (11), *it depends only on the asymptotic form of* $|\Phi_1^{(1)}\rangle$.

Proceeding further, we collect the coordinates $\mathbf{r}_1$ and $\mathbf{r}_2$ of the electrons relative to the nucleus into a single six-dimensional displacement vector $\mathbf{R} = (\mathbf{r}_1, \mathbf{r}_2)$. The wave function $\langle\mathbf{R}|\Phi_1^{(1)}\rangle$ describes the motion of the electrons in the final state, after the atom has absorbed the photon. The asymptotic boundary condition for two-electron escape is most conveniently specified in terms of the hyperspherical coordinates R, α, Ω_1, and Ω_2, where $R = \sqrt{r_1^2 + r_2^2}$, with $r_1 = |\mathbf{r}_1|$, $r_2 = |\mathbf{r}_2|$, where $\alpha = \tan^{-1}(r_1/r_2)$, and where Ω_1 and Ω_2 are, respectively, the solid angles defining the directions of $\mathbf{r}_1$ and $\mathbf{r}_2$. If both electrons escape, they collectively have a (six-dimensional) aymptotic momentum $\mathbf{K}$ which points along $\mathbf{R}$, with $K^2/2 = E_\omega$ (where $K = |\mathbf{K}|$). Denoting the amplitude for two-electron escape as $F(\Omega_1, \Omega_2, \alpha)$, the asymptotic boundary condition is [1–3]

$$\langle\mathbf{R}|\Phi_1^{(1)}\rangle \to \frac{e^{iKR + i\zeta\ln(KR)}}{R^{5/2}} F(\Omega_1, \Omega_2, \alpha),$$

$$R \to \infty,\ \alpha \neq 0, \pi/2 \quad (12)$$

where, with Z the atomic number of the parent nucleus, with k_1 and k_2 the speeds of the electrons relative to the nucleus, and with k_{12} the relative speed of the two electrons,

$$\zeta = \frac{Z}{k_1} + \frac{Z}{k_2} - \frac{1}{k_{12}}. \quad (13)$$

Note that the Pauli principle implies that, if S is the total spin quantum number of the electrons,

$$F(\Omega_1, \Omega_2, \alpha) = (-1)^S F(\Omega_2, \Omega_1, \pi/2 - \alpha). \quad (14)$$

However, the limit $R \to \infty$ does not guarantee that both electrons escape; we must also have $\alpha \neq 0, \pi/2$. If $\alpha = 0$ or $\pi/2$, one electron remains behind, possibly bound to its parent nucleus — corresponding to single ionization. Suppose that electron 1 escapes while electron 2 remains bound. If $\langle\mathbf{r}_2|\psi_m\rangle$ represents a bound state of the residual one-electron ion (or atom), whose energy is ϵ_m, and if $f_m(\Omega_1)$ is the amplitude for electron 1 to emerge into the solid angle Ω_1 and for electron 2 to be in the bound state m, the boundary condition appropriate to single ionization is

$$\langle\mathbf{R}|\Phi_1^{(1)}\rangle \to \sum_m \frac{e^{ik_{1m}r_1 + i\zeta_m \ln(k_{1m}r_1)}}{r_1} f_m(\Omega_1)\langle\mathbf{r}_2|\psi_m\rangle,$$

$$R \to \infty,\ \alpha \to \pi/2 \quad (15)$$

where $k_{1m}^2/2 = E_\omega - \epsilon_m$, $\zeta_m = (Z-1)/k_{1m}$, and the sum is over bound states only. If instead electron 2 escapes and electron 1 remains bound, we interchange the coordinates of the two electrons on the right-hand side of Eq. (15), multiply the amplitude by $(-1)^S$, and let $\alpha \to 0$. Hence to remove the contribution of the single-ionization channel to Γ_1, we simply multiply $|\Phi_1^{(1)}\rangle$ by the projection operator Q which annihilates the bound states of the residual one-electron ion (or atom) that is left behind after one electron has been removed. This projection operator is $Q = 1 - P$ where [4]

