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Characterization of high-energy photoionization in terms of the singularities of the atomic potential. I. Photoionization of the ground state of a two-electron atom

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We describe single and double photoionization of two-electron atoms by photoabsorption at high incident photon energies ω (but still $\omega \ll mc^2$) using a unified approach based on asymptotic Fourier transform (AFT) theory modified by Coulombic interactions. Within this approach the matrix elements for photoabsorption processes at high energies can be understood in terms of the singularities of the many-body Coulomb potential. These singularities (e-e and e-N) result in the singularities of the wave functions and the singularities of the e-γ interaction, which determine the asymptotic behavior of the matrix element. Within our unified approach we explain the dominant contributions, including both the dominant contributions to the total cross section for single ionization and for ionization with excitation, and the dominant contributions to the double ionization spectrum, as a Fourier transform asymptotic in a single large momentum (dependent on the process and the region of the spectrum). These dominant contributions are connected, through AFT, with either the e-N singularity or the e-e singularity. The AFT results are modified by Coulombic interactions. We include these modifications, for the cases of single ionization and of double ionization in the shake-off region at high energies, and extract a slowly convergent factor (Stobbe factor). In this way we obtain rapid convergence of the cross sections to their high-energy behaviors. This also allows us to discuss the convergence of ratios of cross sections.

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I. INTRODUCTION

In this sequence of papers [1,2] we are exploring the understanding of high-energy nonrelativistic photoionization processes, which follows from the theory of asymptotic Fourier transforms (AFT). Basically, the AFT of a function is determined by its singularities. In our case this means that the high-energy behavior of cross sections follows from the Coulomb singularities of the basic electron-nucleus and electron-electron interactions. In our first paper we introduce the ideas of AFT (also using the simpler case of photoionization of an electron bound in a screened Coulombic central potential, for illustration), and we explore correlation issues, focusing on photoionization of the ground state of a two-electron atom. In the second paper [2] we examine further issues that arise in the consideration of high-energy photoionization of a many-electron atom.

Here we consider high-energy photoabsorption in two-electron atoms, including correlation. We will discuss both single ionization, including also ionization with excitation [3] to any bound state, and double ionization. Our main concern is with total cross sections and with the spectrum [4] of double ionization. In recent years, the study of single-photon absorption resulting in single or multiple ionization has attracted much attention [5–17], resulting in a better understanding of electron correlation effects in complex systems and in photoabsorption processes involving these systems. We show here that the issues of the high-energy [18] ionization by photoabsorption can be studied from a unified point of view. The idea is based on the close relation between high-energy photoabsorption matrix elements and the AFT of functions with singularities (by singularity we mean a point where a function is not differentiable). Due to the fact that high photon energy ω necessarily means at least one large outgoing electron momentum, the study of the photoabsorption matrix element at high energies is equivalent to the study of the asymptotics of Fourier transforms (FTs). According to the AFT theory, the asymptotic Fourier transform of a function with singularities is determined by the behavior of the function in the vicinity of these singularities [19,20].

The study of the asymptotics of the FTs that arise in our problems is based on the theory of generalized functions [19]. By definition [20], $f(x_1, \ldots, x_n)$, a function of n variables infinitely differentiable and such that

$$R^l \frac{\partial f}{\partial x^{\alpha_1} \partial x^{\alpha_2} \cdots \partial x^{\alpha_n}} \to 0, \quad R \to \infty, \tag{1}$$

for any l, m and any choice of the indices $\alpha_1, \alpha_2, \ldots, \alpha_n$ $(\alpha_1 + \alpha_2 + \cdots + \alpha_n = m)$, where $R \equiv (x_1^2 + x_2^2 + \cdots + x_n^2)^{1/2}$, is called a good function. (In the terminology of Ref. [20], these are called χ functions.) The theorem (Ref. [19], Theorem 2, p. 15) says that the FT, $g(p_1, \ldots, p_n)$, of a good function $f(x_1, \ldots, x_n)$ is a good function [19,20]. We will call this the AFT theorem. Note this means that asymptotically, the FT $[g(p_1, \ldots, p_n)]$, of a good function decreases faster than any power of $p \equiv (p_1^2 + p_2^2 + \cdots + p_n^2)^{1/2}$.

The functions that appear in our photoionization matrix elements, even considering photoionization of a particle in a potential, are well localized (due to the fact that the bound state is localized), but they are not differentiable everywhere. Namely, they are differentiable everywhere except at coalescence points, where they are singular [21], i.e., nondifferentiable. These coalescence points result from the singularities of the potential of the many-electron Hamiltonian. A slow asymptotic decrease for large p, such as $1/p^n$, of the FT of a well-localized function comes only from the singularities of that function.

In the vicinity of a singularity the functions (whose FT is calculated) may be written in terms of simpler functions f_S (S standing for ''simpler''), whose FT we know, and a remainder O, whose FT is asymptotically negligible. This we call the partitioning (f_S+O) of the functions. According to the generalized-function theory, the FT of a generalized function with singularities is approximated by the FT of these simpler functions f_S, while the size of the FT of the remainder O gives a measure of the accuracy of the approximation. The point is that by taking f_S more accurately in the vicinity of the singularity, one can in principle achieve arbitrary accuracy (see Ref. [19], Theorem 19, p. 52). A special partitioning, i.e., the expansion of wave functions around the origin (which is the position of the e-N singularity) in terms of polynomials has been used previously in both single and double ionizations [22–25]. Here and in Paper II, using AFT theory, we are generalizing these approaches. We may partition (in fact, using Coulombic functions, which are much better functions near the singular point than polynomials) around singular points which, in general, do not have to be at the origin, and we consider all singularities.

There is, however, a point of difference between our asymptotic matrix elements and asymptotic FT. Namely, after pulling out the fast oscillating terms of the plane wave, the function left in the integrand still depends on the large momentum variable $\mathbf{p}$ (coming from the final-state wave function), through pr dependence (as, for example, in confluent hypergeometric functions in the Coulomb case). For this reason it might be more appropriate to talk about a generalization of FT. However, in the large p limit the Coulomb functions that depend on pr are expandable in uniformly convergent series in powers of pr. Although all these powers of pr must be included, as we discuss, we are able to argue that FT theorems apply to each power separately (a power of p is pulled out from each integral and no p's appear any more) and, due to uniform convergence, also to the full function [26]. When the final state cannot be explicitly determined, this argument also applies to partitioning of the final state in terms of full Coulombic functions. The Coulombic modification of the FT results, as we demonstrate in Sec. II B, in a slowly converging factor called the Stobbe factor. By explicitly pulling out the Stobbe factor, fast convergence is achieved. The Stobbe factor is a common factor, independent of initial state, and so this allows us to discuss also the convergence of ratios of cross sections.

Our objectives are: (1) To obtain the leading contribution [i.e., the leading inverse power ($1/p_{large}$) in large momenta] in the high-energy matrix elements that determine the cross sections we are discussing, by using the AFT approach. (2) To show that the leading contributions can be identified by identifying the kinematical regions in which the matrix element is an AFT in just one large momentum p_{large} (there must be at least one large momentum), which is associated (through the AFT theorem) with a singularity of the potential, and to find what knowledge of the singularity structure of the wave functions is needed in order to obtain form independent high-energy results in leading order. (3) To include terms needed to obtain fast convergence (at least as $1/p^2$) of our results to the exact photoabsorption results. In particular, we study how the Stobbe factor appears in correlated systems in photoabsorption situations when one electron takes almost all of the energy (single ionization with excitation and double ionization in the shake-off region).

The potential energy of the two-electron atom,

$$V(\mathbf{r}_1,\mathbf{r}_2)=-\frac{Z\alpha}{r_1}-\frac{Z\alpha}{r_2}+\frac{\alpha}{r_{12}}, \tag{2}$$

where $r_{12}=|\mathbf{r}_1-\mathbf{r}_2|$ is singular (nondifferentiable) at the e-N coalescences ($\mathbf{r}_1=0$ for any $\mathbf{r}_2$, and $\mathbf{r}_2=0$ for any $\mathbf{r}_1$), and at the electron-electron (e-e) coalescence [$\mathbf{r}_{12}=0$ for any $\mathbf{R}=(\mathbf{r}_1+\mathbf{r}_2)/2$]. We call these coalescences as double coalescences (points where two of the three particles meet). There is also a triple coalescence point where all three particles meet ($\mathbf{r}_1=\mathbf{r}_2=0$). The functions that appear in our photoionization matrix elements are singular, i.e., nondifferentiable, at the coalescence points [21,27,28]. The properties of wave functions in the vicinity of double coalescence points (which are of primary importance for the dominant contributions we are studying) are well understood [21,27], and they can be obtained from the Schrödinger equation. They are known as coalescence properties, and in the case of s states they are often called Kato cusp conditions. We are using this term, Kato cusp conditions, more generally, as denoting the exact behavior of the wave functions at a two-particle singularity. (There will also be singularities in the e-γ interaction operator, depending on the form that we take, as we note below.)

The leading contribution, at high energies, to the matrix element in any kinematic situation is determined by the singularities, in variables associated with the AFT, of the potential energy. The AFT results from the oscillating terms of the final state wave function, which oscillate rapidly in any kinematics. As indicated, we are not considering here general kinematics, but the kinematics which gives the dominant contributions to the total cross sections (for single and double ionization), and (in the case of double ionization) which gives the dominant contributions to the spectrum. In the case of the total cross section for high-energy ionization of a two-electron atom, the relevant fast oscillating terms come from the plane waves of the final state, as in the one-electron case. However, when the spectrum for double ionization is considered, in some regions the dominant contributions may come from the spherical waves [29], too. In these dominant kinematics, which determine the spectrum in double ionization and the total cross section, there is a single fast oscillating term linked to just one of the two types of double singularities, through a single AFT, rather than with the triple singularity through a double AFT.

In the case of single ionization of a two-electron atom, we argue here (using the AFT theorem) that the dominant contribution to the total cross section is associated with the e-N

coalescence, as in the one-electron case, whether or not the atom is in its ground state. However, while the dominant contribution to the single-ionization total cross section (when summed over all final bound states, so that excitations are not distinguished) of the ground state of a two-electron atom does not involve final-state electron-electron interactions (and involve initial-state correlation only in a normalization factor), regardless of the form used, the dominant contributions in the case of single ionization of a higher state do generally involve final-state electron–electron interaction. This final-state electron-electron interaction leads to predictions of an energy dependence of the cross sections for single ionization, which are different from the independent particle approximation (IPA) predictions, as we will note in Sec. IV below and discuss further in Paper II.

In the case of double ionization of the ground state of a two-electron atom, the leading contributions to the spectrum and to the total cross section are associated with one of the two singularities (either with e-e or with e-N coalescences), and both singularities contribute. However, as in the single ionization case, we demonstrate that the high-energy double-ionization total cross section of the ground state of a two-electron atom does not involve final-state electron-electron interaction, regardless of the form used. It does now involve initial-state e-e interaction beyond normalization (due to the e-e singularity).

The leading contributions to the spectrum are, as we show, single AFT in just one large momentum. The kinematics of these leading contributions are such that the second Fourier transform is not in an asymptotic region. There are three such kinematic regions. The single large momentum may be the momentum $\mathbf{p}_1$ of one electron (associated with the variable $\mathbf{r}_1$ for which the potential has a singularity at $\mathbf{r}_1=0$, the e-N singularity), while the momentum $\mathbf{p}_2$ of the other electron is small. This region is known as the shake-off region. The single large momentum can also be the relative momentum $\mathbf{p}$ of the two electrons (associated with the relative distance $\mathbf{r}_{12}$ for which the potential has a singularity at $\mathbf{r}_{12}=0$, the e-e singularity), while the total momentum $\mathbf{P}$ is small (quasifree region). Also, the large momentum can be the total momentum $\mathbf{p}$, but with electron momenta $\mathbf{p}_1$ and $\mathbf{p}_2$ nearly perpendicular. This is the final-state-interaction region, in which case the large momentum is associated with the variable $\mathbf{r}_1$ (or $\mathbf{r}_2$) and the e-N singularity. The high-energy total cross section is determined by the contributions from the shake-off and the quasifree region, and the fast oscillating terms come from the plane-wave parts of the two-electron final state. In the final-state-interaction region, which does not contribute to the total cross section in the leading order, the fast oscillating term comes from the product of a plane wave and a spherical wave. The search for dominant contributions to the total cross section and the spectrum therefore reduces to the search for the kinematical regions in which the matrix element is an AFT in just one large momentum, which is associated with a variable for which the potential has just one singularity (e-e or e-N). The fast oscillating terms of these single AFT come from plane waves and spherical waves. There is no region of the spectrum in which the leading contribution would have a fast oscillating term coming only from spherical waves.

The rest of the paper is organized in the following way. We first (Sec. II) apply the AFT approach to the simpler case of photoionization of an electron bound in a screened Coulombic central potential (IPA potential), including identification of the slowly convergent Stobbe factor. Then (Sec. III) we describe the general matrix element (in V, L, and A forms) for single and double ionization, from any state of a correlated He-like system, which will be used throughout the paper, discussing the approximations appropriate for the considered energies and atoms. We proceed to discuss ionization of the ground state of a two-electron atom. We first (Sec. IV) consider single ionization, including ionization with excitation. In discussing double ionization from the ground state, we first (Sec. V) identify the three kinematical regions of observables, which give the leading contributions to the three regions of the spectrum. We then discuss these leading contributions to the spectrum in the three regions separately [contributions due to shake off (Sec. VI), quasifree case (Sec. VII), and final-state interaction (Sec. VIII)], and we discuss the procedures and conditions for obtaining these contributions. In the cases of single ionization (Sec. IV) and of double ionization in the shake-off region (Sec. VI), we also include modifications (due to Coulombic interaction) of the asymptotic Fourier-transform results. Finally (Sec. IX), we discuss the resulting double-ionization cross section and the ratio of double-to-single ionization.

II. ONE-ELECTRON CASE

Here, using our AFT approach, we consider photoionization of an electron bound in a screened Coulombic central potential. We will be able to understand the adequacy of the use of various forms of matrix elements [length (L), velocity (V), or acceleration (A) forms] when using approximate wave functions of various qualities in the vicinity of the singularity at the origin. We will demonstrate that nonrelativistic IPA high-energy photoabsorption is determined [up to corrections $O(1/p^2)\simeq O(1/\omega)$, p being the outgoing electron momentum], by the initial-state normalization and by the point Coulomb singularity. The result, as we demonstrate, is form independent, but whether information about the singularity comes from the interaction (as in A form) or from the initial and final states (as in L and V forms) is form dependent. In this way, we are able to identify the necessary conditions for all three forms to give correctly the high-energy result in the IPA case. We also explicitly obtain the order of the error resulting from the error in the description of the wave functions in the vicinity of the singularity. We will consider this on two levels of accuracy (depending on the accuracy in the description of the wave functions in the vicinity of the singularity), both in single and double ionization. First, we will obtain the leading-order results in $1/p$, using a simple description of the wave functions in the vicinity of the singularity. Then we will use a description that completely includes the strong e-N interaction. The Coulombic modification of the FT results in a slowly converging factor, the Stobbe factor, which we obtain to all orders.

For a single electron in a potential, the matrix element for photoionization by photoabsorption, in the lowest order of the quantum electrodynamic electron-photon interaction, is

$$M=\int \Psi_{\mathbf{p}}^{(-)*}(\mathbf{r})I(\mathbf{r})\Psi_i(\mathbf{r})d^3r, \tag{3}$$

where $\Psi_i(\mathbf{r})=R_{nl}(r)Y_l^m(\hat{\mathbf{r}})$ is the initial bound state, normalized to unit integrated probability density, $\Psi_{\mathbf{p}}^{(-)}(\mathbf{r})=e^{i\mathbf{p}\cdot\mathbf{r}}\Phi_{\mathbf{p}}^{(-)}(\mathbf{r})$ is the final electron continuum state, normalized on the momentum scale [to asymptotically approach a $1/(2\pi)^{3/2}$ amplitude distorted plane wave of momentum $\mathbf{p}$], and $I(\mathbf{r})$ is the interaction operator, given in the three commonly used forms (neglecting retardation [30] for simplicity) as

$$I_V=-i[\boldsymbol{\epsilon}\cdot\boldsymbol{\nabla}], \quad I_L=im\omega\boldsymbol{\epsilon}\cdot\mathbf{r}, \quad I_A=\frac{i}{\omega}\boldsymbol{\epsilon}\cdot\boldsymbol{\nabla}V(r). \tag{4}$$

$V(r)$ is an IPA potential energy of the type $V(r)=-(Z\alpha/r)S(r)$, where $S(r)$ is a screening function that for small r we assumed can be described as a polynomial in r, $S(r)=(1+s_1r+s_2r^2+\cdots)$, i.e., the potential has only a Coulombic divergence and is differentiable except at $\mathbf{r}=0$. The singularity of the potential energy results in singularities in the wave functions $\Psi_{\mathbf{p}}$ and Ψ_i. These functions are not differentiable at the origin. The e-γ interaction operator in the L and V forms is, in this sense, regular, while in A form, it is singular due to the presence of the singular V(r) in it Eq. (4). The large p behavior of the Fourier transform of a slowly varying function of r picks out its behavior near the coalescence point (since $pr\sim1$, large p corresponds to small r), and it only depends on the singular parts of the function. Thus we begin by partitioning the functions $\Psi_i(\mathbf{r})$ and $\Phi_{\mathbf{p}}^{(-)}(\mathbf{r})$ in the vicinity of the coalescence point $\mathbf{r}=0$. The small r behavior of these slowly varying portions of the integrand will determine the asymptotic FT.

Accurate evaluation of the matrix element at high energies requires knowledge of (in general) both initial- and final-state electron wave functions at the singular point, or in general at all singular points, if one goes beyond IPA. However, how much of this knowledge is actually needed in a given calculation depends on the form of the matrix element used for that calculation. As we will demonstrate in considering the leading-order result, with A form we only need knowledge about the normalization of the initial-state wave function at the e-N coalescence. With other forms (V and L), we generally need further information about both the initial and final states. The exception is for s-state ionization using V form, for which we need only the normalization and the slope of the initial-state function at the coalescence.

A. Partitioning in terms of polynomials—leading-order Born results

The partitioning f_S+O in terms of polynomials of the initial (bound) state of quantum numbers (n,l,m) in an IPA potential with Coulombic singularity is

$$\Psi_i(\mathbf{r})=N_i^{IPA}r^l\left[1-\frac{a}{l+1}r+\lambda_2r^2+\lambda_3r^3+O(r^4)\right]Y_l^m(\hat{\mathbf{r}}), \tag{5}$$

where $a=mZ\alpha$. In the simple function f_S [in which the terms are alternately regular and singular, with the first term $r^lY_l^m(\hat{\mathbf{r}})$ being regular], the first two terms are determined solely by the Coulomb singularity of the potential, and therefore they are known independent of screening, except for the overall normalization factor N_i^{IPA} (which depend on the choice of IPA potential). Higher-order terms in the f_S of Eq. (5) do depend on the screening of the IPA potential, which affects the λ_i coefficients. This fact that the two first terms in the parentheses of Eq. (5) are determined by the Coulomb singularity, is well known, and it is a special case of the general behavior of wave functions at coalescence points of many-electron-atoms [21,27]. Namely, in the description of a many-electron atom wave function in the vicinity of any coalescence (which includes any electron-electron coalescence) in terms of the relative coordinate of the two coalescing particles, the first two terms are determined by the singularity of the corresponding part of the Coulomb potential, up to an overall factor [31], and there is a remainder that vanishes more rapidly than linearly in the coordinate.

These two terms, and the normalization constant, are all that we need from the initial-state wave function (we also need information from the final state) in order to determine the leading contribution in $1/p$ for high-energy photoabsorption in V and A forms.

In the final-state electron wave function the situation is very similar, except that in the limit of high momenta the normalization is not affected by screening. Namely, according to Refs. [32–35], the wave function of a high-energy continuum electron state of momentum $\mathbf{p}$ in the vicinity of the Coulomb singularity of the IPA potential is essentially Coulombic. As shown in Ref. [35], using analytic perturbation theory, the corrections to the Coulombic wave function in the vicinity of the nucleus ($r\ll1/a$, where $a=mZ\alpha$ characterizes the unscreened nuclear charge), due to screening, decrease with electron momentum as $O(1/p^2)$ relative to the Coulomb functions. This means that in the vicinity of the Coulomb singularity ($r\ll1/a$) the wave function representing the outgoing electron (which we need) of momentum $p\gg a$ can be written, following Refs. [33,35], as a Coulomb solution plus a remainder,

$$\Psi_{\mathbf{p}}^{(-)}(\mathbf{r})=N_p^Ce^{i\mathbf{p}\cdot\mathbf{r}}\left\{{}_1F_1\left[-i\frac{a}{p},1,-ipr(1+\cos\vartheta)\right]+O\left(\frac{1}{p^2};pr,\cos\vartheta,s_i\right)\right\}, \tag{6}$$

where $O(1/p^2;pr,\cos\vartheta,s_i)$ denotes the remainder, which vanishes faster than $1/p$ (denoted in O by $1/p^2$). Note that we are not assuming pr to be small. In fact, the distances that contribute in our high-energy matrix elements will be $pr\sim1$. The functional dependence of O is also shown; the remainder contains all information on screening, symbolized by the coefficients s_i characterizing the small-distance behavior of the screened potential. According to analytic perturbation theory [33,35], an even more accurate continuum wave function of Coulombic shape, in the region $r \ll 1/a$, is obtained by shifting the electron momentum in Eq. (6) from momentum p to p_C, by an amount determined by the parameters of the screened potential, and by replacing normalization N_p^C (if momentum scale normalization is used) by $\sqrt{p_c/p}N_{p_C}^C$. However, although such a Coulombic function is more accurate, its error still decreases as $1/p^2$ with large momentum p. Therefore we do not need it at this moment here, but we will use it in Sec. II B.

This result, Eq. (6), is important for our approach because it means (as we show below) that the terms in the partitioning of the final state in the vicinity of the coalescence, which contribute to the high-energy matrix element, are not affected by screening. We show this to the leading order in $1/p$, further simplifying f_S in the partitioning of Eq. (6). Due to the fact that the distances involved in the process are $r \sim 1/p$, and since we are considering high energies for which $p \gg (mZ\alpha)$, when we write our wave functions in terms of the scaled variable pr, the terms that will be important for our discussion here involve terms up to linear in the parameter $a/p = mZ\alpha/p$, with further terms contributing in higher orders in $1/p$. We write

$$\Psi_{\mathbf{p}}^{(-)}(\mathbf{r}) = N_p^C e^{i\mathbf{p}\cdot\mathbf{r}}\left[1 - i\frac{a}{p}g^{(-)}[i(pr+\mathbf{p}\cdot\mathbf{r})] + O\left(\frac{1}{p^2}; pr, \cos\vartheta, s_i\right)\right], \tag{7}$$

where $\cos\vartheta = \hat{\mathbf{p}}\cdot\hat{\mathbf{r}}$. O now includes all contributions of order a^2/p^2 and higher from the full Coulomb function of Eq. (6), and

$$g^{(-)}(i\xi) = -\frac{1}{2\pi i}\oint_\Gamma e^{-i\xi t}\ln\left(\frac{t-1}{t}\right)\frac{dt}{t} = \int_0^1 [e^{-i\xi t}-1]\frac{dt}{t}. \tag{8}$$

The contour Γ is a counterclockwisely oriented closed contour encircling the cut [0,1]. By inserting Eqs. (7) and (5) in Eq. (3), using the series expansion form of Eq. (8) for $g^{(-)}(i\xi)$, expanding in $\xi = pr + \mathbf{p}\cdot\mathbf{r}$, we obtain a series of integrals of functions that contain powers of r and angular functions.

The function $g^{(-)}(i\xi)$, Eq. (8), determines all contributions of order a/p to the full Coulombic wave function for $pr \sim 1$. It is therefore equivalent to the first Born term in the perturbation expansion of the Coulomb continuum state. The function $g^{(-)}(i\xi)$ is generally needed in calculating the leading contribution to the high-energy matrix element. However, it contains $\mathbf{p}$ dependence through pr which, at first sight, may not look good, if one wants to view this high-energy matrix element as a FT. However, we can expand this function in powers of pr [by expanding the exponential function in the integral representation, Eq. (8)], apply the FT theorem to each term, and then sum the series. Since these series are uniformly convergent, this is the same as integrating without expansion (see, e.g., Ref. [36], p. 158), which we do.

To achieve a convergent integration of each term in the series, which will then separately satisfy the requirements of the FT theorem, a factor $e^{-\varepsilon r}$ is introduced; after the integration is performed, the limit $\varepsilon \to 0$ is taken. This procedure is consistent with the definition of the FT of generalized functions [19]. For the AFT theorem, we must understand the singularities of the integrand. The singularity properties of the wave functions are immediately identifiable in these series, which involve powers of r and angular functions such as powers of $\hat{\mathbf{p}}\cdot\hat{\mathbf{r}} = \cos\vartheta$ and spherical harmonics. For example, r and $\cos\vartheta$ are singular at the origin (as functions of x, y, and z) but their product is not ($r\cos\vartheta = z$), nor are their squares. (Note also that $r^l Y_l^m$ is regular.)

The leading contribution in any form to the high-energy matrix element can be obtained, using only the first two terms in f_S of the partitioning of initial [Eq. (5)] and of final state [Eq. (7)], while neglecting some of these first two terms may lead to erroneous results in some forms. Higher-order terms in the expansion give higher-order contributions in $1/p$. Therefore the form-independent high-energy matrix element (to the leading order in $1/p$) for photoabsorption in an IPA model is obtained from

$$M = N_i^{IPA} N_p^{C*} \lim_{\varepsilon\to 0}\int e^{-i\mathbf{p}\cdot\mathbf{r}-\varepsilon r}\left[1 + i\frac{a}{p}g^{(-)*}[i(pr+\mathbf{p}\cdot\mathbf{r})]\right] I(\mathbf{r}) r^l\left[1 - \frac{a}{l+1}r\right] Y_l^m d^3r, \tag{9}$$

where $I(\mathbf{r})$ may take forms like Eqs. (4), which also contains different powers of r and angular functions. Integrals that appear in Eq. (9) are elementary, and even when the g function is involved they are easily performed using Eq. (8). For example, when $l=0$, the integrals involved are

$$\int e^{-(\varepsilon + i\mathbf{p}\cdot\mathbf{r})} r^n \boldsymbol{\epsilon}\cdot\hat{\mathbf{r}} d^3r = \frac{2\pi(n+2)!\boldsymbol{\epsilon}\cdot\hat{\mathbf{p}}}{(ip)^{n+3}} C_n, \tag{10}$$

where $C_{-1} = i\pi$, $C_n = 0$ for any odd positive n, and $C_n = -2/(n+1)$ for even $n \geqslant -2$, and

$$\int e^{-(\varepsilon + i\mathbf{p}\cdot\mathbf{r})} g^{(-)*}[i(pr+\mathbf{p}\cdot\mathbf{r})] r^n \boldsymbol{\epsilon}\cdot\hat{\mathbf{r}} d^3r = \frac{2\pi\boldsymbol{\epsilon}\cdot\hat{\mathbf{p}}}{(ip)^{n+3}} D_n, \tag{11}$$

where $D_{-2} = i\pi - 2$, $D_{-1} = -\pi^2/2 - i\pi - 2$, $D_n = 2(n+2)!(1-i\pi)/(n+1)$ for nonnegative even n, and $D_n = 4n!\Sigma_{k=0}^{(n-1)/2}(2k+2)/(n-2k)$ for odd $n > 0$.

Expression (9) gives the leading order in $1/p$ for large p, and this term is form independent. We may look at this expression and compare it with a pure Coulombic potential case to see what determines high-energy photoabsorption in an IPA model with a Coulombic singularity. We see from Eq. (9) that the only difference from the pure Coulombic case is in the initial-state normalization, which depends on the IPA potential. All other terms are determined by the Coulomb singularity. Therefore at high energies, information about screening persists only in the initial-state normalization [34].

In a matrix element form in which the interaction operator is regular (such as V and L forms, and we denote them as I_V^R and I_L^R) rather than singular (as in A form, I_A^S), the contribution from the term in the integrand, which involves the first terms of the simple functions f_S of both the partitionings of Ψ_i and of $\Phi^{(-)}$, vanishes for any l (while in A form, this term gives the leading nonvanishing contribution). The leading nonvanishing contributions in such forms (L or V) involve the product of the first term from $\Phi^{(-)}$ (which is regular and denoted by as R_f) with the second term in Ψ_i (singular, S_i), and the product of the second term from $\Phi^{(-)}$ (singular, S_f) with the first term in Ψ_i (regular, R_i). These two contributions are of the same order in $1/p$. In summary, in leading order in $1/p$ one obtains the leading nonvanishing contribution from

$$M=\int e^{-i\mathbf{p}\cdot\mathbf{r}-\varepsilon r}[R_f+S_f]\begin{bmatrix} I_L^R \\ I_V^R \\ I_A^S \end{bmatrix}[R_i+S_i]$$

$$\Rightarrow\int e^{-i\mathbf{p}\cdot\mathbf{r}-\varepsilon r}\begin{bmatrix} R_f I_L^R S_i + S_f I_L^R R_i \\ R_f I_V^R S_i + S_f I_V^R R_i \\ R_f I_A^S R_i \end{bmatrix}. \tag{12}$$

Note that the results, Eqs. (9) and (12), reflect that it is the singularity region that is important. This means that if one wants to improve results, one needs to partition functions in terms of functions that better describe behavior in the vicinity of the singularity [37]. Partitioning of the wave functions in terms of functions that are more accurate in the vicinity of the singularity provides more accurate results.

B. Partitioning in terms of Coulombic functions—the Stobbe factor

The ratio of the first correction to the leading contribution is of the order of $1/p$, and it gives a very slow convergence of the photoionization matrix elements and cross sections. In fact, it converges as $\pi a/p \sim \pi\sqrt{E_K/\omega}$, where E_K is the K-shell binding energy. Due to this slow convergence, and also due to the possibility of considering large Z, we may include the e-N interaction completely in both the initial and final states, by performing the partitioning of the wave functions in the vicinity of the singularity in terms of Coulombic functions. Formally, this means that we write for the initial-state wave function

$$\Psi_i^{IPA}(\mathbf{r})=\frac{N_i^{IPA}}{N_i^C}\Psi_i^C(\mathbf{r})+O[r^{l+2}], \tag{13}$$

where $\Psi_i^C(\mathbf{r})$ is a normalized Coulombic wave function with the same quantum numbers as $\Psi_i^{IPA}(\mathbf{r})$, and $O[r^{l+2}]$ represents the difference between the Coulombic and screened wave functions. The terms represented by O are small in the vicinity of the singularity, as we discuss below.

For the final state we take the Coulombic part of Eq. (6), but with shifted energy and with corrected normalization [33,35]. As already mentioned, according to Refs. [33,35], the exact IPA wave function is Coulombic in the vicinity of the e-N singularity except for corrections $O(1/p^2)$. A fairly accurate function (containing the dominant but not all terms of relative order $1/p^2$) is obtained by using shifted momentum p_C rather than the true momentum p. Momentum p characterizes the electron at large distances from the nucleus. If we want to describe the screened wave function in the vicinity of the nucleus by a Coulombic function, we should use, according to Refs. [33,35], shifted momentum p_C. In addition, if the function is normalized on the momentum scale, the normalization is affected, and it is given by $N_p^{IPA}=\sqrt{p_C/p}N_{p_C}^C$. The final state is, therefore, described by

$$\Psi_{\mathbf{p}}^{(-)}(\mathbf{r})=\sqrt{\frac{p_C}{p}}\Psi_{\mathbf{p}_C}^{(-)}(\mathbf{r})+O\left(\frac{1}{p^2}\right), \tag{14}$$

where the shifted momentum p_C is given by Ref. [33],

$$\frac{p^2}{2m}-\frac{p_C^2}{2m}=|E_B^C|-|E_B^{IPA}|, \tag{15}$$

where E_B^C (E_B^{IPA}) is the hydrogenlike (IPA) binding energy of the state that is ionized.

We thus arrive at the following approximation for the IPA matrix element:

$$M=\frac{N_i^{IPA}}{N_i^C}\sqrt{\frac{p_C}{p}}\int\Psi_{\mathbf{p}_C}^{C(-)*}(\mathbf{r})I_A(\mathbf{r})\Psi_i^C(\mathbf{r})d^3r\left[1+O\left(\frac{1}{p^2}\right)\right]$$

$$\equiv\frac{N_i^{IPA}}{N_i^C}\sqrt{\frac{p_C}{p}}M^C(p_C)\left[1+O\left(\frac{1}{p^2}\right)\right]. \tag{16}$$

From Eq. (16), it immediately follows that at high energies,

$$d\sigma^{IPA}=\left(\frac{N_i^{IPA}}{N_i^C}\right)^2 d\sigma^C\left[1+O\left(\frac{1}{p^2}\right)\right], \tag{17}$$

where $d\sigma^C$ is the differential cross section obtained from Coulombic H-like wave functions calculated at shifted momentum p_C, and where O designates how rapidly the error decreases at high energies. The error in Eq. (17) is determined by the errors in the wave functions. According to the results presented in Ref. [33], the difference between screened and Coulombic functions [when un-normalized functions, i.e., the same first coefficient in the expansion is taken, are compared] is very small (and for a potential with a polynomial expansion for small r decreases as $1/p^2$). This means that dominant terms of the relative order $1/p^2$ are included; only small terms of relative order $1/p^2$ remain in $O(1/p^2)$.

An important point, relevant for later discussion, is the relatively fast convergence of the ratios of photoabsorption cross sections to the results for ratios predicted by lowest-order results (Born results in A form). The most slowly converging factor in the cross sections is $\exp(-\pi a/p)$ (Stobbe factor), and it is included in $d\sigma^C$. This factor comes from the final-state Coulombic interaction, which means that in partitioning wave functions around the coalescence, we get this factor by collecting all Coulombic interaction in the final state for each term in the partition of the initial state, as argued in Ref. [38]. The factor is therefore present for any state. The fact that the dominant slowly convergent factor is the same for all states explains the much more rapid convergence of ratios of cross sections.

Our comparison of the results obtained with Eq. (17) for He with exact IPA results [39] shows agreement within about 1% already around 1 keV. This illustrates the fast convergence of this procedure, especially when compared with the lowest-order result, which gives about 50% disagreement in the same energy range. The shapes of the wave functions at the distances involved are basically Coulombic. We will employ and generalize this important point in our subsequent approach. High-energy photoabsorption is essentially Coulombic. This means that the high-energy behavior (we are talking here about the keV range) of cross sections is determined by the properties of functions near the singularity, which is Coulombic. Screening effects enter, of course, but in a simple way, as a constant factor, in these IPA examples. By straightforward generalization of these findings in high-energy many-body calculations, one can significantly simplify calculations involving e-e correlation, as we show in following sections, in considering photoabsorption by a two-electron systems.

III. MATRIX ELEMENT FOR SINGLE AND DOUBLE IONIZATION AND TWO-ELECTRON WAVE FUNCTIONS

In our study, we are assuming nonrelativistic electrons. We are neglecting L-S coupling and we factorize the two-electron wave functions into a spin part (which, in a two-electron system, can be a symmetric triplet or an antisymmetric singlet) and a coordinate part. Further, since $\omega \ll m$, we neglect the interaction of radiation with electron spin. This means that the initial state and final state are either both spin singlets (symmetric coordinate part) or both spin triplets (antisymmetric coordinate part).

Within this description, the matrix element for single or double photoionization by photoabsorption on a two-electron atom (in the lowest order of electron-photon interaction), where at least one electron of momentum $\mathbf{p}_1$ is ejected, is

$$M=\int \Psi_{\mathbf{p}_1,\lambda}(\mathbf{r}_1,\mathbf{r}_2) I^{2e}(\mathbf{r}_1,\mathbf{r}_2)\Psi_i(\mathbf{r}_1,\mathbf{r}_2)d^3r_1 d^3r_2 . \tag{18}$$

Here $\Psi_i(\mathbf{r}_1,\mathbf{r}_2)$ is the coordinate part of the initial-state wave function. $\Psi_{\mathbf{p}_1,\lambda}(\mathbf{r}_1,\mathbf{r}_2)$ is the coordinate part of the two-electron wave function in the final state, where λ denotes the quantum numbers of the remaining bound electron in the case of single ionization, or it denotes the momentum $\mathbf{p}_2$ of the other electron in the case of double ionization. I^{2e} is the photon-electron interaction, which in V, L, and A forms of the matrix element are

$$I_V^{2e}=-i[e^{i\mathbf{k}\cdot\mathbf{r}_1}\boldsymbol{\epsilon}\cdot\boldsymbol{\nabla}_1+e^{i\mathbf{k}\cdot\mathbf{r}_2}\boldsymbol{\epsilon}\cdot\boldsymbol{\nabla}_2], \tag{19a}$$

$$\begin{aligned} I_L^{2e}=&\, im\left(\omega-\frac{k^2}{2m}\right)(\boldsymbol{\epsilon}\cdot\mathbf{r}_1 e^{i\mathbf{k}\cdot\mathbf{r}_1}+\boldsymbol{\epsilon}\cdot\mathbf{r}_2 e^{i\mathbf{k}\cdot\mathbf{r}_2})\\ &-(e^{i\mathbf{k}\cdot\mathbf{r}_1}\boldsymbol{\epsilon}\cdot\mathbf{r}_1\mathbf{k}\cdot\boldsymbol{\nabla}_1+e^{i\mathbf{k}\cdot\mathbf{r}_2}\boldsymbol{\epsilon}\cdot\mathbf{r}_2\mathbf{k}\cdot\boldsymbol{\nabla}_2), \end{aligned} \tag{19b}$$

$$\begin{aligned} I_A^{2e}=&\frac{1}{\omega-\dfrac{k^2}{2m}}\Bigg[iZ\alpha\left(\frac{\boldsymbol{\epsilon}\cdot\hat{\mathbf{r}}_1}{r_1^2}e^{i\mathbf{k}\cdot\mathbf{r}_1}+\frac{\boldsymbol{\epsilon}\cdot\hat{\mathbf{r}}_2}{r_2^2}e^{i\mathbf{k}\cdot\mathbf{r}_2}\right)\\ &-i\alpha\frac{\boldsymbol{\epsilon}\cdot\hat{\mathbf{r}}_{12}}{r_{12}^2}(e^{i\mathbf{k}\cdot\mathbf{r}_1}-e^{i\mathbf{k}\cdot\mathbf{r}_2})-\frac{1}{m}(e^{i\mathbf{k}\cdot\mathbf{r}_1}\mathbf{k}\cdot\boldsymbol{\nabla}_1\boldsymbol{\epsilon}\cdot\boldsymbol{\nabla}_1\\ &+e^{i\mathbf{k}\cdot\mathbf{r}_2}\mathbf{k}\cdot\boldsymbol{\nabla}_2\boldsymbol{\epsilon}\cdot\boldsymbol{\nabla}_2)\Bigg], \end{aligned} \tag{19c}$$

where $\boldsymbol{\epsilon}$ is photon polarization and $\mathbf{k}$ is photon momentum. Note that, as in the one-electron case, the A form of the electron-photon interaction is singular, and note that these singularities correspond to and result from the singularities of the potential energy. In Eqs. (19), we have shown retardation included to all orders. When $\omega \ll m$ and thus $|\mathbf{k}| \ll p_{large}$, we may neglect retardation entirely (put $\mathbf{k}=0$ in the interaction term) for the leading contributions determined by the e-N singularity. This means that we may neglect retardation both in evaluating the leading contribution to the single-ionization total cross section and, in the case of double ionization, when calculating the shake-off and the final-state-interaction contributions to the spectrum, neglecting the (retardation-dependent) quasifree contribution. Without retardation [30], the two-electron forms are just the sums of the one-electron forms, Eq. (4),

$$I_{L,V,A}^{2e}=I_{L,V,A}^{1e}(\mathbf{r}_1)+I_{L,V,A}^{1e}(\mathbf{r}_2), \tag{20}$$

which, e.g., in A form, is

$$I_A^{2e}=\frac{iZ\alpha}{\omega}\left(\frac{\boldsymbol{\epsilon}\cdot\hat{\mathbf{r}}_1}{r_1^2}+\frac{\boldsymbol{\epsilon}\cdot\hat{\mathbf{r}}_2}{r_2^2}\right). \tag{21}$$

Note that, neglecting retardation, the electron-photon interaction in A form does not contain the e-e singularity. The e-e singularity is present in the wave functions but, neglecting retardation, this singularity would not give contributions in leading order in any form, as we will see subsequently. For the leading contributions due to the e-e singularity (which gives the leading contribution in the quasifree region of the spectrum), we need to include retardation at least to first order, as we do in Sec. VII in V and A forms.