$$P = P_1 + P_2 - P_1P_2, \quad (16)$$

and where P_j is the operator which projects onto the subspace of bound states occupied by the jth electron; in position space we have

$$P_j = \sum_m \langle\mathbf{r}_j|\psi_m\rangle \int d^3r_j' \langle\psi_m|\mathbf{r}_j'\rangle, \quad (17)$$

where the sum is over all bound states of the residual one-electron ion (or atom). Note that P_j is rather simple (it involves a sum over bound states that are known exactly). The operator Q, while removing the single-ionization channels, leaves unchanged the asymptotic behavior of two-electron escape, i.e., Eq. (12). Consequently, the rate for double escape is

$$\Gamma_1^{++} = i\langle\Phi_1^{(1)}|Q(H_a - H_a^\dagger)Q|\Phi_1^{(1)}\rangle \quad (18)$$

$$= 2\mathrm{Im}\langle\Phi_1^{(1)}|Q(E_\omega - H_a)Q|\Phi_1^{(1)}\rangle. \quad (19)$$

Note that $(E_\omega - H_a)Q|\Phi_1^{(1)}\rangle$ is of order $O(1/R^2)Q|\Phi_1^{(1)}\rangle$, and although we could drop E_ω on the right-hand side of Eq. (19), since it is real and therefore does not contribute to the imaginary part of $\langle\Phi_1^{(1)}|Q(E_\omega - H_a)Q|\Phi_1^{(1)}\rangle$, its presence is required to ensure that the real part of this expression is finite.

Recalling that T is the total kinetic energy operator for the electrons, we have, from Eq. (18),

$$\Gamma_1^{++} = i\langle\Phi_1^{(1)}|Q(T - T^\dagger)Q|\Phi_1^{(1)}\rangle. \quad (20)$$

Using Green's theorem to convert the volume integral to a surface integral and using the asymptotic form of $Q|\Phi_1^{(1)}\rangle$, given by Eq. (12), we obtain

$$\Gamma_1^{++} = K \oint |F(\Omega_1, \Omega_2, \alpha)|^2 \sin^2(\alpha)\cos^2(\alpha) d\Omega_1 d\Omega_2 d\alpha. \quad (21)$$

We can determine $|\Phi_1^{(1)}\rangle$ by solving the inhomogeneous equation [see Eq. (9)]

$$(E_\omega - H_a)|\Phi_1^{(1)}\rangle = V_+|\Psi_0\rangle, \tag{22}$$

subject to *outgoing*-wave boundary conditions. Actually, we only require a knowledge of $Q|\Phi_1^{(1)}\rangle$, not the full $|\Phi_1^{(1)}\rangle$. If we put $|\Phi_1^{(1)}\rangle = (P+Q)|\Phi_1^{(1)}\rangle$ in Eq. (22), and premultiply by P and Q in turn, we can eliminate $P|\Phi_1^{(1)}\rangle$ to give an equation for $Q|\Phi_1^{(1)}\rangle$ directly:

$$(E_\omega - \tilde{H}_a)Q|\Phi_1^{(1)}\rangle = Q[1 + H_aPG_a(E_\omega)P]V_+|\Psi_0\rangle, \tag{23}$$

where $\tilde{H}_a$ includes the "optical potential:"

$$\tilde{H}_a = QH_aQ + QH_aPG_a(E_\omega)PH_aQ. \tag{24}$$

To summarize, the rate for double escape can be obtained without invoking the complicated boundary conditions that apply to double escape; we only need to solve an inhomogeneous equation [Eq. (22) or (23)] subject to outgoing-wave boundary conditions. After determining $|\Phi_1^{(1)}\rangle$, we can evaluate the volume integral on the right-hand side of Eq. (19). While it may appear that all we have done is replace $|\Phi_1^{(1)}\rangle$ by $Q|\Phi_1^{(1)}\rangle$ in the volume integral, we stress that in deriving Eq. (19) it was essential to transform to the surface integral as an intermediate step.

B. Energy and angular distributions

The integrand on the right-hand side of Eq. (21) is proportional to the triply differential cross section:

$$\frac{d^3\sigma}{d\Omega_1 d\Omega_2 d\alpha} \propto K|F(\Omega_1,\Omega_2,\alpha)|^2, \tag{25}$$

corresponding to the probability of ejecting the two electrons into the directions Ω_1 and Ω_2, while the ratio of their momenta is $\tan\alpha = k_1/k_2$. We now show that it is possible—at least in principle—to extract the triply differential cross section, without explicitly invoking the boundary condition. To this end we introduce $Q_\chi \equiv \chi \circ Q$, where, in coordinate space, $\chi \equiv \chi(\Omega_1,\Omega_2,\alpha)$ is a *real* multiplicative function depending only on angles, i.e., on α, Ω_1, and Ω_2. (Note that Q_χ is, in general, not a projection operator.) We define

$$\Gamma_1^{++}[\chi] \equiv \mathrm{Im}[\langle Q\Phi_1^{(1)}|(E_\omega - H_a)|Q_\chi\Phi_1^{(1)}\rangle + \langle Q_\chi\Phi_1^{(1)}|(E_\omega - H_a)|Q\Phi_1^{(1)}\rangle]. \tag{26}$$

We have

$$\Gamma_1^{++}[\chi] = \frac{i}{2}[\langle\Phi_1^{(1)}|Q_\chi(T-T^\dagger)Q|\Phi_1^{(1)}\rangle + \langle\Phi_1^{(1)}|Q(T-T^\dagger)Q_\chi|\Phi_1^{(1)}\rangle] \tag{27}$$

$$= K\oint |F(\Omega_1,\Omega_2,\alpha)|^2\chi(\Omega_1,\Omega_2,\alpha) \times \sin^2(\alpha)\cos^2(\alpha)d\Omega_1 d\Omega_2 d\alpha, \tag{28}$$

where in the second step we again used Green's theorem, noting now that the radial derivative (normal to the hypersurface) commutes with χ. To extract the triple differential cross section we could choose $\chi(\Omega_1,\Omega_2,\alpha)$ to be proportional to a δ function in the angles, but it is perhaps more convenient to proceed as follows. We introduce the complete set of (real) polynomials that are orthogonal with respect to the weight appearing in the surface integral of Eq. (28). These polynomials are

$$\Pi_{NLM\sigma}^{\lambda l}(\Omega_1,\Omega_2,\alpha) \equiv \frac{2}{\sqrt{\pi}}U_N(\cos 2\alpha)\mathcal{Z}_{LM\sigma}^{\lambda l}(\Omega_1,\Omega_2), \qquad M \geq 0,\ \sigma = \pm, \tag{29}$$

where $U_N(x)$ is the Chebyshev polynomial of the second kind and where, if $\mathcal{Y}_{LM}^{\lambda l}(\Omega_1,\Omega_2)$ is the spherical harmonic which couples the one-particle spherical harmonics $Y_{\lambda,m}(\Omega_1)$ and $Y_{l,m'}(\Omega_2)$, so that $M = m + m'$ and $|\lambda - l| \leq L \leq \lambda + l$,

$$\mathcal{Z}_{L|M|+}^{\lambda l}(\Omega_1,\Omega_2) = \frac{\mathcal{Y}_{LM}^{\lambda l}(\Omega_1,\Omega_2) + [\mathcal{Y}_{LM}^{\lambda l}(\Omega_1,\Omega_2)]^*}{\sqrt{2}(1-\delta_{M,0}) + 2\delta_{M,0}}, \tag{30}$$

$$\mathcal{Z}_{L|M|-}^{\lambda l}(\Omega_1,\Omega_2) = \frac{\mathcal{Y}_{LM}^{\lambda l}(\Omega_1,\Omega_2) - [\mathcal{Y}_{LM}^{\lambda l}(\Omega_1,\Omega_2)]^*}{\sqrt{2}i}, \qquad M > 0. \tag{31}$$