In calculating the dominant contributions (to the total cross section and spectrum), the inclusion of lowest-order retardation is needed in calculating the quasifree contribution to the double-ionization spectrum, which also contributes to the total double-ionization cross section. Other dominant contributions to the total cross section (the shake-off contribution) can be treated neglecting retardation because, as we discuss in Sec. IX, the retardation correction to the shake-off contribution is of relative order $O(k^2/p^2_{large}) \sim O(v^2/c^2)$ in comparison to the nonretarded term in the shake off region [40,41].

In our analysis, we start with exact initial- and final-state wave functions. Our procedure of evaluating the leading contributions at high energies through expansion in terms of simpler functions around singular points allows us to identify the information from the two-electron wave functions needed to obtain the leading contributions in *V*, *L*, or *A* forms. We may then use approximate wave functions that contain such information.

We write the exact final-state two-electron wave function in the form

$$\Psi_{\mathbf{p}_1,\lambda}(\mathbf{r}_1,\mathbf{r}_2)=\frac{1}{\sqrt{2}}[\Psi^{(-)}_{\mathbf{p}_1}(\mathbf{r}_1)\Psi^{(-)}_{\lambda}(\mathbf{r}_2)D_{\mathbf{p}_1,\lambda}(\mathbf{r}_1,\mathbf{r}_2)+\zeta(\mathbf{r}_1\leftrightarrow\mathbf{r}_2)], \tag{22}$$

where $\zeta=1$ for symmetric states and $\zeta=-1$ for antisymmetric states, $\Psi^{(-)}_{\mathbf{p}}(\mathbf{r})=e^{i\mathbf{p}\cdot\mathbf{r}}\Phi^{(-)}_{\mathbf{p}}(\mathbf{r})$ represents an outgoing electron in a pure Coulombic potential of a nucleus with charge *Z*, λ denotes $\mathbf{p}_2$ when double ionization is considered and denotes (n,l,m) quantum numbers of a bound electron in a pure Coulombic potential with charge *Z* when single ionization is considered. The third factor $D_{\mathbf{p}_1,\lambda}(\mathbf{r}_1,\mathbf{r}_2)$ contains all final-state *e*-*e* interactions. The form, Eq. (22), is convenient because, in our calculations, we will argue that we may use the approximate $3C$ function [10,42], which is a product of three Coulomb one-particle functions, i.e., *D* is approximated by a Coulomb function in the *e*-*e* interaction; we will argue that $3C$ functions suffice for the high-energy situations considered here. Namely, as we argue in Appendix B, the $3C$ function is accurate, neglecting terms of the order $Zm\alpha^2/E_f$, where E_f is the total energy of the two electrons in the final state and, therefore, the $3C$ function contains accurately terms of order $Zm\alpha/p_{large}$ in the *e*-*N* interaction and terms of order $m\alpha/p_{large}$ in the *e*-*e* interaction ($p_{large}\simeq\sqrt{2mE_f}$).

By substituting Eq. (22) into Eq. (18) and using the symmetry of the initial state (which is the same as the symmetry of the final state), the matrix element can be written in the form, asymmetric in final electron states [43],

$$M=\sqrt{2}\int\Psi^{(-)*}_{\mathbf{p}_1}(\mathbf{r}_1)\Psi^{(-)*}_{\lambda}(\mathbf{r}_2)D^{*}_{\mathbf{p}_1,\lambda}(\mathbf{r}_1,\mathbf{r}_2)I^{2e}\times(\mathbf{r}_1,\mathbf{r}_2)\Psi_i(\mathbf{r}_1,\mathbf{r}_2)d^3r_1d^3r_2. \tag{23}$$

We use Eq. (23) to study the leading contributions to the matrix element for high-energy single and double ionization of the two-electron system with the Coulombic interaction of Eq. (2).

IV. SINGLE IONIZATION AND *e*-*N* COALESCENCE

In high-energy single ionization [3] of a two-electron atom, there is one fast emerging electron, and we therefore, as in the ionization in a potential case, are concerned with a single asymptotic Fourier transform with respect to a variable that can be taken as the electron-nucleus coordinate (we are here assuming a nucleus of infinite mass). The difference from ionization in a potential is that there is another variable. We wish to examine the role of the *e*-*N* coalescence and the *e*-*e* correlations in determining the high-energy behavior of the cross section.

In this section we discuss the total cross section for ionization from the ground state of the atom [44]. It is helpful to realize that the role of the *e*-*N* coalescence and *e*-*e* correlations, which we will describe here for single ionization, is the same as in double ionization in the shake-off region, discussed in Sec. VI. (In both situations, one electron takes almost all photon energy.) We will partition exact wave functions in terms of Coulombic wave functions starting from the full matrix element [Eq. (24)]. We obtain a factorization of the matrix element [Eq. (27)], into an absorption factor and a correlation factor, accurate to the order used in the partitioning. We then discuss the convergence of the obtained correlation factor to the high-energy limit. We will use this later in Sec. IX to discuss the convergence of the cross sections. At the end of this section we briefly note the form dependence of the obtained results.

The cross section for single ionization in general depends on both initial- and final-state electron-electron interaction. But when the initial state is the ground state, as we are considering here, high-energy ionization with excitation into bound *s* states (also including the case without excitation of the remaining electron) is determined by initial-state correlation only. For this reason the sudden approximation (which does not include the *e*-*e* interaction in the final state) is applicable in calculating high-energy ionization from the ground state of a He-like system with excitations into *s* states (and also in the shake-off double ionization total cross section) [22,45–47]. Excitations to non-*s* states, as demonstrated below, do depend on final-state interaction. However at high energies the total cross section for single ionization of the ground state (when the final state of the bound electron is not observed, i.e., summing over all final states), is dominated by contributions involving only excitations into *s* states, and therefore it is determined only by initial state correlation. We show this in *V*, *L*, and *A* forms.

We consider the dominant contribution to the matrix element for single ionization using Eq. (23), neglecting retardation in order to simplify our expressions, yet without losing generality for the energies considered ($\omega\ll m$). The three forms of the matrix element are obtained by substituting Eqs. (20) for $I^{2e}(\mathbf{r}_1,\mathbf{r}_2)$ into Eq. (23), with $\lambda=(n,l,m)$ the quantum numbers of the final-state bound electron. The matrix element for single ionization with excitation into the bound (n,l,m) state is thus

$$M^{+}_{nlm}=\sqrt{2}\int e^{-i\mathbf{p}_1\cdot\mathbf{r}_1}\Phi^{(-)*}_{\mathbf{p}_1}(\mathbf{r}_1)\Psi^{*}_{nlm}(\mathbf{r}_2)D^{(-)*}_{\mathbf{p}_1,nlm}(\mathbf{r}_1,\mathbf{r}_2)\times[I^{1e}(\mathbf{r}_1)+I^{1e}(\mathbf{r}_2)]\Psi_i(\mathbf{r}_1,\mathbf{r}_2)d^3r_1d^3r_2. \tag{24}$$

The procedure of evaluation of the leading contribution to the single-ionization matrix element is the same as in the one-electron case. Due to the large photon energy, the outgoing electron momentum $\mathbf{p}_1$ must be large. The term exp $(-i\mathbf{p}_1\cdot\mathbf{r}_1)$ is fast oscillating unless $p_1 r_1 \lesssim 1$. The dominant contribution for large p_1 is obtained in the vicinity of the e-N coalescence $\mathbf{r}_1=0$. Note that this connection distinguishes $I^{1e}(\mathbf{r}_1)$ (which is in the variable $\mathbf{r}_1$) from $I^{1e}(\mathbf{r}_2)$. The matrix element Eq. (24) is the sum of two terms $M^+ = M_d^+ + M_{ex}^+$, a direct term, (M_d^+) involving $I^{1e}(\mathbf{r}_1)$, and an exchange term (M_{ex}^+) involving $I^{1e}(\mathbf{r}_2)$. The leading contributions that concern us are obtained from M_d^+. However, when approximate wave functions are used in Eq. (24), the term M_{ex}^+ may give spurious contributions (in L and V forms) of leading order. In order to see this, we will keep track (in our discussion) of both M_d^+ (direct term) and M_{ex}^+ (exchange term).

To obtain the dominant contributions to the total cross sections, we write the integrands around $\mathbf{r}_1=\mathbf{0}$ in terms of simpler functions, as discussed in the Introduction and in Sec. II. In the vicinity of the Coulombic singularity, we represent the exact wave function (except for its normalization) in terms of a Coulombic function for that electron plus a remainder. This representation is sufficient to give a fast convergence of the cross sections, as we demonstrate [48]. This means that for small enough r_1 and fixed r_2,

$$\Psi_i(\mathbf{r}_1,\mathbf{r}_2)=\frac{1}{N_i^C}\Psi_i(0,\mathbf{r}_2)\Psi_i^C(\mathbf{r}_1)+O(r_1^2;\hat{\mathbf{r}}_1,\mathbf{r}_2), \quad (25)$$

where $\Psi_i^C(\mathbf{r}_1)$ is a hydrogenlike bound-state wave function satisfying the same Kato condition at the coalescence as the original function. $O(r_1^2;\hat{\mathbf{r}}_1,\mathbf{r}_2)$ means that the remainder vanishes faster than r_1 (e.g., like r_1^2), and it is a function of angles $\hat{\mathbf{r}}_1$ and of $\mathbf{r}_2$, too.

The partitioning, Eq. (25), of the exact two-electron wave function is obtained with the following arguments. When one electron approaches the nucleus $[r_1 \ll r_0$, where r_0 is the size of the atom, $r_0=1/(mZ\alpha)\equiv 1/a]$, while the other is at large distances $[r_2 \gg r_1$, and r_2 is not much smaller than $r_0]$, then the ground-state wave function can be written as $\Psi_i(\mathbf{r}_1,\mathbf{r}_2) = \Psi_i(0,\mathbf{r}_2)(1-ar_1)Y_0^0(\hat{\mathbf{r}}_1)+O(r_1^2;\hat{\mathbf{r}}_1,\mathbf{r}_2)$, which is just the statement of the e-N Kato cusp condition. We have then replaced $(1-ar_1)Y_0^0$ with a Coulombic wave function Ψ_i^C/N_i, which for small r_1 has the same behavior $(1-ar_1+\cdots)Y_0^0$ independent of energy for any s state (we can take the K-shell function). We will use partition equation (25) in integrations over all distances r_2, and therefore also over $r_2 \lesssim r_1$, for which partition equation (25) is not correct. However, the region $r_2 \lesssim r_1$ for $r_1 \ll r_0$ of the function $\Psi_i(\mathbf{r}_1,\mathbf{r}_2)$ corresponds to the triple coalescence point, which gives a negligible contribution to the observables we are discussing. We will use partitioning similar to Eq. (25) throughout the paper, in the vicinity of both coalescences and for both initial- and final-state wave functions [49]. Note that we are assuming functions that satisfy the Kato conditions at the nucleus exactly. Some problems with approximate functions which do not satisfy Kato conditions at the nucleus, which have been used in some calculations, are noted below, and they are discussed further in Appendix A in connection with the form dependence of results.

For the final state, the same procedure leads to a partitioning similar to Eq. (25),

$$\Psi_f(\mathbf{r}_1,\mathbf{r}_2)=\Psi_f(0,\mathbf{r}_2)\Psi_{\mathbf{p}}^C(\mathbf{r}_1)+O\left(\frac{1}{p_1^2}\right), \quad (26)$$

where $O(1/p_1^2)$, in analogy with the IPA case discussed in Sec. II, denotes the remainder that vanishes faster than a/p_1 as p_1 increases. In analogy with the IPA case, we expect that the contribution of these $O(1/p_1^2)$ and $O(r_1^2)$ of Eqs. (25) and (26) will be small.

Writing $\Psi_f(\mathbf{r}_1,\mathbf{r}_2)$ in the form of Eqs. (22), and using Eqs. (25) and (26), we obtain a factorization of the high-energy matrix element, Eq. (24),

$$M_{nlm}^+ = M_{corr}M_{abs}^C + O\left(\frac{1}{p_1^2}\right). \quad (27)$$

Here M_{abs}^C is the Coulombic photoabsorption matrix element, determined by the singularity at the nucleus, which includes retardation and a Stobbe factor,

$$M_{abs}^C = \int \Psi_{\mathbf{p}_1}^C(\mathbf{r}_1)I^{1e}(\mathbf{r}_1)\Psi_i^C(\mathbf{r}_1)d^3r_1. \quad (28)$$

M_{corr} contains initial- and final-state correlations that remain important at high energies:

$$M_{corr}=\frac{\sqrt{2}}{N_i^C}\int \Psi_{nlm}^{(-)*}(\mathbf{r}_2)D_{\mathbf{p}_1,\lambda}(0,\mathbf{r}_2)\Psi_i(0,\mathbf{r}_2)d^3r_2. \quad (29)$$

The results [Eqs. (27)–(29)] are obtained from Eq. (24) by performing the partition in terms of simpler functions describing the e-N singularity in both M_d^+ and M_{ex}^+. Neglecting the terms denoted by $O(r_1^2)$ in Eq. (25) and $O(1/p_1^2)$ in Eq. (26), the exchange term vanishes regardless of the form used. This is due to orthogonality of $\Psi_{\mathbf{p}}^C(\mathbf{r}_1)$ and $\Psi_i^C(\mathbf{r}_1)$ [50]. Our discussion proceeds neglecting terms $O(1/p_1^2)$ in Eq. (27).

First we discuss what the results [Eqs. (27)–(29)] mean. The absorption part [Eq. (28)] describes the absorption process that is determined, at high energies, by the Coulombic shape (hydrogenlike) of the wave functions at the coalescence. However, due to initial-state and final-state e-e interaction, these wave functions have normalizations (the wave-function normalization is defined through the expansion described earlier) that are different from the normalization of H-like functions. These normalizations enter photoabsorption at high energies through M_{corr}. The initial-state correlation enters M_{corr} through $\Psi_i(0,\mathbf{r}_2)$, which means that correlation is important between the electrons when one electron is at the e-N coalescence while the other electron is at some position $\mathbf{r}_2$. The point is that at the position from which the electron is removed (at high energies), the shape of the wave function for that electron is Coulombic, and its value is affected by a constant factor (normalization) associated with the position of the second electron.

M^C_{abs} is the single-electron Coulombic photoabsorption matrix element [51] which is known. We therefore need only to evaluate M_{corr}. We are interested in obtaining cross sections accurate neglecting the order $1/p^2$. For this purpose, we may use $3C$ functions [42] for the final two-electron state, as is argued in Appendix B. The $3C$ functions have been successfully applied to double-ionization calculations of He at high energies (around 1 keV and above) [10].

The advantage of using $3C$ functions for the final state is that the integration in Eq. (29) can be performed analytically, which simplifies our discussion. Expression (27) itself is accurate within $O(1/p_1^2)$, where, as in the IPA case, we expect these $O(1/p_1^2)$ terms in Eq. (27) to be small. However, we cannot demonstrate how large these terms are by using the $3C$ functions, which lack terms of the order $1/p_1^2$, which might be large even in the keV region (as we will discuss in Sec. VI in connection with double ionization).

Denoting by $R_{nl}(r_2)$ the radial component of the hydrogenlike state $\Psi_{nlm}(\mathbf{r}_2)$ and writing $\Psi(0,\mathbf{r}_2) = (1/\sqrt{4\pi})R_i(r_2)$ (we are taking into account that this is a spherically symmetric function), we obtain that

$$M_{corr}=\frac{\sqrt{2}}{N_i^C}\begin{cases}\displaystyle\int R_{n0}(r_2)R_i(r_2)r_2^2dr_2+\frac{im\,\alpha}{p_1}X(a)+O\left(\frac{1}{p_1^2}\right), & l=0,\\[2ex] \displaystyle -i\frac{m\alpha}{p_1}\,\frac{\sqrt{4\pi}}{l(l+1)}Y_l^{m}{}^{*}(\hat{\mathbf{p}}_1)\int R_{nl}(r_2)R_i(r_2)r_2^2dr_2+O\left(\frac{1}{p_1^2}\right), & l\neq 0.\end{cases} \tag{30}$$

In Eq. (30) $X(a)$ denotes a real quantity accurately given by $3C$ functions, which (due to the imaginary factor $im\,\alpha/p_1$) contributes as $1/p^2$ to the cross section (and for this reason, we do not show it explicitly); $O(1/p_1^2)$ denotes all terms that decrease faster than $1/p_1$, which $3C$ functions cannot reproduce correctly. Equation (30) explicitly shows the leading terms of M_{corr}. We will use these results in Sec. IX in discussing the total cross section for single ionization.

We see from Eqs. (30) and (27) that the total cross section for single ionization from the ground state of a He-like atom, at high energies, involves only $l=0$ bound states of the remaining electron. This is a well-known result used in the study of high-energy ionization with excitation and (through the completeness relation) in obtaining shake-off double ionization of two-electron atoms from the ground state [22,23,45]. Also, we see that this result, for $l=0$, does not depend on the final-state interaction. (We show in Appendix A that final-state interaction is not important at high energies, regardless of the form used.) Further, we see that excitations to any $l\neq 0$ state have just one additional power of $1/p_1$, i.e., excitations, in high-energy single ionization, to $l\neq 0$ states decrease as $1/p^4$ for all *l*. This is an important result that tells us that final-state interactions can move an electron from an $l=0$ state to an $l\neq 0$ state, with negligible transfer of energy, with just one additional power of $1/p_1$. This fact and its consequences are further discussed in Paper II, in examining single ionization from higher states and the modification of high-energy IPA results [52].