Note that the $\mathcal{Z}_{LM\sigma}^{\lambda l}$, with $M \geq 0$ and $\sigma = \pm$, are *real* two-particle spherical harmonics. The polynomials $\Pi_{NLM\sigma}^{\lambda l}(\Omega_1,\Omega_2,\alpha)$ satisfy the usual orthogonality relation on the hypersurface:

$$\oint \Pi_{N'L'M'\sigma'}^{\lambda' l'}(\Omega_1,\Omega_2,\alpha)\Pi_{NLM\sigma}^{\lambda l}(\Omega_1,\Omega_2,\alpha)\sin^2(\alpha) \times \cos^2(\alpha)d\Omega_1 d\Omega_2 d\alpha = \delta_{N'L'M'\lambda'l'\sigma',NLM\lambda l\sigma}. \tag{32}$$

We can expand $|F(\Omega_1,\Omega_2,\alpha)|^2$ in the form

$$K|F(\Omega_1,\Omega_2,\alpha)|^2 = \sum_{NLM\lambda l\sigma} a_{NLM\lambda l\sigma}\,\Pi_{NLM\lambda l\sigma}(\Omega_1,\Omega_2,\alpha), \tag{33}$$

where in general the sums over L, M, and σ are restricted by symmetry considerations. The coefficients of this expansion can be evaluated by inserting $\chi = \Pi_{NLM\lambda l\sigma}(\Omega_1,\Omega_2,\alpha)$ in the volume integral of Eq. (26); utilizing the orthogonality property above yields

$$a_{NLM\lambda l\sigma}(\Omega_1,\Omega_2,\alpha) = \Gamma_1^{++}[\Pi_{NLM\lambda l\sigma}]. \tag{34}$$

Once these coefficients have been determined we know the triply differential cross section.

C. Multiphoton ionization

To the extent that the interaction $V(t)$ is periodic there are no temporal boundaries, and the solution $|\Phi(t)\rangle$ to the time-dependent Schrödinger equation is given by the Floquet ansatz [5]:

$$|\Phi(t)\rangle = e^{-i\mathcal{E}t}\sum_m e^{-im\omega t}|\Phi_m\rangle, \tag{35}$$

where $\mathcal{E}$ is the quasienergy eigenvalue and where the harmonic components $|\Phi_m\rangle$ satisfy the coupled equations [5]

$$(\mathcal{E}+m\omega-H_a)|\Phi_m\rangle = V_+|\Phi_{m-1}\rangle + V_-|\Phi_{m+1}\rangle. \tag{36}$$

Within the framework of perturbation theory we may, to leading nonvanishing order, replace $|\Phi_m\rangle$ by $|\Phi_m^{(|m|)}\rangle$, where

$$|\Phi_0^{(0)}\rangle = |\Psi_0\rangle, \tag{37}$$

and where $|\Phi_m^{(|m|)}\rangle$ is of $|m|$th order and for $m \geq 1$ is given by

$$(E_{m\omega}-H_a)|\Phi_m^{(m)}\rangle = V_+|\Phi_{m-1}^{(m-1)}\rangle, \quad m \geq 1, \tag{38}$$

where $E_{m\omega} = E_0 + m\omega$. The flux formula, Eq. (18), could be immediately generalized to N-photon ionization were $|\Phi_N^{(N)}\rangle$ to satisfy the correct asymptotic boundary conditions. Unfortunately, $|\Phi_N^{(N)}\rangle$ does not satisfy the correct asymptotic boundary conditions when $N > 1$. The reason is that, since we have assumed the interaction $V(t)$ to persist for all time, an electron that has escaped from the nucleus will nevertheless continue to move in the radiation field and may therefore absorb and emit *virtual* photons. Consequently, the index N of $|\Phi_N^{(N)}\rangle$ refers to the total number of real *and* virtual photons absorbed. Within the framework of perturbation theory, an electron, as it leaves the nucleus, may absorb $N-m$ real photons, and m virtual photons, where $m = N_{\min}, \ldots, N$, with $N_{\min}$ the minimum number of photons which the atom must absorb to singly ionize; only for $N = 1$ are no virtual photons absorbed.

The way to circumvent this problem is to transform the Hamiltonian so that an electron at asymptotically large distances does not experience the radiation field. This is most conveniently done if $V(t)$ is expressed in the velocity gauge, and therefore we write

$$V(t) = \frac{1}{c}\mathbf{A}(t)\cdot\mathbf{P}, \tag{39}$$

where $\mathbf{A}(t)$ is the vector potential and where $\mathbf{P}$ is the total canonical momentum operator for the electrons. [We are free to remove the $\mathbf{A}^2(t)$ term by a gauge transformation.] The wave functions that describe the motion of free electrons in the presence and absence of the radiation field are related by the unitary operator $e^{-i\mathbf{a}(t)\cdot\mathbf{P}}$, where

$$\mathbf{a}(t) = \frac{1}{c}\int^t dt'\,\mathbf{A}(t'). \tag{40}$$

Thus we introduce the state vector

$$|\Phi'(t)\rangle \equiv e^{i\mathbf{a}(t)\cdot\mathbf{P}}|\Phi(t)\rangle. \tag{41}$$

The Hamiltonian of the atom interacting with the field is transformed from $H_a + V(t)$ to $T + W'(t)$, where, with W the sum of the atomic potentials, $W'(t)$ is the space-translated potential

$$W'(t) = e^{i\mathbf{a}(t)\cdot\mathbf{P}}We^{-i\mathbf{a}(t)\cdot\mathbf{P}}. \tag{42}$$

If we write

$$|\Phi'(t)\rangle = e^{-i\mathcal{E}t}\sum_m e^{-im\omega t}|\Phi'_m\rangle \tag{43}$$

and

$$W'(t) = \sum_m e^{-im\omega t}W'_m, \tag{44}$$

the new harmonic components $|\Phi'_m\rangle$ satisfy the coupled equations

$$(\mathcal{E}+m\omega-T-W'_0)|\Phi_m\rangle = \sum_{n\neq 0} W_n|\Phi'_{m-n}\rangle. \tag{45}$$

Within the framework of perturbation theory we may, to leading nonvanishing order, replace $|\Phi'_m\rangle$ by $|\Phi'^{(|m|)}_m\rangle$, where

$$|\Phi'^{(0)}_0\rangle = |\Psi_0\rangle, \tag{46}$$

and where $|\Phi'^{(|m|)}_m\rangle$ is of $|m|$th order and for $m \geq 1$ is given by

$$(E_{m\omega}-H_a)|\Phi'^{(m)}_m\rangle = \sum_{n=1}^{m} W'^{(n)}_n|\Phi'^{(m-n)}_{m-n}\rangle, \quad m \geq 1, \tag{47}$$

where $W'^{(n)}_n$ is the leading order, i.e., nth order, approximation to W'_n, with $W'^{(0)}_0 = W$. Since the right-hand side of Eq. (47) vanishes at asymptotically large distances, $|\Phi'^{(N)}_N\rangle$ satisfies the correct asymptotic boundary conditions, i.e., Eqs. (12) and (15) with E_ω replaced by $E_{N\omega}$. It follows that the rate for double ionization by N photons is

$$\Gamma^{++}_N = i\langle\Phi'^{(N)}_N|Q(H_a-H_a^\dagger)Q|\Phi'^{(N)}_N\rangle \tag{48}$$

$$= 2\mathrm{Im}\langle\Phi'^{(N)}_N|Q(E_{N\omega}-H_a)Q|\Phi'^{(N)}_N\rangle, \tag{49}$$

where the presence of $E_{N\omega}$ on the right-hand side of Eq. (49), while not contributing to the imaginary part of $\langle\Phi'^{(N)}_N|Q(E_{N\omega}-H_a)Q|\Phi'^{(N)}_N\rangle$, ensures that the real part of this expression is finite.