Let us note the form dependence of the results. We have not yet fixed the form of photoabsorption matrix element. We restrict for the moment the discussion to the dependence of the result, Eq. (27), for which the exchange term vanishes in any form, and afterwards discuss the form dependence of the exchange term. The forms [Eq. (20)], which neglect retardation, are similar to the one-electron forms [Eq. (4)], except that energies involved in Eq. (20) are two-electron $E_1+E_2-E_i=\omega$ (where E_1 is outgoing electron energy, E_2 is final-state bound electron energy, and E_i is initial state binding energy), while in one-electron forms the energies involved are one-electron ones, $E_1-E_K=\omega$, where E_K is, for the case of ground-state ionization which we consider here, binding energy of a *K*-shell electron. The difference in the fast electron energy (in the two and in the one electron case) is just $E_2-E_i+E_K\simeq a^2/2m$. Since the absorption factor M^C_{abs} in Eq. (27) is invariant in one electron forms, we conclude that the result Eq. (27) varies with forms Eq. (20) as $O(a^2/p_1^2)$ (i.e., varies within the order of neglected terms). This is just additional confirmation that our results are form invariant to the order we consider.

The contribution of the exchange term M^+_{ex} is also of an order which we have neglected in Eq. (27), as we discuss in Appendix A. There we show that M^+_{ex} can however be a source of spurious contributions, which may dominate the contribution described by Eq. (27), when approximate functions are used. This we discuss in Appendix A, including also the dicsussion of M^{++}_{ex} in the shake-off region, which is closely related to single ionization with excitation, and for which spurious contributions have been observed in numerical calculations of double ionization [22,45] (see Sec. VI).

Since the exchange term can be neglected in high-energy single ionization of the ground state of a He-like system, and since the remaining (direct term) matrix element has the same form as in the one-electron case, we may utilize the discussion of the Stobbe factor of Sec. II. This we do in Sec. IX.

V. IDENTIFYING THE THREE REGIONS OF THE DOUBLE-IONIZATION SPECTRUM

We now turn our attention to double ionization of the ground state of a He-like atom. In general, if both ionized electrons are of high-energy, the matrix element will correspond to a double AFT, giving an asymptotic $1/p_{large}^7$ behavior ($p_{large} \sim \sqrt{2m\omega}$). However, there will be kinematic situations in which the matrix element reduces to a single AFT. If our interest is the resulting electron spectrum (integrated over electron angles), in all regions of the spectrum single AFT contributions will dominate. There are three situations that need to be distinguished [53–55]: (1) the end points of the spectrum, in which one electron is fast and the other one is slow (shake off), and a single AFT contribution is associated with e-N coalescence, giving a contribution in the matrix element $1/p_{large}^3$ (as in single ionization of the ground state), which results in a $1/\omega^{7/2}$ contribution to the spectrum; (2) the middle of the spectrum, with electrons having nearly equal and opposite momenta (total momentum $\mathbf{p}_1+\mathbf{p}_2 \sim 0$) (quasifree region), and an AFT associated with the e-e coalescence giving a contribution $(1/p_{large}^3)(k/p_{large})$, where k is the photon momentum (this contribution is not allowed in dipole approximation), which results in a $1/\omega^{5/2}$ contribution to the spectrum; (3) the remainder of the spectrum, with electrons having perpendicular momenta, in which case an AFT is associated with the e-N coalescence and gives a matrix element of the order $1/p_{large}^6$, which results in a $1/\omega^{13/2}$ contribution to the spectrum.

These dominant contributions to the spectrum can be identified, as we will demonstrate for each region separately in Secs. VI, VII, and VIII, by identifying the singularities and by identifying kinematics in which only one large momentum in the system is associated with just one two-particle coalescence (singularity). By minimizing the dimension of the asymptotic FT, one singles out the dominant contributions. In order to understand what this means, let us consider the ordinary AFT of a function $f(\mathbf{r}_1,\mathbf{r}_2)$ with singularities at $\mathbf{r}_1=0$, at $\mathbf{r}_2=0$, and at $\mathbf{r}_{12}=\mathbf{r}_1-\mathbf{r}_2=0$ (we choose the same singularities as the functions in our photoabsorption matrix element have; we continue to call these singularities two-particle coalescence points in view of our physical picture of the process), i.e., we consider

$$F(\mathbf{p}_1,\mathbf{p}_2)=\int e^{-i\mathbf{p}_1\cdot\mathbf{r}_1-i\mathbf{p}_2\cdot\mathbf{r}_2} f(\mathbf{r}_1,\mathbf{r}_2)\,d^3r_1\,d^3r_2, \quad (31)$$

in the asymptotic region of $E=p_1^2+p_2^2\rightarrow\infty$. Minimizing the dimension of AFT means finding kinematics in which only one momentum will be large for $E\rightarrow\infty$, associated with a two-particle coalescence. Some evident choices are p_1 large (p_2 small) or p_2 large (p_1 small). We then check whether that large momentum (let us say p_1) is associated with a singularity (through the $\mathbf{p}_1\cdot\mathbf{r}_1$ phase). Since it is, we will get a single AFT. [This would correspond to the SO region, i.e., the edge region of the spectrum.] However, these are not the only choices. Another choices becomes apparent by rewriting the argument of the oscillating term in Eq. (31) as $i\mathbf{p}_1\cdot\mathbf{r}_1+i\mathbf{p}_2\cdot\mathbf{r}_2=i\mathbf{p}_{12}\cdot\mathbf{r}_{12}+i\mathbf{P}\cdot\mathbf{R}$, where $\mathbf{r}_{12}=\mathbf{r}_1-\mathbf{r}_2$, $\mathbf{R}=(\mathbf{r}_1+\mathbf{r}_2)/2$, $\mathbf{p}_{12}=(\mathbf{p}_1-\mathbf{p}_2)/2$, and $\mathbf{P}=\mathbf{p}_1+\mathbf{p}_2$. We may have kinematic situations in which p_{12} is large (P is small) or P is large (p_{12} is small), and so we can examine whether that large momentum is associated with a two-particle singularity. Large relative momentum p_{12} is associated with a two-particle coalescence, since $\mathbf{r}_{12}$ is a two-particle singularity that is distinct from the singularities in $\mathbf{r}_1$ and $\mathbf{r}_2$. [This would correspond to the QF region, i.e., the central region of the spectrum.] But large P is not associated with a two-particle coalescence. It is associated with a singularity at $\mathbf{R}=0$ and that singularity is present only when both $\mathbf{r}_1=0$ and $\mathbf{r}_2=0$; it is a three-particle coalescence. With the kind of FT shown in Eq. (31), in the kinematics in which total momentum is large, and with a function with singularities as we have assumed, the AFT is not a single AFT.

In order to argue that the only single AFT, obtained with plane waves and three-particle Coulombic singularities, are those in the kinematics: (1) $\mathbf{p}_1$ large, $\mathbf{p}_2$ small; (2) $\mathbf{p}_2$ large, $\mathbf{p}_1$, small; and (3) $\mathbf{p}_{12}$ large, $\mathbf{P}$ small, one may start from the assumption that there is another kinematical situation in which some momentum $\mathbf{q}$ is large while $\mathbf{Q}$ is small, where $\mathbf{q}$ and $\mathbf{Q}$ are linearly independent. Then we can express $\mathbf{p}_1=b\mathbf{q}+c\mathbf{Q}$ and $\mathbf{p}_2=b'\mathbf{q}+c'\mathbf{Q}$. With this, the plane-wave phase $\varphi=\mathbf{p}_1\cdot\mathbf{r}_1+\mathbf{p}_2\cdot\mathbf{r}_2$ becomes $\varphi=(b\mathbf{r}_1+b'\mathbf{r}_2)\cdot\mathbf{q}+(c\mathbf{r}_1+c'\mathbf{r}_2)\cdot\mathbf{Q}$. Now, as explained above, we examine whether the large momentum $\mathbf{q}$ is associated with a two-particle coalescence. This requires $b\mathbf{r}_1+b'\mathbf{r}_2$ to be $\mathbf{r}_1$, $\mathbf{r}_2$, or $\mathbf{r}_{12}$ (this determines b and b') as these are the only such coalescences, from which one finds that $\mathbf{q}$ (the large momentum) is $\mathbf{p}_1$, $\mathbf{p}_2$, or $\mathbf{p}_{12}$.

In the high-energy photoabsorption matrix element integral, which we view as a generalized AFT, there are also other kinds of oscillations (in addition to the plane waves) as we will discuss below, which have other oscillatory behaviors, i.e., spherical waves. There are kinematic situations in which the oscillatory term of the spherical wave would modify the plane-wave oscillatory terms in such a way that we get a single AFT even in the kinematical region where both p_1 and p_2 are large. The kind of AFT we get in the final-state-interaction (FSI) region (which we consider in Sec. VIII) and which can also lead to a single AFT is

$$F(\mathbf{p}_1,\mathbf{p}_2,q)=\int e^{-i\mathbf{p}_1\cdot\mathbf{r}_1-i\mathbf{p}_2\cdot\mathbf{r}_2+iqr_{12}} f(\mathbf{r}_1,\mathbf{r}_2)\,d^3r_1\,d^3r_2, \quad (32)$$

where $r_{12}=|\mathbf{r}_1-\mathbf{r}_2|$, and q is a parameter in this example (in the real calculation in Sec. VIII it is relative momentum). We will take both p_1 and p_2 as large. In such a situation, without the modifying term $\exp(iqr_{12})$, we obtained the double AFT. However, with the modifying oscillatory term we may get a single AFT. If $q \ll p_1, p_2$, then the additional oscillating term will not modify the fast oscillating terms $\exp(-i\mathbf{p}_1\cdot\mathbf{r}_1-i\mathbf{p}_2\cdot\mathbf{r}_2)$. However, if $q\simeq p_1$ (or $q\simeq p_2$), it will strongly modify (nearly cancel) the oscillations $\exp(-i\mathbf{p}_1\cdot\mathbf{r}_1)$ [or $\exp(-i\mathbf{p}_2\cdot\mathbf{r}_2)$] in the region in which $\mathbf{p}_1\cdot\mathbf{r}_1\simeq qr_{12}$ (or $\mathbf{p}_2\cdot\mathbf{r}_2\simeq qr_{12}$). We will show later (Sec. VIII) how this cancellation of spherical wave and plane wave occurs in the FSI region. In double ionization, this type of modification of the plane-wave oscillations comes with an additional $1/p^2_{large}$ factor (which is associated with the scattering amplitude). Although this contribution dominates the contribution from two singularities (three-particle coalescence), it is smaller (higher powers in $1/p_{large}$) than the contributions from the edge and the central region.

These types of single AFT are the only ones that appear in determining dominant contributions to the spectrum, assuming that it is correct to write matrix elements as Born terms (including first order in e-e and e-N interactions) and a remainder that vanishes faster than the Born terms for large momenta. Then these are the only oscillating factors, neglecting higher-order terms in Born expansion. Given these oscillations, the question is what are the kinematics in which these oscillations reduce to single AFT. For the plane-wave oscillations we saw that the dominant contributions (single AFT) are obtained only in SO and QF kinematics. With modified oscillations [Eq. (32)] there are also two kinematic regions in which it reduces to single AFT. One is for orthogonal outgoing electron momenta that give the dominant contribution in the FSI region of the spectrum. The other is for nearly equal and nearly parallel outgoing electron momenta that contribute in the quasifree region. Since the modified AFT, Eq. (32), comes with an additional $1/p^2_{large}$ factor (unlike the QF contribution determined by the plane-wave oscillations), it is negligible and we do not discuss it here.

VI. THE SHAKE-OFF CONTRIBUTION TO DOUBLE IONIZATION AND THE *e-N* COALESCENCE

In the edge region of the spectrum for double ionization, the momentum of one electron is very large while the momentum of the other electron is small ($p_1 \sim p_{large} = \sqrt{2m\omega}$, while $p_2 \lesssim a$, or vice versa). The shake-off mechanism provides the dominant contribution in this region, called the shake-off (SO) contribution. Here, double ionization can be described in terms of the sudden approximation, and the cross section factorizes as in a two-step process [56]. In the first step, photoabsorption occurs with the ejection of a single electron. The nucleus and the electron are involved in the absorption process and have to be close to each other in order to exchange a large momentum (much larger then the average momentum of the bound electrons), as required by energy and momentum conservation. Afterwards, the nucleus and the electron have nearly equal and opposite momentum, while the electron (having much smaller mass) takes almost all the photon energy and is moving at high velocity. The nucleus has very low velocity (and the second electron is still associated with it). In the second step, the second electron (in a state that reflects the initial state correlation) shakes off, taking generally a small amount of energy and momentum, reflecting the momentum distribution of that electron in the initial state. The leading contribution in this region of the spectrum is, therefore, associated with the kinematics in which the fast electron momentum (say $\mathbf{p}_1$) and the nucleus momentum are nearly equal and opposite. The other electron shakes off. The SO contribution, like single ionization, is a FT in just one large momentum $\mathbf{p}_1$, and it is determined by the e-N coalescence.

The evaluation of the SO contribution follows the same procedure that we used in calculating the dominant (shake-up) contribution to the cross sections for single ionization and ionization with excitation, Sec. IV. In both cases, the singularity that determines the dominant contribution is the e-N singularity, and the second electron (the electron not involved in the absorption) takes a small portion of the photon energy and is left in one of the eigenstates of the one-electron nuclear point Coulomb Hamiltonian, i.e., in both cases the electron shakes (up or off). The entire discussion of the dominant contribution in the edge region, the results in different forms (such as the importance of the final-state e-e interaction in L form), the needed quality of approximate wave functions, and the possible sources of spurious contributions can all simply be taken from the discussion of single ionization with excitation in Sec. IV. However, since these issues have been widely discussed in double ionization and some of them have not been fully resolved (e.g., the importance of the final-state e-e interaction in the SO region in L form [57]), we briefly repeat the arguments and point to the understanding of these issues provided by the AFT approach. In addition, at the end of this section, we discuss how large is the SO region and we discuss, using the AFT approach, the contributions of the triple-coalescence singularity. These considerations will be used in Sec. VIII, in which we discuss the importance of the final-state interaction away from the SO region.

As in Sec. IV, we start with the matrix element

$$M^{++} = \sqrt{2}\int e^{-i\mathbf{p}_1\cdot\mathbf{r}_1 - i\mathbf{p}_2\cdot\mathbf{r}_2}\Phi^{(-)*}_{\mathbf{p}_1}(\mathbf{r}_1)\Phi^{(-)*}_{\mathbf{p}_2}(\mathbf{r}_2)D^{(-)*}_{\mathbf{p}_1,\mathbf{p}_2} \times(\mathbf{r}_1,\mathbf{r}_2)[I^{1e}(\mathbf{r}_1)+I^{1e}(\mathbf{r}_2)]\Psi_i(\mathbf{r}_1,\mathbf{r}_2)d^3r_1d^3r_2, \tag{33}$$

neglecting retardation, and writing explicitly plane-wave oscillating terms of both outgoing electrons. In the edge region, one momentum (say $\mathbf{p}_1$) is large while the other is small. Therefore the fast oscillating term $\exp(i\mathbf{p}_1\cdot\mathbf{r}_1)$, from the plane wave of the final state associates (through the FT theorem) this large momentum with the coalescence (singularity) $\mathbf{r}_1 = 0$.

We now write the integrand of the matrix element integral around this coalescence in terms of simpler functions (partitioning in terms of Coulomb functions and a remainder; as in the other cases Coulombic functions are sufficiently accurate for our purposes). Using the same reasoning that led to Eqs. (27)–(29) for single ionization with excitation from the ground state, by using Eqs. (25) and (26) (but with the other electron now also being in the continuum), we obtain a factorization of the matrix element in the edge region of the ground-state double-ionization spectrum

$$M^{++}_{SO} = M_{corr}M^{C}_{abs} + O\left(\frac{1}{p_1^2}\right), \tag{34}$$

where $O(1/p_1^2)$ represents the order of terms that we are now neglecting. M^C_{abs} is the Coulombic photoabsorption matrix element determined by the singularity at the nucleus (which includes retardation and a Stobbe factor),

$$M^{C}_{abs}=\int \Psi^{(-)*C}_{\mathbf{p}_1}(\mathbf{r}_1)I^{1e}(\mathbf{r}_1)\Psi^{C}_{i}(\mathbf{r}_1)d^3r_1, \tag{35}$$

while M_{corr} contains initial- and final-state correlation important at high energies:

$$M_{corr}=\frac{\sqrt{2}}{N^{C}_{i}}\int \Psi^{(-)*}_{\mathbf{p}_2}(\mathbf{r}_2)D^{(-)*}_{\mathbf{p}_1,\mathbf{p}_2}(0,\mathbf{r}_2)\Psi_i(0,\mathbf{r}_2)d^3r_2. \tag{36}$$

As in Sec. IV, the functions Ψ^{C}_{i} and $\Psi^{C}_{\mathbf{p}_1}$ are single-electron Coulomb functions used in partitioning of the exact wave function in the vicinity of the nucleus taken, so that Kato conditions at the nucleus are satisfied.

Note that the only difference from the single-ionization case (Sec. IV) is in the final state of the second electron, which is here a slow continuum electron, instead of a bound electron, in the field of the nuclear charge. As in Sec. IV, we are interested in obtaining cross sections accurate, neglecting the order $1/p^2$. For this purpose we may use $3C$ functions [42] for the final two-electron state. As argued in Appendix B, the $3C$ functions are accurate neglecting terms of order $1/p_1^2$, which is consistent with the accuracy of Eq. (34). The $3C$ functions have been successfully applied to double-ionization calculations of He at high energies (around 1 keV and above) [10]. In the limit $p_1\rightarrow\infty$, $p_2\sim a$, the function $D_{\mathbf{p}_1,\mathbf{p}_2}(0,\mathbf{r}_2)$ approaches $1+O(1/p_1)$ and M_{corr} approaches the shake-off limit,

$$M_{corr}=\frac{\sqrt{2}}{N^{C}_{i}}\int \Psi^{(-)*}_{\mathbf{p}_2}(\mathbf{r}_2)\Psi_i(0,\mathbf{r}_2)d^3r_2. \tag{37}$$

We will discuss the convergence of the cross section toward this SO limit in Sec. IX. We note that, as in the ionization-excitation case, the first correction to the shake-off limit [Eq. (37)] is a relative $1/p_1^2$ correction in the cross section. The slowly converging term (the Stobbe factor that converges as $\pi ma/p_1$) obtained from M_{abs} is not affected by the correlation factor.

Let us note the form dependence of the result [Eq. (34)], which is determined by the form dependence of the absorption factor M_{abs}, as in single ionization (Sec. IV). The forms [Eq. (20)], that neglect retardation are similar to the one-electron forms [Eq. (4)] except that energies involved in Eq. (20) are two-electron $E_1+E_2-E_i=\omega$, while in one-electron forms the energies involved are one-electron $E_1-E_K=\omega$, where E_K is, for the case of ground-state ionization that we consider here, the binding energy of a K-shell electron. The difference in the fast electron energy (in the two- and in the one-electron cases) is just $E_2-E_i+E_K\simeq a^2/2m$, since also $E_2\simeq a^2/2m$ in the SO region. Since the absorption factor M^{C}_{abs} in Eq. (35) is invariant in one-electron forms, we conclude that calculations of the leading term in Eq. (34) vary with the forms [Eq. (20)] by amounts $O(a^2/p_1^2)$, as would be expected.