We can express Γ^{++}_N in terms of the original harmonic components $|\Phi^{(m)}_m\rangle$, as follows. For simplicity, assume that the light is linearly polarized, in which case we can write

$$\mathbf{a}(t) \equiv \mathbf{a}_0\sin(\omega t). \tag{50}$$

It follows that, with $J_n(x)$ the regular Bessel function,

$$e^{-i\mathbf{a}(t)\cdot\mathbf{P}} = \sum_n e^{-in\omega t}J_n(\mathbf{a}_0\cdot\mathbf{P}). \tag{51}$$

From Eqs. (35), (41), (43), and (50), we have

$$|\Phi'_m\rangle = \sum_n J_{m-n}(\mathbf{a}_0\cdot\mathbf{P})|\Phi_n\rangle, \tag{52}$$

and hence within the framework of perturbation theory we have, expanding the Bessel function in a power series

and keeping only the leading term,

$$|\Phi'^{(m)}_m\rangle = \sum_{n=0}^{m} \frac{(2^{-1}\mathbf{a}_0\cdot\mathbf{P})^{(m-n)}}{(m-n)!}|\Phi^{(n)}_n\rangle, \quad m \geq 0. \tag{53}$$

Consequently, combining Eqs. (48), (49), and (53), we obtain the final result

$$\Gamma^{++}_N = i \sum_{n=N_{\min}}^{N}\sum_{n'=N_{\min}}^{N} \frac{1}{2^{2N-n-n'}(N-n)!(N-n')!}\langle\Phi^{(n)}_n|(\mathbf{a}_0\cdot\mathbf{P})^{(N-n)}Q(H_a - H_a^\dagger)Q(\mathbf{a}_0\cdot\mathbf{P})^{(N-n')}|\Phi^{(n')}_{n'}\rangle \tag{54}$$

$$= 2\mathrm{Im}\sum_{n=N_{\min}}^{N}\sum_{n'=N_{\min}}^{N} \frac{1}{2^{2N-n-n'}(N-n)!(N-n')!}$$
$$\times\langle\Phi^{(n)}_n|(\mathbf{a}_0\cdot\mathbf{P})^{(N-n)}Q(E_{N\omega} - H_a)Q(\mathbf{a}_0\cdot\mathbf{P})^{(N-n')}|\Phi^{(n')}_{n'}\rangle. \tag{55}$$

Recall that $N_{\min}$ is the minimum number of photons which the atom must absorb to singly ionize, and note that we have used the fact that for $n < N_{\min}$, or/and $n' < N_{\min}$, we have $\langle\Phi^{(n)}_n|(\mathbf{a}_0\cdot\mathbf{P})^{(N-n)}Q(H_a - H_a^\dagger)Q(\mathbf{a}_0\cdot\mathbf{P})^{(N-n')}|\Phi^{(n')}_{n'}\rangle = 0$. For $N = 1$ we recover Eq. (19) from Eq. (55). The $|\Phi^{(m)}_m\rangle$ can be obtained by solving Eq. (38).

III. APPLICATION

We have calculated the cross section for double ionization of He by one photon, and also the total cross section, using Eqs. (19) and (10), respectively. We solved Eq. (22) by expanding $|\Psi_0\rangle$ and $|\Phi^{(1)}_1\rangle$ on a basis composed of the functions $S^\kappa_{nl}(r_1)S^\kappa_{\nu\lambda}(r_2)\mathcal{Y}^{\lambda l}_{LM}(\Omega_1,\Omega_2)$, where $S^\kappa_{nl}(r)$ is a (complex) radial Sturmian function [6] (which is a polynomial of degree $n-l-1$ multiplied by $e^{i\kappa r}$). As usual, we chose κ to lie in the upper right quadrant of the complex plane, so as to describe both closed and open channels [5, 7].