The discussion of the form dependence of the exchange term [which vanishes at the level of accuracy obtained with Eqs. (25) and (26), as already explained in Sec. IV] follows the discussion of Sec. IV. The discussion in Appendix A is applicable in the SO region here, too. We may just repeat the conclusion that if the e-N coalescence is treated incorrectly in the initial or final state, a spurious contribution appears. While the relative contribution of this spurious contribution in A form and (for the ground state) in V form is negligible, it may be the dominant contribution (a spurious $1/p^2$ contribution) in L form. However (see Appendix A), in the SO region, if the wave functions satisfy the Kato e-N cusp conditions (as, for example, an uncorrelated product of the Coulombic wave functions does), there is no spurious $1/p^2$ contribution. (This was also shown by Åberg [22] for double ionization in the SO region). Of particular importance is the finding (Appendix A) that an exact initial-state wave function with uncorrelated final-state wave functions gives the correct high-energy result, Eq. (33) [58]. The finding is important because it demonstrates that the sudden approximation (which neglects the final-state e-e interaction, and which has been widely used in obtaining the high-energy double-to-single ionization ratio) is form invariant. However, the needed representation of the fast electron is form dependent, i.e., the fast electron cannot, in general, simply be represented by plane waves.

The leading contribution in the SO region of double ionization of He is of the same order $1/p^3_{large}$ as the leading shake-up contribution for single ionization of He, since the leading contribution is determined by the leading contribution of the absorption factor M^{C}_{abs}, which is the same, in high-energy limit, in both shake processes. The leading contributions in both cases are a FT in just one large momentum associated with the same e-N singularity and the fast oscillating term comes from the plane-wave part of the final state.

We may now look at what happens to the SO contribution, Eq. (33), in which final-state interaction is neglected and which is connected to the e-N coalescence, when the other momentum ($\mathbf{p}_2$ in this case) also becomes large (here we assume no specific kinematics), i.e., when $p_1\gg p_2\gg a$. This analysis helps us understand how large is the SO region and it will help in understanding the importance of the final-state interaction in situations where $p_2\gg a$, which we now neglect, but will consider in Sec. VIII. When $p_2\gg a$, the correlation factor M_{corr} [Eq. (36)] becomes an asymptotic FT in $\mathbf{p}_2$, too. The fast oscillating term $\exp(i\mathbf{p}_2\cdot\mathbf{r}_2)$ connects the leading contribution to the coalescence $\mathbf{r}_2=0$. By expanding $\Psi(0,\mathbf{r}_2)$ and $\Phi(\mathbf{r}_2)$ around $\mathbf{r}_2=0$, we obtain

$$M_{corr}\sim\int e^{-(\eta r_2+i\mathbf{p}_2\cdot\mathbf{r}_2)}\left[1-i\frac{a}{p_2}g(\mathbf{r}_2)+O\left(\frac{a^2}{p_2^2}\right)\right]\Psi(0,0)\times[1+a'r_2+O(r_2^2)]d^3r_2\sim\frac{1}{p^4_{large}}, \tag{38}$$

where now $a\neq a'$. (We will see in the paragraph below that this is correct for initial state. This is then sufficient to say that the result [Eq. (38)] decreases at least as $1/p^4_{large}$ or faster.) From Eq. (38), we see that the correlation factor adds four more powers and, together with the absorption factor that decreases asymptotically as $1/p_1^3$, results in matrix element which decreases as $1/p_{large}^7$.

The contribution [Eq. (38)] comes from the configuration region in which both electrons are in the vicinity of the nucleus. We may therefore call this contribution a triple-coalescence contribution. However, due to the order in which the limits were taken, we have $r_1 \ll r_2 \ll 1/a$. We may ask what is the contribution from the triple coalescence when both electrons are at a similar, but small distances from the nucleus. The answer is that such a contribution is again of the order $1/p_{large}^7$. The argument is as follows. At the triple-coalescence point, the ground-state wave function can be expanded in terms of hypergeometric coordinates [28],

$$\Psi(r,\vartheta,\varphi)=\sum_{k=0}^{\infty} r^k \sum_{p=0}^{[k/2]} \psi_{kp}(\vartheta,\varphi)(\ln r)^p = 1-a(r_1+r_2) + \frac{m\alpha}{2} r_{12} + O(r^2), \tag{39}$$

where $r=\sqrt{r_1^2+r_2^2}$ is the hyper-radius, ϑ and φ are hyper-angles, and $O(r^2)$ denotes terms that decrease faster than r when r is vanishing (in fact, these terms vanish at least as $r^2 \ln r$). We see that the leading terms in this expansion are, in fact, just powers in r_1, r_2, and r_{12}. If we use the A form of the matrix element (which is singular in r_1, r_2, and r_{12}, and the singularity is described by the powers of these coordinates), the leading contribution of AFT of Eq. (39) comes from a product of powers (of coordinates) and therefore is a power in $1/p_{large}$ in any kinematics. Product of powers (of different coordinates) can then be integrated independently [59]. We point out again that the triple singularity is not reached in all kinematics when the final-state interaction is negligible, but only in kinematics in which all momenta (p_1, p_2 relative momentum p_{12} and total momentum P) are large. In such cases, there is a $1/p_{large}^7$ contribution from the triple coalescence.

We will now demonstrate, in the next two sections, that due to final-state interaction (in the intermediate region), and due to the $\mathbf{r}_{12}=0$ singularity (in the central region of the spectrum), the leading contributions away from the edge region are also connected with just one singularity [unlike in Eq. (38)] and are of a lower power than $1/p_{large}^7$.

VII. THE QUASIFREE CONTRIBUTION TO DOUBLE IONIZATION AND THE *e-e* COALESCENCE

As in our earlier examples, another kinematic situation when a double FT reduces to a single AFT occurs when total momentum of the two outgoing electrons ($\mathbf{P}=\mathbf{p}_1+\mathbf{p}_2$) is small ($P\sim a$). In this case the relative momentum of the two electrons is large ($p_{12}=p_{large}$). The two electrons leave the atom with nearly equal and opposite momentum, and the nucleus is a passive spectator not receiving energy or momentum [53]. While a photon cannot be absorbed by one free electron, it can be absorbed by two free electrons, although not in dipole approximation.

With these momenta, the plane-wave oscillating term of the final-state wave function $\exp(i\mathbf{p}_1\cdot\mathbf{r}_1+i\mathbf{p}_2\cdot\mathbf{r}_2)$ can be written, using coordinates $\mathbf{r}_{12}$ and $\mathbf{R}$, as $\exp(i\mathbf{p}_{12}\cdot\mathbf{r}_{12}+i\mathbf{P}\cdot\mathbf{R})$. The matrix element is a FT in just one large momentum $\mathbf{p}_{12}$, associated with the coordinate $\mathbf{r}_{12}$ in which the potential energy is singular at $\mathbf{r}_{12}=0$ (singularity when two electrons meet). The modifications of the fast plane-wave oscillations can, in principle, contribute (just as in the SO region discussed in the preceding section), but these modifications always come with additional powers in $1/p_{large}$. Here we are interested in the leading contribution.

To evaluate the leading contribution to the spectrum in the equal energy sharing region of the spectrum, we may start from the exact nonrelativistic matrix element, Eq. (23). We again represent the integrand near the coalescence ($\mathbf{r}_{12}=0$) in terms of simpler functions and a remainder. As simple functions we again use Coulombic functions or pieces of Coulombic functions, for initial and final states, which satisfy the Kato condition at the singularity. This is sufficient for our purposes if V form or A form of the matrix element is considered. (For L form, one needs better knowledge of the wave functions in the vicinity of the coalescence.) The e-γ interaction is expanded in powers of $\mathbf{r}_{12}$. It is hence more convenient to express the wave functions and the electron-photon interaction operator in terms of the coordinates $\mathbf{r}_{12}$ and $\mathbf{R}$. We will keep retardation to first order in its expansion around the singularity at $\mathbf{r}_{12}=0$ (and we will see that we get no contribution in zero order). For the final-state wave function, we again use the $3C$ function which is, as argued in Appendix B, accurate neglecting terms of order $Zm\alpha/E_f$. The functions $\Psi_{\mathbf{p}_i}^{(-)}=\exp(i\mathbf{p}_i\cdot\mathbf{r}_i)\Phi_{\mathbf{p}_i}^{(-)}(\mathbf{r}_i)$ $(i=1,2)$ are regular at $\mathbf{r}_{12}=0$, except at the triple coalescence, which we have argued gives contributions of higher powers in $1/p_{large}$. Note also that, due to $p_i \gg a$, we can expand $\Phi_{\mathbf{p}_i}^{(-)}(\mathbf{r}_i)$ in a/p_i, or use the g function as explained in Sec. II, i.e., we can make the approximation $\Phi_{\mathbf{p}_i}^{(-)}(\mathbf{r}_i)=N_i[1-(a/p_i)g_i]$. For the term containing the e-e interaction, we use the approximate form $D_{\mathbf{p}_1,\mathbf{p}_2}(\mathbf{r}_1,\mathbf{r}_2)=N_D[1+(m\alpha/2p_{12})g]$, which correctly describes the $\mathbf{r}_{12}$ singularity to this order. The g_i functions from $\Phi_{\mathbf{p}_i}^{(-)}(\mathbf{r}_i)$ contribute in higher order in $1/p_{large}$, while the g function from the e-e interaction term is important for the proper description of the coalescence, and it will be needed for a proper treatment in V form.

The leading contribution can thus be obtained from

$$M_{QF}^{++}=\sqrt{2}N_f\int e^{-(\varepsilon r_{12}+i\mathbf{p}_{12}\cdot\mathbf{r}_{12}+i\mathbf{P}\cdot\mathbf{R})} \times\left[1-i\frac{\nu}{p_{12}}g^{(-)*}[i(p_{12}r_{12}+\mathbf{p}_{12}\cdot\mathbf{r}_{12})]+O\left(\frac{\nu^2}{p_{12}^2}\right)\right] \times I^{2e}(\mathbf{r}_{12},\mathbf{R})\tilde{\Psi}(0,\mathbf{R})[1+\nu r_{12}+O(r_{12}^2)]d^3r_{12}d^3R, \tag{40}$$

where $\tilde{\Psi}(\mathbf{r}_{12},\mathbf{R})=\Psi(\mathbf{r}_1,\mathbf{r}_2)$ and $\nu=m\alpha/2$. In Eq. (40), we use the partition $\tilde{\Psi}(\mathbf{r}_{12},\mathbf{R})=\tilde{\Psi}(0,\mathbf{R})[1+\nu r_{12}+O(r_{12}^2)]$ [28], which follows from the Kato conditions. The neglected terms vanish faster than r_{12} for $r_{12}\rightarrow 0$. The central region of the spectrum, in which the matrix element for double ionization is dominated by the contribution of Eq. (40), is (at nonrelativistic energies) determined by the condition [53]

$$\frac{|E_1-E_2|}{\omega}\leqslant\left(\frac{\omega}{m}\right)^{1/2}, \tag{41}$$

obtained from free-electron kinematics (i.e., assuming absorption of a photon by two free electrons at rest).

In *A* form, the electron-photon interaction operator [Eq. (19)] may be expressed in $\mathbf{r}_{12},\mathbf{R}$ coordinates and expanded around the singularity $\mathbf{r}_{12}=0$. Keeping first order in retardation and the leading (singular) term in r_{12}, we obtain

$$I_A^{2e}=-\frac{i\alpha}{\omega}\frac{\boldsymbol{\epsilon}\cdot\hat{\mathbf{r}}_{12}\mathbf{k}\cdot\mathbf{r}_{12}}{r_{12}^2}. \tag{42}$$

Note that in obtaining Eq. (42) we have neglected some terms that are of first order in retardation, but are regular. These neglected terms, due to singular terms in wave functions, will lead to contributions in higher powers in $1/p_{12}$.

The leading contribution to the matrix element in the central region come from the singular term, Eq. (42), combined with the the first terms (the unit terms, i.e., the "$1-s$") in the expansion of the wave functions. The leading contribution in the QF region [53,54] is

$$M_{QF}=N_f\pi\nu\frac{\boldsymbol{\epsilon}\cdot\hat{\mathbf{p}}_{12}}{p_{12}^3}\frac{\mathbf{k}\cdot\hat{\mathbf{p}}_{12}}{p_{12}}\int\tilde{\Psi}(0,\mathbf{R})e^{i\mathbf{P}\cdot\mathbf{R}}d^3R. \tag{43}$$

Here the factor $\mathbf{k}\cdot\hat{\mathbf{p}}_{12}/p_{12}$ comes from first-order retardation. If one neglects retardation [puts the singular term in Eq. (42) identically to zero], the leading contribution in the central region would be of order $1/p_{12}^7$ (the first nonvanishing $\mathbf{k}$-dependent contribution involves three more powers in r_{12}), i.e., of the same order as the contribution from the triple coalescence.

In *V* form, the electron-photon interaction operator, Eq. (19) (written in terms of $\mathbf{r}_{12},\mathbf{R}$ coordinates, expanded around the coalescence $\mathbf{r}_{12}=0$, and taken to first order in retardation) is

$$I_V^{2e}=-i[\boldsymbol{\epsilon}\cdot\boldsymbol{\nabla}_R+(\mathbf{k}\cdot\mathbf{r}_{12})\boldsymbol{\epsilon}\cdot\boldsymbol{\nabla}_{12}]. \tag{44}$$

As explained earlier in connection with the *e*-*N* coalescence contributions (single-ionization and double-ionization SO contribution), the plane-wave approximation for the fast electrons gives the correct leading contribution for *s* states (but not for higher states). We show here that when the *e*-*e* coalescence is important, as in the central region, such an approximate wave function may give spurious contributions in the same order as the leading contribution [Eq. (43)]. These spurious contributions can be present in this order even when retardation is neglected.

By substituting I_V^{2e} into the matrix element, Eq. (40), the term $\mathbf{k}\cdot\mathbf{r}_{12}\boldsymbol{\epsilon}\cdot\boldsymbol{\nabla}_{12}$ (together with the first singular term from the initial state "νr_{12}" and the regular term "1" from the final state) give the leading contribution, Eq. (43). However, there are two terms (one term being the product of $\boldsymbol{\epsilon}\cdot\boldsymbol{\nabla}_R$ from I_V, the singular term "g" from final state, and the unit term from the initial state, and the other term the product of $\boldsymbol{\epsilon}\cdot\boldsymbol{\nabla}_R$ from I_V, the unit term "1" from final state, and the singular term from the initial state "νr_{12}") of the order $\boldsymbol{\epsilon}\cdot\mathbf{P}/p_{12}^4$, which do not contain retardation, and which cancel with each other. Therefore if an approximate initial-state wave function or an approximate final-state wave function is used, a term proportional to $\boldsymbol{\epsilon}\cdot\mathbf{P}/p_{12}^4$ may appear, resulting in a spurious structure in the central region even in dipole approximation. For example, such structure in dipole approximation was obtained in Ref. [60] using approximate initial-state wave functions with *V* form. Other examples of appearance of spurious contributions in the central region are discussed in Ref. [61]. This may happen, for example, if uncorrelated final-state wave functions are used, or if the initial-state wave function does not have proper expansion around the coalescence (i.e., if it does not satisfy the *e*-*e* Kato cusp condition).

The QF and the SO contributions are similar in the following sense. Each of them corresponds to an AFT in just one large momentum. Each is associated with a corresponding singularity through a fast oscillating term from the plane-wave parts of the final-state wave function. These are the only such contributions since the potential only has these two singularities. The difference between the QF and SO mechanisms is in the different pair of particles involved in the coalescence.

VIII. THE FINAL-STATE-INTERACTION CONTRIBUTION TO DOUBLE IONIZATION AND THE *e*-*N* COALESCENCE

While the end points and the center of the spectrum, dominant in determining the total cross section, are due respectively to the shake off and the quasifree mechanisms, the main part of the spectrum is determined in another way. As the momentum of the second electron increases, the probability amplitude to have this electron produced through the shake-off mechanism (which is, as we discussed, equivalent to the sudden approximation that neglects final-state interaction), with momentum $p_2\gg a$, decreases as $1/p_2^4$, as discussed in Sec. VI, Eq. (38). In this situation, however, the influence of the final-state interaction becomes important, and it dominates over the shake-off mechanism. [This intermediate region of the spectrum is called the final-state-interaction (FSI) region.] We can see this already starting from Eqs. (34), (35), and (36), derived with the assumption that $p_2\ll p_1$ [62]. We increase p_2 and look for the dominant kinematics in the region of the spectrum $p_1\gg p_2\gg a$ (Sec. VIII A). Note that due to the assumption $p_2\ll p_1$ (which we will later remove) we are looking only a small part of the spectrum, next to the edge. But this helps us see how SO evolves into the FSI region. We will then remove the assumption $p_2\ll p_1$ (in Sec. VIII B) and we will look at the rest of the FSI region, in which p_1 and p_2 are of comparable size.

A. FSI when $p_1 \gg p_2 \gg a$

We first look at what happens to our SO result [Eqs. (35) and (36)] as the momentum of the slower electron also becomes large, i.e., when $p_1 \gg p_2 \gg a$. We need to look only at the correlation factor [Eq. (36)], which we now write, making explicit the plane-wave oscillating term [43] as

$$M_{corr} = \frac{\sqrt{2}}{N_i^C} \int e^{-i\mathbf{p}_2 \cdot \mathbf{r}_2} \Phi_{\mathbf{p}_2}^{(-)*}(\mathbf{r}_2) D_{\mathbf{p}_1,\mathbf{p}_2}(0,\mathbf{r}_2) \Psi_i(0,\mathbf{r}_2) d^3 r_2 . \tag{45}$$

In the limit $p_1 \gg p_2 \gg a$, the fast oscillating plane-wave term $\exp(-i\mathbf{p}_2 \cdot \mathbf{r}_2)$, unless modified by oscillating terms from $\Phi_{\mathbf{p}_2} D_{\mathbf{p}_1,\mathbf{p}_2}$, results in $1/p_2^{n+3}$ powers for singular terms containing r_2^n, and it therefore gives at most a $1/p_2^4$ contribution [63]. The powers come from the $\mathbf{r}_2 = 0$ singularity. In order to find terms that are larger than $1/p_2^4$, one needs to look at the oscillating terms in $\Phi_{\mathbf{p}_2} D_{\mathbf{p}_1,\mathbf{p}_2}$ which can modify the fast oscillating plane-wave term so that it becomes a smooth function at least for some kinematics. Since $\exp(-i\mathbf{p}_2 \cdot \mathbf{r}_2)\Phi_{\mathbf{p}_2}$ is fast oscillating everywhere for $p_2 \gg a$, the needed modification can come only from fast oscillations of $D_{\mathbf{p}_1,\mathbf{p}_2}$. We can represent these oscillations accurate to first order in the *e*-*e* interaction by employing the 3*C* model, as demonstrated in Appendix B. In the 3*C* model the fast oscillations of the function $D_{\mathbf{p}_1,\mathbf{p}_2}$ occur for large values of its argument, $\mathbf{p}_{12} \cdot \mathbf{r}_{12} + p_{12} r_{12} \gg 1$, (see Appendix B). In the asymptotic region [accurate to the leading order in $\nu = m\alpha/2$ (*e*-*e* interaction)], neglecting terms that decrease faster than $1/r_{12}$, we have

$$D_{\mathbf{p}_{12},nlm}(\mathbf{r}_1,\mathbf{r}_2) = e^{-i(\nu/p_{12})\ln(p_{12}r_{12} + \mathbf{p}_{12}\cdot\mathbf{r}_{12})} + \frac{f_{p_{12}}(\hat{\mathbf{p}}_{12}\cdot\hat{\mathbf{r}}_{12})}{r_{12}} \times e^{-i(p_{12}r_{12} + \mathbf{p}_{12}\cdot\mathbf{r}_{12}) + i(\nu/p_{12})\ln(2p_{12}r_{12})}, \tag{46}$$

where $f_{p_{12}}$ is the *e*-*e* scattering amplitude,

$$f_{p_{12}}(\hat{\mathbf{p}}_{12}\cdot\hat{\mathbf{r}}_{12}) = \frac{\nu}{p_{12}^2(1 + \hat{\mathbf{p}}_{12}\cdot\hat{\mathbf{r}}_{12})} \times e^{i(\nu/p_{12})\ln[(1/2)(1 + \hat{\mathbf{p}}_{12}\cdot\hat{\mathbf{r}}_{12}) + i\pi - 2i\eta_0]}, \tag{47}$$

and where $\eta_0 = \arg\Gamma(1 + i\nu/p_{12})$.