TABLE I. Total cross sections for ionization of helium by a single photon (frequency ω) obtained from theory (this paper) and from interpolation of the measured data given in Ref. [8]. Numbers between square brackets indicate powers of 10.

	$\sigma_{\rm tot}$ (Mb)	
$\hbar\omega$ (eV)	Theory	Experiment
88.538	0.567	0.538
91.259	0.524	0.501
93.980	0.484	0.465
99.422	0.416	0.403
106.225	0.348	0.334
113.028	0.294	0.286
119.831	0.250	0.249
126.634	0.214	0.218
133.437	0.184	0.188
140.239	0.160	0.163
147.042	0.140	0.142
153.845	0.123	0.123
160.648	0.109	0.107
167.451	9.63[-2]	9.36[-2]
174.254	8.58[-2]	8.36[-2]

In Table I we present results for the total cross section (single plus double ionization) and we compare to the data recently measured and compiled by Samson *et al.* [8]. The contribution of double ionization to the total cross section is roughly, on average, about 3% (see Fig. 1) but the discrepancy between our calculated results and the experimental data is smaller than 3% at the higher photon energies.

In Fig. 1 we present results for the ratio of cross sections for double to single ionization, and we compare to both theoretical [9, 10] and experimental [11–17] data of others. The experimental data are quite scattered. Numerous calculations have been reported for double photoionization of helium (see, e.g., [18–23]) and we cannot present all results; we have chosen to compare with two sets of recently published results. The calculations of Hino *et al.* [9] were based on many body perturbation theory. Their results are in excellent agreement with ours, but it is unclear whether this is fortuitous; besides, our results, while obtained from an *ab initio* approach,

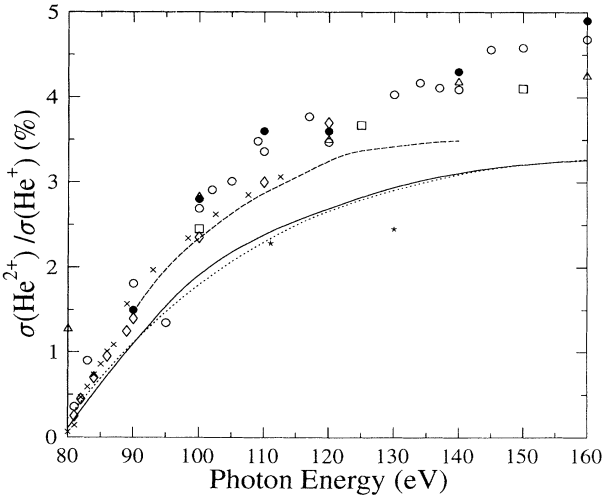

FIG. 1. Ratio of cross sections for double to single ionization of helium (by one photon) vs photon energy in eV. Theory: present, solid line; Ref. [9], dotted line; and Ref. [10], short broken line. Experiment: Refs. [11], (◇); [12], (⋆); [13], (□); [14], (•); [15], (×); [16], (△); and [17], (○).

are not converged to better than a few percent with respect to the size of the Sturmian basis set. The calculations of Proulx and Shakeshaft [10] were obtained from an approach which explicitly incorporated the boundary conditions, but within a stationary phase limit [1]. Again a Sturmian basis was used. We suspect that inexact convergence (of the basis) is at the root of why the results of Proulx and Shakeshaft are significantly higher than the present results.

In conclusion, we have formulated a method for calculating cross sections for double ionization which does not require the explicit inclusion of the asymptotic boundary conditions for two-electron escape. We have tested the method in an application to one-photon double ionization of He. In principle, we could calculate differential cross sections, but we did not do so since they are most conveniently calculated in hyperspherical coordinates, as described in Sec. II B.

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