In the configuration regions in which the function $D_{\mathbf{p}_1,\mathbf{p}_2}$ is not asymptotic, the final-state interaction gives just a correction to the SO contribution, which is small. Restricting to integration within the asymptotic region for $D_{\mathbf{p}_1,\mathbf{p}_2}$, and inserting Eq. (46) into Eq. (45), we obtain

$$M_{corr} = \frac{\sqrt{2}}{N_i^C} \int e^{-i\mathbf{p}_2\cdot\mathbf{r}_2} \Phi_{\mathbf{p}_2}^{(-)*}(\mathbf{r}_2) \left[e^{i(\nu/p_{12})\ln(p_{12}r_2 - \mathbf{p}_{12}\cdot\mathbf{r}_2)} + \frac{f_{p_{12}}(-\hat{\mathbf{p}}_{12}\cdot\hat{\mathbf{r}}_2)}{r_2} e^{+i(p_{12}r_2 - \mathbf{p}_{12}\cdot\mathbf{r}_2) + i(\nu/p_{12})\ln(2p_{12}r_2)} \right] \times \Psi_i(0,\mathbf{r}_2) d^3 r_2 . \tag{48}$$

The first term in the parentheses, involving only a logarithmic phase, is slowly oscillating and it therefore will not modify the fast oscillating plane-wave $\exp(-i\mathbf{p}_2\cdot\mathbf{r}_2)$, hence only giving small contributions. Note also that spherical waves from $\Phi_{\mathbf{p}_2}$ together with spherical waves from $D_{\mathbf{p}_1,\mathbf{p}_2}$ give already a $1/p_{large}^4$ factor, due to the $1/p_{large}^2$ factor contained in both spherical waves; we therefore do not consider such oscillating terms. We proceed, keeping only the second term. The integration only includes the regions in which the function D has asymptotic behavior, and these regions are defined by the requirement that $p_2 r_2 (1 - \hat{\mathbf{p}}_2 \cdot \hat{\mathbf{r}}_2) \gg 1$. We will calculate just the leading contribution, to determine its $1/p_2$ dependence, and therefore we approximate $\Phi_{\mathbf{p}_2}(\mathbf{r}_2) \simeq 1/(2\pi)^3$. We are calculating

$$M_{corr} = \frac{\sqrt{2}}{(2\pi)^3 N_i^C} \int e^{-i(\mathbf{P}/2)\cdot\mathbf{r}_2 + ip_{12}r_2 + i(\nu/p_{12})\ln(2p_{12}r_2)} \times \frac{f_{p_{12}}(-\hat{\mathbf{p}}_{12}\cdot\hat{\mathbf{r}}_2)}{r_2} \Psi_i(0,\mathbf{r}_2) d^3 r_2 , \tag{49}$$

where $\mathbf{P} = \mathbf{p}_1 + \mathbf{p}_2$. Note the modified oscillating term. In the asymptotic region the *e*-*e* scattering function $f_{p_{12}}(-\hat{\mathbf{p}}_{12}\cdot\hat{\mathbf{r}}_2)$, given by Eq. (47), is a smooth function, i.e., in the asymptotic region it is away from its singularity at $\hat{\mathbf{p}}_{12}\cdot\hat{\mathbf{r}}_2 = 1$.

We now perform the radial integration over r_2, i.e., we are calculating

$$\rho(\mathbf{P}\cdot\hat{\mathbf{r}}_2, p_{12}) = \int e^{-i(\mathbf{P}/2)\cdot\mathbf{r}_2 + ip_{12}r_2} \frac{1}{r_2} \Psi(0,\mathbf{r}_2) r_2^2 dr_2 , \tag{50}$$

where we have dropped the slowly oscillating logarithmic term that only contributes with additional powers in ν/p_{12}. For large momenta (both $p_1 \gg a$ and $p_2 \gg a$), the function $\rho(\mathbf{P}\cdot\hat{\mathbf{r}}_2, p_{12})$ has a maximum at $\mathbf{P}\cdot\hat{\mathbf{r}}_2/2 - p_{12} = 0$.

In order to get some impression of the behavior of this function, we can use some realistic examples for $\Psi(0,\mathbf{r}_2)$. If we use a model (Hylleraas) in which $\Psi(0,\mathbf{r}_2)$ can be expressed, to a good accuracy, as $\Psi(0,\mathbf{r}_2) = C\exp(-\lambda r_2)$ [64] [$\lambda \simeq m\alpha(Z - 0.53)$], we get

$$\rho(\mathbf{P}\cdot\hat{\mathbf{r}}_2, p_{12}) = \frac{C}{(\lambda - ip_{12} + i(\mathbf{P}/2)\cdot\hat{\mathbf{r}}_2)^2}, \tag{51}$$

which has the kind of behavior we have discussed. We are now left with the angular integration in Eq. (49) over angles that do not include singularity of $f_{p_{12}}(-\hat{\mathbf{p}}_{12}\cdot\hat{\mathbf{r}}_2)$, so that this function is slowly changing. Using a peaking approximation we can make the following estimate for the integral in Eq. (49). For arbitrary kinematics, in the limit $p_1 \gg a$ and $p_2 \gg a$, [we write $M_{corr}=\sqrt{2}I/((2\pi)^3 N_i^C)$],

$$|I| \leqslant \left| f_{p_{12}}(-\hat{\mathbf{p}}_{12}\cdot\hat{\mathbf{r}}_2^{max}) \int \mu(\mathbf{P}\cdot\hat{\mathbf{r}}_2, p_{12})\, d\Omega_2 \right|$$
$$= \left| f_{p_{12}}(-\hat{\mathbf{p}}_{12}\cdot\hat{\mathbf{r}}_2^{max}) \frac{4\pi C}{(\lambda - i p_{12})^2 + (P/2)^2} \right|, \qquad (52)$$

where $\hat{\mathbf{r}}_2^{max}$ denotes that direction, among all directions satisfying $\mathbf{P}\cdot\hat{\mathbf{r}}_2/2 - p_{12} = 0$, in which $f_{p_{12}}$ has maximal value.

As illustrated by Eq. (52), in general there will be two additional powers in $1/p_{large}$, except when the kinematics is such that $P/2 = p_{12}$. In such a case $\hat{\mathbf{r}}_2^{max} = \hat{\mathbf{P}}$ and we obtain that the dominant contribution to M_{corr} for the kinematics $P/2 = p_{12}$, which gives the leading contribution to the spectrum, for $p_1 \gg p_2 \gg a$, is

$$M_{corr} = \frac{\sqrt{2}}{(2\pi)^3 N_i^C} f_{p_{12}}(-\hat{\mathbf{p}}_{12}\cdot\hat{\mathbf{P}})\, \mu(p_{12}, \Delta), \qquad (53)$$

where

$$\mu(p_{12},\Delta) = \int \rho(\mathbf{P}\cdot\hat{\mathbf{r}}_2, p_{12})\, d\Omega_2 = \frac{2\pi i}{p_{12}} \int e^{i\Delta r_2} \Psi(0, r_2)\, dr_2, \qquad (54)$$

and where $\Delta = p_{12} - (P/2)$. In obtaining Eq. (54), the angular integration was performed using the fact that $\Psi(0, r_2)$ is angle independent for the ground state; only the leading order in $1/p_{12}$ is being kept.

The correlation part of the matrix element, in the dominant kinematics, factorizes further into a final-state e-e interaction part (represented by the free e-e scattering amplitude) and an initial-state correlation represented by the function $\mu(p_{12}, \Delta)$. This means that the dominant contribution to the matrix element for photoabsorption in the limit $p_1 \gg p_2 \gg a$, in the dominant kinematics ($P/2 = p_{12}$, which is equivalent to saying that $\mathbf{p}_1$ is orthogonal to $\mathbf{p}_2$), is

$$M_{FSI} = \frac{\sqrt{2}}{(2\pi)^3 N_i^C} f^*_{p_{12}}(-\hat{\mathbf{p}}_{12}\cdot\hat{\mathbf{P}})\, \mu(p_{12}, \Delta) M_{abs}, \qquad (55)$$

where M_{abs} is the absorption part given by Eq. (35). The result [Eq. (55)] has been obtained for the situation $p_1 \gg p_2 \gg a$, in which exchange can be neglected in the leading order. In a more symmetric situation the same factorization as in Eq. (55) is obtained [55], as we also show below, except that the e-e scattering is represented by the full e-e scattering amplitude for electrons in the spin-singlet state, which is $f_{p_{12}}(-\hat{\mathbf{p}}_{12}\cdot\hat{\mathbf{P}}) + f_{p_{12}}(\hat{\mathbf{p}}_{12}\cdot\hat{\mathbf{P}})$.

B. The rest of the FSI region

We now remove the assumption $p_2 \ll p_1$. We demonstrate that in the limits $p_1 \gg a$ and $p_2 \gg a$, but with no restrictions on the relative size of p_1 and p_2, the dominant contribution to the spectrum (but away from the quasifree region, $p_1 \simeq p_2$) comes from the kinematics in which the outgoing electron momenta are perpendicular (which implies that both P and p_{12} are large), and we show that the leading contribution in that kinematics is

$$M_{FSI} = \frac{\sqrt{2}}{(2\pi)^3 N_i^C} [f^*_{p_{12}}(-\hat{\mathbf{p}}_{12}\cdot\hat{\mathbf{P}})$$
$$+ f^*_{p_{12}}(\hat{\mathbf{p}}_{12}\cdot\hat{\mathbf{P}})]\, \mu(p_{12}, \Delta) M_{abs}. \qquad (56)$$

The arguments follow exactly those leading to Eq. (55). However, in obtaining Eq. (55) we have already started from a partitioning in the vicinity of one singularity (the singularity connected with the momentum of the faster electron). Now we just need to clarify the roles of the singularities $\mathbf{r}_1 = 0$ and $\mathbf{r}_2 = 0$.

We are looking at the regions where not only both $\mathbf{p}_1$ and $\mathbf{p}_2$ are large but also $\mathbf{p}_{12}$ and $\mathbf{P}$ are large. We substitute the asymptotic expansion for the final-state wave function and the asymptotic behavior of the final-state e-e interaction [Eq. (46)] into Eq. (18) (with $\lambda \equiv \mathbf{p}_2$). We use the argument from Sec. V that without modification of the plane-wave oscillations the intermediate region is determined by the triple coalescence, and that such modification comes from the e-e interaction term. We obtain for the leading contribution [43],

$$M_{FSI} = -\frac{\sqrt{2}}{(2\pi)^3} \int e^{-i(\mathbf{P}\cdot\mathbf{R} + i\mathbf{p}_{12}\cdot\mathbf{r}_{12} - p_{12} r_{12} - \mathbf{p}_{12}\cdot\mathbf{r}_{12})}$$
$$\times \frac{f^*_{p_{12}}(\hat{\mathbf{p}}_{12}\cdot\hat{\mathbf{r}}_{12})}{r_{12}} [I^{1e}(\mathbf{r}_1)$$
$$+ I^{1e}(\mathbf{r}_2)]\Psi(\mathbf{r}_1, \mathbf{r}_2)\, d^3 r_1 d^3 r_2, \qquad (57)$$

where we have written the plane-wave oscillating factors in terms of $\mathbf{P}$ and $\mathbf{p}_{12}$ for convenience for combining them with the oscillating terms of the scattering wave. We have dropped the logarithmic phases that do not contribute in the leading order. Note that the integral containing the e-γ interaction $I(\mathbf{r}_2)$ can be obtained from the integral containing $I(\mathbf{r}_1)$ by interchanging $\mathbf{p}_1$ and $\mathbf{p}_2$. We explicitly show only the contributions containing $I(\mathbf{r}_1)$. For the e-γ interaction, we are assuming V form or A form, since we are neglecting e-N interaction in the final state (we are not treating the final-state e-N coalescence correctly), and in L form this will lead to spurious contributions as discussed in Sec. VI.

The evaluation of the leading contribution follows the procedure of the partitioning around the e-N coalescence. The leading contributions to Eq. (57) come from two regions: (1) a region in which r_1 is small and r_2 is large ($r_1 \simeq 1/p_{large}$, $r_2 \simeq 1/a$), and (2) a region in which r_2 is small and r_1 is large. These two regions that we denote as $(0, r_2)$

and $(r_1,0)$ are disconnected, and we can simply add the contributions in the two regions to get the leading contribution to M_{FSI}.

$$M_{FSI}=\frac{\sqrt{2}}{(2\pi)^6 N_i^C}[I_{(0,r_2)}+I_{(r_1,0)}]+(\mathbf{p}_1\leftrightarrow\mathbf{p}_2), \qquad (58)$$

where the contribution from the $\mathbf{r}_1=0$ singularity is

$$I_{(0,r_2)}=\int e^{-i(\mathbf{P}/2)\cdot\mathbf{r}_1-ip_{12}r_1\cos\vartheta_{12}-i(\mathbf{P}/2)\cdot\mathbf{r}_2+ip_{12}r_2}I(\mathbf{r}_1)\times\frac{f^*_{p_{12}}(-\hat{\mathbf{p}}_{12}\cdot\hat{\mathbf{r}}_2)}{r_2}\Psi_i^C(\mathbf{r}_1)\Psi(0,\mathbf{r}_2)d^3r_1d^3r_2, \qquad (59)$$

and the contribution from the $\mathbf{r}_2=0$ singularity is

$$I_{(r_1,0)}=\int e^{-i(\mathbf{P}/2)\cdot\mathbf{r}_2-ip_{12}r_2\cos\vartheta_{12}-i(\mathbf{P}/2)\cdot\mathbf{r}_1+ip_{12}r_1}I(\mathbf{r}_1)\times\frac{f^*_{p_{12}}(\hat{\mathbf{p}}_{12}\cdot\hat{\mathbf{r}}_1)}{r_1}\Psi_i^C(\mathbf{r}_2)\Psi(\mathbf{r}_1,0)d^3r_1d^3r_2, \qquad (60)$$

and where $\nu=m\alpha/2$. The integrations in these expressions are restricted to the regions in which the *e*-*e* interaction is in the asymptotic region. Note that the expansion of r_{12} around $\mathbf{r}_1=0$ (the same is true for $\mathbf{r}_2=0$) gives two terms that we should keep, i.e., at the $\mathbf{r}_1=0$ singularity the two terms are $p_{12}r_{12}=p_{12}r_2-p_{12}r_1\cos\vartheta_{12}+O(r_1/r_2)\cdots$, where ϑ_{12} is the angle between $\mathbf{r}_1$ and $\mathbf{r}_2$. We cannot neglect the term $p_{12}r_1\cos\vartheta_{12}$ since Pr_1 and $p_{12}r_1$ are of the same magnitude.

We can now perform the analysis that led to Eq. (55). Terms like $p_{12}r_1\cos\vartheta_{12}$ in the phase of the oscillating factor,

$$e^{-i(\mathbf{P}/2)\cdot\mathbf{r}_1-ip_{12}r_1\cos\vartheta_{12}},$$

which we did not have in the situation where $p_1\gg p_2\gg a$, make no change in the argument. In the dominant region $(P/2=p_{12})$, they give a phase $\mathbf{P}\cdot\mathbf{r}_1/2$, which together with the already existing phase term $\mathbf{P}\cdot\mathbf{r}_1/2$, gives the correct phase $\mathbf{P}\cdot\mathbf{r}_1$ with the total absorption momentum $[-i(\mathbf{P}/2)\cdot\mathbf{r}_1-ip_{12}r_1\cos\vartheta_{12}=-i\mathbf{P}\cdot\mathbf{r}_1]$. Namely, after photon absorption, one electron has the whole total momentum $\mathbf{P}$, which is then distributed between electrons through *e*-*e* scattering. In the dominant kinematics $(P/2=p_{12})$, which can be established as in the asymmetric situation, and which is the same for both $I_{(0,r_2)}$ and $I_{(r_1,0)}$, we get

$$I_{(0,r_2)}=\int e^{-i\mathbf{P}\cdot\mathbf{r}_1}I(\mathbf{r}_1)\Psi_i^C(\mathbf{r}_1)d^3r_1\int e^{-i(\mathbf{P}/2)\cdot\mathbf{r}_2+ip_{12}r_2}\times\frac{f^*_{p_{12}}(-\hat{\mathbf{p}}_{12}\cdot\hat{\mathbf{r}}_2)}{r_2}\Psi(0,\mathbf{r}_2)d^3r_2, \qquad (61)$$

$$I_{(r_1,0)}=\int e^{-i(\mathbf{P}/2)\cdot\mathbf{r}_2}\Psi_i^C(\mathbf{r}_2)d^3r_2\int e^{-i(\mathbf{P}/2)\cdot\mathbf{r}_1+ip_{12}r_1}I(\mathbf{r}_1)\times\frac{f^*_{p_{12}}(\hat{\mathbf{p}}_{12}\cdot\hat{\mathbf{r}}_1)}{r_1}\Psi(\mathbf{r}_1,0)d^3r_1. \qquad (62)$$

Equation (61) is just the expression we considered in the asymmetric case. The contribution, Eq. (62), can be neglected since both integrals appearing in it are of higher order in $1/p_{large}$ than the corresponding integrals in Eq. (61).

As discussed here, and in Refs. [53–55], a more equal energy sharing between electrons occurs primarily due to the subsequent final-state interaction rather than through the shake-off mechanism. The final-state interaction mechanism of double ionization can be viewed (like shake-off) as a two-step process. In the first step photoabsorption occurs, as in the case of the shake-off mechanism. But in the second step the fast electron interacts with (scatters off) the second electron (final-state correlation), leading to double ionization and establishing a more equal energy sharing between the two electrons. In both the shake-off and the final-state-interaction mechanisms, an electron and the nucleus are involved in photoabsorption. However, the double ionization in the shake-off mechanism is a consequence of initial-state correlation, while in the final-state interaction mechanism the double ionization is a consequence of final-state correlation. In this FSI region the leading contribution is associated with the kinematics in which the two-electron momenta are nearly orthogonal to each other. This leading contribution, called the FSI contribution, is determined by the *e*-*N* coalescence. The matrix element is again a single FT in just one large momentum associated with just one singularity. We should note that the contribution of the final-state interaction mechanism to the total cross section for double ionization, at high energies, is negligible in comparison to the contribution of the shake-off mechanism.

As discussed in Sec. V, the dominant contributions in the three regions of the spectrum are a consequence of the existence of the singularities. There we have shown that the ordinary AFT (of a function with the same singularities as in the photoabsorption matrix element) in the intermediate region, away from both the edge region (in which the dominant contribution is determined by the *e*-*N* singularity) and the central region (the quasifree region in which the dominant contribution is determined by the *e*-*e* singularity), is determined by the triple singularity at $r_1=r_2=0$, corresponding to a double AFT. However, our matrix element differs from the ordinary AFT in that the plane-wave fast oscillating behavior can be modified due to spherical waves. What matters here is the modification resulting from the final state spherical wave due to the *e*-*e* interaction term, which results in a single AFT in a large momentum associated with just one (*e*-*N*) singularity, giving a contribution that dominates in the spectrum in comparison to the contribution from the triple coalescence. Within the assumption of a perturbative expansion for the final-state two-electron continuum wave function, there are no other contributions of the same order as the contribution [Eq. (56)] in this region of the spectrum.

IX. GROUND-STATE IONIZATION TOTAL CROSS SECTIONS AND DOUBLE-TO-SINGLE IONIZATION RATIOS R_{SO} AND R

The total cross section for single or double ionization in photoabsorption of a high-energy photon of momentum **k** by a two electron atom is

$$\sigma=\frac{(2\pi)^2\alpha}{m^2\omega}\sum_{\lambda}\int d^3p_1\frac{1}{2}\sum_{\epsilon}|M|^2\delta(\omega-|E_B|-\epsilon_1-\epsilon_\lambda), \tag{63}$$

where the nonrelativistic transition matrix element in the lowest order in the photon-electron interaction is given by Eq. (18). The symbol Σ_λ means summation over hydrogenlike discrete states n when single photoionization is considered and means $\int d^3p_2$ when double photoionization is considered. [Bound states are normalized to unity. The single-electron continuum is normalized asymptotically to an amplitude $1/(2\pi)^{3/2}$ and the two-electron continuum is normalized asymptotically on an amplitude $1/(2\pi)^3$.]

Substituting Eq. (30) into Eq. (63) we obtain an expression for the single-ionization total cross section at high photon energies (but $\omega \ll m$), within the $3C$ model, involving excitations to all subshells. However, since the $3C$ model neglects terms of the order $Z(m\alpha)^2/p^2$, we neglect, for simplicity, all terms from the correlation factor that vanish as $1/p^2$, i.e., we take only excitations to $l=0$ bound states. Also, we neglect binding energies E_n of the final-state bound electron compared to the kinetic energy of the outgoing electron. Thus, we obtain a common absorption factor for all excitations. This leads to factorization of the cross section for single-ionization of He, and we obtain an expression for the single ionization total cross section at high photon energies (but with $\omega \ll m$),

$$\sigma^{+}=\frac{1}{(N_1^C)^2}\left[\sum_n\left|\int \Phi_n^*(\mathbf{r})\Psi_i(\mathbf{r},0)d^3r\right|^2\right]\sigma_{1s}^C(\omega), \tag{64}$$

where $\sigma_{1s}^C(\omega)$ is the photoabsorption cross section from the ground state of hydrogenlike He. The cross section $\sigma_{1s}^C(\omega)$ in Eq. (64), resulting from the absorption matrix element, Eq. (30), includes both retardation and the slowly converging Stobbe factor.

We now calculate the double-ionization total cross sections. This means integration in Eq. (63) over the whole spectrum of final electron energies. But, before doing that, we may consider restricting ourselves to just the SO region, and we define the SO total cross section σ_{SO}^{2+}. This is an observable, which has been measured [65] by counting only the events where momentum is transferred to the nucleus (e-N coalescence is involved in photoabsorption). As in single-ionization case, we neglect all terms from the correlation factor which vanish as $1/p_{large}^2$, i.e., we take Eq. (37) for the correlation factor. Also, we neglect the kinetic energy of the slow electron, $E_2 \sim a^2/2m$, compared to the kinetic energy of the fast electron. As in single ionization, we obtain a common factor $\sigma_{1s}^C(\omega)$ for all contributing $E_2 \sim a^2/2m$. This leads to factorization of the σ_{SO}^{2+} cross section. When calculating the SO double-ionization total cross section σ_{SO}^{2+}, we can simply use Eq. (64), replacing the summation over discrete states n by summation over continuum states. Alternatively (due to the above simplifications), as has been done in Ref. [45], we may employ the completeness relation for the states Φ. We obtain

$$\sigma_{SO}^{++}=\frac{1}{(N_1^C)^2}\left[\int|\Psi_i(\mathbf{r},\mathbf{0})|d^3r-\sum_n\left|\int \Phi_n^*(\mathbf{r})\Psi_i(\mathbf{r},0)d^3r\right|^2\right]\sigma_{1s}^C(\omega). \tag{65}$$

Our analysis of SO double ionization and single ionization gave a factorization of the matrix elements into absorption and correlation factors, which leads to a similar factorization of cross sections. This factorization is accurate, neglecting terms that vanish as $1/p_{large}^2$. Since the SO double-ionization cross section and single-ionization cross section have the same factor $\sigma_{1s}^C(\omega)$ (which include retardation and the slowly converging Stobbe factor) at high energies, it cancels in the ratio. The cancellation of retardation was demonstrated in numerical calculations [40] that were consistent with the shake-off assumption. The shake-off ratio $R_{SO}=\sigma_{SO}^{2+}/\sigma^{+}$ therefore involves only the correlation factors. At high energies [22,45–47,66],

$$R_{SO}=\frac{\int|\Psi_i(\mathbf{r}_1,0)|^2d^3\mathrm{r}_1}{\sum_n\left|\int \Phi_n^*(\mathbf{r}_1)\Psi_i(\mathbf{r}_1,0)d^3\mathrm{r}_1\right|^2}-1. \tag{66}$$

The cross sections σ^{+}, σ_{SO}^{2+}, and also the ratio R_{SO} approach their asymptotic forms, Eqs. (64)–(66), faster than $1/p_{large}$ (in fact, the $3C$ model gives an approach as $1/p_{large}^2$). Various numerical calculations [see, e.g., [10], and references therein], are consistent with such a conclusion. These calculations agree that, in the case of He, the constant SO ratio, $R_{SO}=1.67\%$, which can be obtained even in the lowest-order Born approximation, is reached within few percent at 5 keV and approaches a constant as $1/p_{large}^2$. In contrast, at such an energy the lowest-order Born approximation for cross sections is still more than 25% away from the correct value (as we obtain in our IPA calculations) and the error decreases only as $1/p_{large}$. Fast convergence of the ratio is due to cancellations of the Stobbe factors.

The contribution of the FSI region to the total cross section is negligible in the high-energy limit. The double-ionization cross section in the FSI region obtained from Eq. (56) [55] is

$$\frac{d\sigma^{2+}(\omega)}{dE_1}=\kappa\sigma_{1s}^C(\omega)\frac{d\sigma_{ee}^{+}(\omega,E_1)}{dE_1}, \tag{67}$$

factorized as the product of the cross section $\sigma_{1s}^C(\omega)$ for single photoabsorption (which reflects the mechanism of absorption of the photon) and $d\sigma_{ee}^{+}(\omega,\epsilon_1)/d\epsilon_1$, the cross sections for single ionization by electron impact [55],

$$\frac{d\sigma_{ee}^{+}(\omega,E_1)}{dE_1}=\frac{2\pi\alpha^2}{2\omega}\left[\frac{1}{\omega-E_1}+\frac{1}{E_1}\right]^2, \qquad (68)$$

where κ in Eq. (67) is

$$\kappa=\frac{\displaystyle\int \frac{1}{r^2}|\Psi_i(0,\mathbf{r})|^2 d^3r}{\displaystyle 4\pi\int |\Psi_i(0,\mathbf{r})|^2 d^3r}. \qquad (69)$$

By integrating Eq. (67) over the whole energy region, but excluding the SO region (integrate from E_0 to $\omega-E_0$ where E_0 defines the SO region; E_0, is several times $a^2/2m$), in which Eq. (67) is not valid, one obtains

$$\sigma_{FSI}^{2+}\simeq\frac{2\pi\alpha^2}{\omega E_0}\sigma_{1s}^{C}(\omega), \qquad (70)$$

which shows that the FSI contribution to the total cross section is negligible at high energies ω.

The full total cross section for double ionization σ^{2+} includes both the SO and the QF contributions. The matrix element, Eq. (18), can be approximated by M_{SO} and by M_{QF} in the two different dominant kinematical regions. The overlap (interference term) of these two contributions is negligible. In fact, this interference term is much smaller than the contribution of the final-state interaction term, which has also been neglected here. We may therefore proceed following Ref. [54], substituting Eq. (43) in Eq. (63) for the He double-ionization total cross section $(\lambda=\mathbf{p}_2)$. We perform the integration over all outgoing electron energy and momenta in order to obtain the σ_{QF}^{2+} contribution to the total double-ionization cross section. Neglecting the binding energy E_B and the energy of the center of mass of the two electrons, $P^2/(4m)$, in comparison to their energy p^2/m in the center-of-mass frame, we obtain the leading contribution σ_{QF}^{2+} to the total cross section for double ionization by photoabsorption through the quasifree mechanism

$$\sigma_{QF}^{2+}=\frac{2^9\pi^2 m\alpha^3\omega}{15(m\omega)^{7/2}}\int |\Psi_i(\mathbf{r}_1,\mathbf{r}_1)|^2 d^3\mathrm{r}_1. \qquad (71)$$

The dominant contributions to the total cross section σ^{2+} for double ionization of the ground state of a He-like atom by photoabsorption, at high but nonrelativistic energies, are given by summing Eqs. (65) and (71).

Taking the single-ionization total cross section to the same order (or to all orders) in retardation [30] as in calculating σ_{QF}^{2+}, the ratio $R=\sigma^{2+}/\sigma^{+}$ is obtained as

$$R=R_{SO}+C_Z\frac{\omega}{m}, \qquad (72)$$

for $\omega\ll m$, where the constant R_{SO} is the shake-off result for the ratio and

$$C_Z=\frac{8\sqrt{2}}{5Z^2}\,\frac{\displaystyle\int |\Psi_i(\mathbf{r}_1,\mathbf{r}_1)|^2 d^3\mathrm{r}_1}{\displaystyle\sum_n \left|\int \Phi_n^{*}(\mathbf{r}_1)\Psi_i(\mathbf{r}_1,0)d^3\mathrm{r}_1\right|^2}. \qquad (73)$$

Here m is the electron mass, $\Phi_n(\mathbf{r}_1)$ is a bound-state hydrogenlike electron wave function (in a potential of charge Z), and the summation is over all bound states. We may estimate the magnitude of the constant C_Z by using approximate ground-state wave functions in Eq. (73). For the function $\Psi_i(\mathbf{r}_1,\mathbf{r}_2)=\exp[-Z(r_1+r_2)+|\mathbf{r}_1-\mathbf{r}_2|/2]$, (here we use atomic units) [28], both the e-e and e-N Kato conditions are exactly fulfilled. Then Eq. (73) gives $C_Z=[(2Z-1)/(2Z)]^3\sqrt{2}/(5Z^2)$. (The binding energy of He given by this simple wave function is 77.7 eV.) In the case of He, this gives $C_Z=0.030$. Since for He, $R_{SO}=0.0167$, this means that at $\omega=15$ keV, the ratio $R=0.0176$, which is about 5% above the constant shake-off ratio [67]. In this energy region, the deviation will increase linearly with ω. We note that in order to observe this linear rise, one should not restrict oneself, as in Ref. [65], to counting only the events in which the momentum is transferred to the nucleus. Observing events in which the momentum is transferred to, another electron is required. To our knowledge, such measurement has not been performed.

X. CONCLUSIONS

We have described within a unified nonrelativistic approach single and double photoionization of two-electron atoms by photoabsorption at high photon energies ω (but still $\omega\ll m$). We have demonstrated that high-energy ionization by photoabsorption can be understood in terms of the singularities of the many-body Hamiltonian. In particular, the SO and the QF contribution to the double-to-single ratio R, Eq. (72), are explained in terms of the e-N singularity (SO) and e-e singularity (QF) which both contribute to the double ionization total cross section. Our discussion was not dependent on the choice of the form (length L, velocity V, acceleration A, etc.) of the photoionization matrix element.

Since photoabsorption at high photon energies requires at least one large outgoing electron momentum, we have argued that the analysis is equivalent to the analysis of the asymptotics of Fourier transforms. Based on Fourier-transform theory, we have shown that a slow asymptotic decrease for large momentum p, such as $1/p^n$, is connected with the singularities of the e-N and e-e Coulomb potentials. We have demonstrated how this slow asymptotic decrease can be obtained by writing the wave functions and interactions in terms of simpler functions (plus remainders whose contributions decrease faster) around singularities. Our approach clarifies which singularities need to be considered for dominant contributions and demonstrates that this is determined by the kinematics of the outgoing electron momenta. With this approach we can identify the dominant terms, and avoid omitting any of them, and we can also avoid the uncontrolled introduction of spurious contributions. We have illustrated how both of these problems have arisen in the use of approximate wave functions.

We have applied our approach to study the high-energy total cross section for single ionization and the total cross section and spectrum for double ionization of the ground state of a two-electron atom. We have demonstrated that the approach, as well as the final results, are gauge and form independent. However, the dependence of the final results on the quality of initial- and final-state wave functions at singularities varies with gauge and form. We have found that acceleration form, which places the singularities of the Hamiltonian in the e-γ interaction, has the least requirement on the quality of wave functions at the singularity, in all situations considered. In the case of total cross sections for single ionization and for the shake-off limit for the double ionization of the ground state, acceleration form requires only the proper normalization of the initial state at the e-N singularities (which are three-dimensional manifolds, not just points). In contrast, velocity form requires knowledge of both normalization and slope at the singularities, while length form requires even more detailed knowledge of the ground-state wave function at the singularities.

Within our unified approach, we have explained the dominant contributions to the total cross sections (for single and double ionization) and the dominant contributions to the double-ionization spectrum, as a FT asymptotic in a single large momentum (dependent on the process and the region of the spectrum). These dominant contributions are connected, through AFT, with either the e-N singularity or the e-e singularity. The asymptotic Fourier transform results are modified by Coulombic interactions. We have included these modifications, for the cases of single ionization and double ionization in the shake-off region at high energies, and in this way we have obtained rapid convergence of the cross sections with increasing energy. This has allowed us to discuss also the convergence of ratios of cross sections. We have discussed the importance of final-state e-e and e-N interaction. We have discussed the importance of retardation corrections as well as the cancellation of retardation contributions in the shake-off double-to-single ratio.

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APPENDIX A: FORM DEPENDENCE OF THE MATRIX ELEMENT IN THE SHAKE REGION

Here we discuss the form dependence of the matrix element for ionization of a two-electron atom in the region where one electron takes almost all the photon energy while the other just shakes (either shakes up or shakes off). The discussion is valid for both single ionization with excitation and for the SO region of double ionization. In particular, we consider the exchange part of the matrix element M_{ex}, which can be a source of spurious contributions that dominate the contribution from the direct terms discussed in Secs. IV and V, when approximate functions are used. We also show that an exact initial-state wave function with uncorrelated Coulombic final-state wave functions gives an accurate high-energy result in the shake regions, regardless of the form used.

The exchange term is

$$M_{ex}^{+}=\sqrt{2}\int e^{-i\mathbf{p}_1\cdot\mathbf{r}_1}\Phi_{\mathbf{p}_1}^{(-)*}(\mathbf{r}_1)\Psi_{\lambda}^{*}(\mathbf{r}_2)\times D_{\mathbf{p}_1,\lambda}^{*}(\mathbf{r}_1,\mathbf{r}_2)I^{1e}(\mathbf{r}_2)r_1\Psi_i(\mathbf{r}_1,\mathbf{r}_2)d^3r_1d^3r_2, \tag{A1}$$

where λ denotes the quantum numbers of the remaining bound electron in the case of single ionization, or it denotes the momentum $\mathbf{p}_2$ of the other electron in the case of double ionization. According to the AFT theorem, the dominant contributions to this part of the matrix element, at high energies, come from singularities. The fast oscillating terms come from the plane wave, and in some configuration regions also from the e-e interaction term, Eq. (46), modifying the plane wave oscillating term. While the plane wave oscillating term connects the dominant contribution with the $\mathbf{r}_1=0$ singularity, the oscillating term from the e-e interaction can modify these fast oscillations in such a way so as to give additional contributions from the $\mathbf{r}_2=0$ singularity.

Since the modification of the plane wave, due to the e-e interaction, comes with two additional powers in $1/p_1^2$ [see Eq. (47)], such contribution would not modify our result, Eq. (27). For the discussion of the final-state interaction modification of the plane-wave oscillating term, see Sec. VIII. We here discuss the form dependence of the contributions from the plane-wave oscillating term ($\mathbf{r}_1=0$ singularity) to Eq. (A1). This is of interest because contributions from the $\mathbf{r}_1=0$ singularity to the exchange term with approximate wave functions (which do not satisfy Kato condition, and which have been used in some calculations of photoabsorption) can lead to spurious contributions.

The leading contributions from the $\mathbf{r}_1=0$ singularity to the exchange terms can be obtained by characterizing wave functions near the singularity. We will show that if one uses an approximate initial-state wave function that does not satisfy the Kato cusp condition, then one can get an erroneous leading-order result. We suppose that initial state near $\mathbf{r}_1=0$ is $\Psi_i(\mathbf{r}_1,\mathbf{r}_2)=\Psi_i(0,\mathbf{r}_2)(1-a'r_1)Y_0^0(\hat{\mathbf{r}}_1)+O(r_1^2;\hat{\mathbf{r}}_1,\mathbf{r}_2)$, where $a'\neq a=mZ\alpha$ [see Eq. (25) for the partitioning and characterization of exact wave function near $\mathbf{r}_1=0$]. For the final state we take an equivalent partitioning in terms of Coulombic functions and explicitly keep only the leading terms shown in Eq. (7). We obtain

$$\begin{aligned}M_{ex}^{+}=\sqrt{2}N_f\int\ & e^{-(\varepsilon r_1+i\mathbf{p}_1\cdot\mathbf{r}_1)}\left[1+i\frac{a}{p_1}g^{(-)*}\right.\\ &\left.\times[i(p_1r_1+\mathbf{p}_1\cdot\mathbf{r}_1)]+O\left(\frac{1}{p_1^2}\right)\right]\Psi_{nlm}^{*}(\mathbf{r}_2)\\ &\times\left[1-i\frac{m\alpha}{p_1}g^{(-)*}\left[\frac{i}{2}(p_1r_2-\mathbf{p}_1\cdot\mathbf{r}_2)\right]\right.\\ &\left.+O\left(\frac{1}{p_1^2}\right)\right]I^{1e}(\mathbf{r}_2)\Psi(0,\mathbf{r}_2)\\ &\times[1-a'r_1+O(r_1^2)]d^3r_1d^3r_2.\end{aligned}\tag{A2}$$

The leading contributions to the matrix element at high energies are determined by the leading singular terms in the variable $\mathbf{r}_1$. Following the procedure explained in Sec. II, we obtain powers $1/p_1^{n+3}$ from singular terms involving powers r_1^n in Eq. (A2), when we integrate over $\mathbf{r}_1$ [see Eqs. (10) and (11)].

In all forms, the powers in $1/p_1$ of Eq. (A2) are determined by the p_1 dependence of the interaction term [see Eq. (20), in A form the interaction term contains the power $1/\omega \sim 1/p_1^2$, in V form it contains no powers, and in L form it contains $\omega \sim p_1^2$] and the leading power from the integral

$$\begin{aligned}\int\ & e^{-(\varepsilon r_1+i\mathbf{p}_1\cdot\mathbf{r}_1)}\left(1+i\frac{a}{p_1}g^{(-)*}[i(p_1r_1+\mathbf{p}_1\cdot\mathbf{r}_1)]\right.\\ &\left.+O\left(\frac{1}{p_1^2}\right)\right)[1+a'r_1+O(r_1^2)]d^3r_1\sim(a-a')\frac{1}{p_1^4}.\end{aligned}\tag{A3}$$

This spurious contribution, arising in the exchange term from asymmetric description of the e-N singularity ($a'\neq a$) appears in all forms, but in A form it is of the order $1/p_1^6$, in V form it is of the order $1/p_1^4$, and in the L form it is of the order $1/p_1^2$. In L form, this spurious contribution would be the leading contribution to the matrix element. With wave functions that satisfy the e-N Kato cusp condition, these contributions, however, cancel; and, in fact, leave in A form a $1/p_1^7$ power contribution from the exchange term, in V form a $1/p_1^4$ power, and in L form a $1/p_1^3$ power, at high energies. Therefore the contribution of the exchange term is manifestly of higher order in A and V forms, while in L form it is of the same order as the leading contribution for ionization with excitation into s states, $1/p_1^3$. Even this $1/p_1^3$ contribution is obviously a spurious contribution that must vanish. In order to show this explicitly, one needs more detailed knowledge of the wave functions at the coalescence. However, as we show now, neglecting final-state interaction and assuming exact initial-state wave function, we get no spurious terms of the order $1/p_1^3$ (i.e., of the same order as the dominant term) when considering ionization with excitation into a bound s state, i.e., we need no final-state e-e interaction even in L form. An exact initial-state wave function with uncorrelated Coulombic final-state wave functions gives an accurate high-energy result in the shake regions.

We assume that the initial state is exact and that final states are uncorrelated Coulombic states with the correct e-N singularity. As we have shown above, the V form result for ground state ionization does not depend on final-state e-e interaction. Therefore we may analyze the behavior of the difference between the approximate V-form and L-form matrix elements when final state interaction is neglected. If the difference vanishes, we can conclude that L-form result also does not depend on final-state interaction. This difference can be obtained by using the relation $\mathbf{p}_1+\mathbf{p}_2=\mathrm{Im}[H,(\mathbf{r}_1+\mathbf{r}_2)]$, where H is the exact nonrelativistic Hamiltonian for a two-electron atom. We now get

$$\begin{aligned}\Delta M_S=M_S^V-M_S^L=im\int\ & e^{-i\mathbf{p}_1\cdot\mathbf{r}_1}\Phi_{\mathbf{p}_1}^{(-)*}(\mathbf{r}_1)\Psi_{\mathbf{p}_2}(\mathbf{r}_2)\frac{\alpha}{r_{12}}\\ &\times[\boldsymbol{\epsilon}\cdot\mathbf{r}_1+\boldsymbol{\epsilon}\cdot\mathbf{r}_2]\Psi_i(\mathbf{r}_1,\mathbf{r}_2).\end{aligned}\tag{A4}$$

Due to the fact that the function $1/r_{12}$, as well as $\boldsymbol{\epsilon}\cdot\mathbf{r}_1$, are regular at $r_1=0$ for all $r_2\neq 0$, the e-N singularity that determines the leading contributions to ΔM_S comes from the initial- and final-state wave functions. As in the single-ionization case, the leading singular power is r_1, which would result in a leading contribution to ΔM_S of order $1/p_1^4$. This would be sufficient for showing that the difference decreases faster than the matrix element (which decreases as $1/p_1^3$), but, in fact, such terms cancel and the leading contribution to ΔM_S is of order $1/p_1^5$. Therefore M^V and M^L are the same at high energies even with approximate uncorrelated Coulombic final-state wave functions (which have the correct e-N singularity).

APPENDIX B: THE 3C FUNCTION

Here we argue that the $3C$ function, used in our discussions, is accurate neglecting terms of the order $Z(m\alpha)^2/E_f$, where $E_f\simeq p_{large}^2/2m$ is the total energy of the two electrons in the final state, and that the $3C$ function contains accurately terms of the order $Zm\alpha/p_{large}$ in the e-N interaction and terms of the order $m\alpha/p_{large}$ in the e-e interaction. With such accuracy of the $3C$ functions we obtained photoabsorption matrix elements, determining the spectrum of double ionization, accurately neglecting terms of order $1/p_{large}^2$.

We write the exact solution of the Schrödinger equation, describing two electrons in the final state with momenta $\mathbf{p}_1$ and $\mathbf{p}_2$, in the forms

$$\begin{aligned}\Psi_f(\mathbf{r}_1,\mathbf{r}_2)&=\Psi_{\mathbf{p}_1}^{(-)}(\mathbf{r}_1)\Psi_{\mathbf{p}_2}^{(-)}(\mathbf{r}_2)D_{\mathbf{p}_1,\mathbf{p}_2}(\mathbf{r}_1,\mathbf{r}_2)\\ &=e^{i(\mathbf{p}_1\cdot\mathbf{r}_1+\mathbf{p}_2\cdot\mathbf{r}_2)}\Phi_{\mathbf{p}_1}^{(-)}(\mathbf{r}_1)\Phi_{\mathbf{p}_2}^{(-)}(\mathbf{r}_2)D_{\mathbf{p}_1,\mathbf{p}_2}(\mathbf{r}_1,\mathbf{r}_2)\\ &=\Phi_{\mathbf{p}_1}^{(-)}(\mathbf{r}_1)\Phi_{\mathbf{p}_2}^{(-)}(\mathbf{r}_2)d_f(\mathbf{r}_1,\mathbf{r}_2),\end{aligned}\tag{B1}$$

where $\Psi_{\mathbf{p}}^{(-)}(\mathbf{r})=e^{i\mathbf{p}\cdot\mathbf{r}}\Phi_{\mathbf{p}}^{(-)}(\mathbf{r})$ represents an outgoing electron in a pure Coulombic potential of a nucleus with charge

Z. The factor $D_{\mathbf{p}_1,\mathbf{p}_2}(\mathbf{r}_1,\mathbf{r}_2)$ contains all final-state e-e interaction. The $3C$ model means that the final-state correlation is approximately described by

$$D_{\mathbf{p}_1,\mathbf{p}_2}(\mathbf{r}_1,\mathbf{r}_2)=\Gamma\left(1-i\frac{\nu}{p_{12}}\right)e_1^{-\pi\nu/2p_{12}}F_1 \times\left[i\frac{\nu}{p_{12}},1,-i(p_{12}r_{12}+\mathbf{p}_{12}\cdot\mathbf{r}_{12})\right], \tag{B2}$$

where $\nu=m\alpha/2$ and $\mathbf{p}_{12}=(\mathbf{p}_1-\mathbf{p}_2)/2$ (with $\mathbf{p}_2=0$ when single ionization is considered).

We are here discussing the quality of the $3C$ function in terms of the function $d_f=\exp[i(\mathbf{p}_1\cdot\mathbf{r}_1+\mathbf{p}_2\cdot\mathbf{r}_2)D_{\mathbf{p}_1,\mathbf{p}_2}]$, which in the limit $Z\to 0$ (neglecting e-N interaction) describes two electrons with Coulombic interaction. In this discussion, our approach is similar to Ref. [10]. However, we are able to show explicitly, without making any assumption on the $D_{\mathbf{p}_1,\mathbf{p}_2}$ function, that the terms that are neglected in $3C$ are of the order $Z(m\alpha)^2/E_f$ and higher. In contrast, in Ref. [10] it is assumed that the function $D_{\mathbf{p}_1,\mathbf{p}_2}$ depends only on the relative coordinate of the two electrons, and it is only argued that for $p_{large}\gg Z$, the exact function approaches $3C$. We are going a step further.

We now substitute the form, Eq. (B1) (with d_f), into the Schrödinger equation

$$\left(-\frac{1}{2m}\nabla_1^2-\frac{1}{2m}\nabla_2^2-\frac{Z\alpha}{r_1}-\frac{Z\alpha}{r_2}+\frac{\alpha}{r_{12}}\right)\Psi_f(\mathbf{r}_1,\mathbf{r}_2) =E_f\Psi_f(\mathbf{r}_1,\mathbf{r}_2). \tag{B3}$$

Since $\Phi_{\mathbf{p}}(\mathbf{r})$ is the Coulomb wave function, i.e.,

$$\Phi_{\mathbf{p}}(\mathbf{r})=N_p\,{}_1F_1\left[-i\frac{a}{p},1,-i(pr+\mathbf{p}\cdot\mathbf{r})\right], \tag{B4}$$

where $a=mZ\alpha$, we obtain the equation for the function d_f,

$$\left[-\frac{1}{4m}\nabla_R^2-\frac{1}{m}\nabla_{12}^2+\frac{\alpha}{r_{12}}-E_f\right]d_f(\mathbf{r}_{12},\mathbf{R}) =\left[i\frac{2a}{m}(p_1K_1+p_2K_2)-\frac{a}{m}[(\mathbf{M}_1+\mathbf{M}_2)\cdot\boldsymbol{\nabla}_R +2(\mathbf{M}_1-\mathbf{M}_2)\cdot\boldsymbol{\nabla}_{12}]\right]d_f(\mathbf{r}_{12},\mathbf{R}). \tag{B5}$$

The function d_f and Eq. (B5) are written in terms of the (more convenient) relative coordinate $\mathbf{r}_{12}$ and the coordinate of the center of mass $\mathbf{R}$ of the two electrons,

$$K_i=\frac{1+\hat{\mathbf{p}}_1\cdot\hat{\mathbf{r}}_1}{2}H_i,\quad \mathbf{M}_i=\frac{\hat{\mathbf{p}}_i+\hat{\mathbf{r}}_i}{2}H_i. \tag{B6}$$

H_i is the ratio of confluent hypergeometric functions,

$$H_i=\frac{{}_1F_1\left[1-i\dfrac{a}{p_i},2,-i(p_ir_i+\mathbf{p}_i\cdot\mathbf{r}_i)\right]}{{}_1F_1\left[-i\dfrac{a}{p_i},1,-i(p_ir_i+\mathbf{p}_i\cdot\mathbf{r}_i)\right]}, \tag{B7}$$

which appear after dividing the equation by $\Phi_{\mathbf{p}_1}\cdot\Phi_{\mathbf{p}_2}$. For $p_i>a$, H_i, and therefore K_i and M_i, are bounded, i.e., $|H_i|$, $|K_i|$, $|\mathbf{M}_i|\leqslant 2$ for all distances and angles. This can be shown by writing

$$H_i=\frac{{}_1F_1\left[1-i\dfrac{a}{p_i},2,-ix\right]}{{}_1F_1\left[-i\dfrac{a}{p_i},1,-ix\right]} =\frac{i}{x}\left[e^{-ix}\frac{{}_1F_1\left[i\dfrac{a}{p_i},2,ix\right]}{{}_1F_1\left[-i\dfrac{a}{p_i},1,-ix\right]}-1\right], \tag{B8}$$

and noting that the numbers in brackets are of unit amplitude, which means that for $x>1$, $|H|<2$. Then it is easy to see numerically that $|H|<2$ for any x if $a<p$. However, for $a>p$ (as may happen for the slow electron in the SO region), the upper bound on H rises. In numerical calculation, we find that maximum of H appears at $ar(1+\hat{\mathbf{p}}\cdot\hat{\mathbf{r}})=1.445$ which results in a maximum of the size of $2/x\sim 2a/1.445p$ [this also follows from Eq. (B8)]. This means that even for p several times smaller than a, the size of H is not much bigger than 2. Due to the boundedness of these functions, we can discuss the order of the approximation made by neglecting some terms in Eq. (B5).

In the situations we are considering in this paper, the energy E_f is large: $E_f\gg a^2/(2m)$. We ask the order of the approximation made by neglecting the e-N interaction completely [putting the right-hand side of Eq. (B5) to zero, i.e., $a=0$]. Equivalently, we are asking the order of the approximation made by using the $3C$ function for a two-electron system with E_f large [note that with $a=0$, Eq. (B5) becomes the equation for the free two-electron system].

We assume that for large E_f, the function d_f does not differ very much from its first-order approximation d_f^0. Without any detailed analysis of the neglected terms, we may easily estimate that the order of the approximation made by putting $a=0$ in Eq. (B5) is given by the ratio of the neglected (bounded) right side (which is of the order ap_{large}/m, if we take for simplicity the value of K's and M's to be 1) and the bounded term on the left side (which is $E_f\simeq p_{large}^2/2m$). The order of the approximation is a/p_{large}, which would mean that some terms of this magnitude might have been neglected. It also means that the first-order approximation d_f^0 for the function d_f is the wave function of the free two-electron system. [This conclusion was reached in Ref. [10], using the same comparison of the terms, but with additional assumptions as explained above.] This accuracy of d_f^0, and therefore of the $3C$ function used in our work, would not be sufficient to justify our conclusions. However, making a more detailed analysis, we now show that the order of the neglected terms is in fact $a\nu/m$, and not ap_{large}/m as it seems at first sight. Therefore, the order of the approximation is, in fact, $a\nu/p_{large}^2$, and hence the use of the $3C$ function in our discussions is justified.

We write the exact function d_f as

$$d_f = d_f^0 + v_f, \tag{B9}$$

where the first-order approximation is the free two-electron wave function

$$d_f^0(\mathbf{r}_{12},\mathbf{R}) = N_{p_{12}} e^{i(\mathbf{P}\cdot\mathbf{R}+\mathbf{p}_{12}\cdot\mathbf{r}_{12})} \times {}_1F_1\left[i\frac{\nu}{p_{12}}, 1, -i(p_{12}r_{12}+\mathbf{p}_{12}\cdot\mathbf{r}_{12})\right], \tag{B10}$$

and v_f includes all higher-order corrections. Since v_f is small, we assume that the next higher-order corrections can be obtained by an iterative procedure using Eq. (B9) with Eq. (B5). In lowest order, we neglect the right-hand side of Eq. (B5) and obtain d_f^0. Then, in a next iteration we put on the right side $d_f = d_f^0$ and calculate d_f^1.

By inserting d_f^0 for d_f on the right side of Eq. (B9), we obtain

$$\left[-\frac{1}{4m}\nabla_R^2 - \frac{1}{m}\nabla_{12}^2 + \frac{\alpha}{r_{12}} - E_f \right] d_f^1(\mathbf{r}_{12},\mathbf{R}) = -\frac{4a\nu}{m}\mathbf{M}_{12}\cdot(\mathbf{M}_1 - \mathbf{M}_2)\, d_f^0(\mathbf{r}_{12},\mathbf{R}), \tag{B11}$$

where $\mathbf{M}_{12}$, defined similarly to $\mathbf{M}_i$,

$$\mathbf{M}_{12} = \frac{\hat{\mathbf{p}}_{12}+\hat{\mathbf{r}}_{12}}{2} \frac{{}_1F_1\left[1+i\frac{\nu}{p_{12}}, 2, -i(p_{12}r_{12}+\mathbf{p}_{12}\cdot\mathbf{r}_{12})\right]}{{}_1F_1\left[i\frac{\nu}{p_{12}}, 1, -i(p_{12}r_{12}+\mathbf{p}_{12}\cdot\mathbf{r}_{12i})\right]}, \tag{B12}$$

is also bounded, $|\mathbf{M}_{12}| \leqslant 2$ if $p_{12} > \nu$. The corrections to d_f^0, in the second iteration, are given by the inhomogeneous term on the right side of the Eq. (B11), and we see that this term is of the order $a\nu/m$. All terms proportional to the momenta of electrons cancel and the leading correction to d_f^0 involves both the interaction with the nucleus and the interaction between the two electrons. By neglecting this inhomogeneous term in Eq. (B11) [which leads again to d_f^0], we, in fact, neglect terms of the order $a\nu/p_{large}^2$ in the function d_f. This neglect is valid in all situations considered in this work. However in the SO region, when one of the electrons (e.g., p_2) is slow, the coefficient of these neglected terms can be large (due to the large size of H_2 if $p_2 \ll a$). This can influence the accuracy of calculation if a situation $p_2 \ll a$ is considered. However, when the total cross section is considered (as in this work), the contribution from momenta $p_2 \ll a$ is suppressed by its small phase-space factor.

Therefore, all terms of order a/p_{large} (first order in e-N interaction) and all terms of order ν/p_{large} (first order in e-e interaction) are correctly represented by the $3C$ function, as we expected, knowing that these terms must be Coulombic (as if the third particle was not present) at the coalescence of the two particles. We have used this result in Secs. IV and V–VII. This result also means that the spherical waves present in the $3C$ function are accurate including the first order in a/p_{large} and ν/p_{large}. We need this accuracy of the spherical waves (including first order in ν/p_{large}) in considering the FSI region in Sec. VIII.

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[1] We will refer to the present paper and the following paper [2] as Paper I or II when suitable.

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[3] We will call all photoabsorption processes with one outgoing electron as single ionization, regardless of the final state of the He$^+$ ion. When the final He$^+$ ion is in an excited (ground) state, we call the process single ionization with excitation (without excitation).

[4] By the spectrum we mean the singly differential cross section for one detected electron as a function of energy in double ionization in photoabsorption at given incident photon energy, integrated over both electron angles.

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[29] Spherical waves are the continuum state pieces that asymptotically behave as $\exp(ipr)/r$.

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[31] As discussed later in considering ionization of a two-electron atom, the overall factor is generally a function of all the other coordinates describing the atomic system, except the relative coordinate describing the coalescence. In IPA, this factor is just a constant, dependent on screening.

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[37] This is one of the points of difference from a perturbative approach (e.g., Born expansion). The Born expansion gives equal weight to all regions, while the AFT approach tells us that it is the singularity region that is important for high-energy photoabsorption.

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[43] Note that the form of the matrix element [Eq. (23)], from which particular matrix elements for particular photoabsorption processes (or particular kinematical situations) are derived, is asymmetric in the final-state quantum numbers. This form contains the same physics as in the fully symmetric form and is not an approximation. It is derived from the fully symmetric matrix element using the symmetry of the exact wave functions, as explained in the text. However, with the form of Eq. (23), the symmetry of the singularities $\mathbf{r}_1 = 0$ and $\mathbf{r}_2 = 0$ of the integrand [Eq. (23)] is not manifest, and we will get in some situations the full leading contribution from only one of them, e.g., $\mathbf{r}_1 = 0$. In the fully symmetric form of the matrix element, any leading contribution comes half from one singularity, and the other half from the other singularity; but the result is the same.

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[48] This is analogous to the IPA case, where the screening effects on the Coulombic shape of the wave functions in the vicinity of the coalescence were argued to be small.

[49] Equation (25) is also the dominant term in the expansion of the initial-state wave function in terms of angular momentum l of the electron approaching the nucleus (only the $l = 0$ term is retained). In the case of the ground state of He, the probability to find an electron approaching the nucleus with $l = 0$ is dominant, while the probability for higher angular momenta is negligible and is not discussed here for simplicity. These higher angular momenta do not contribute to the order we are interested in this paper. More general partitioning is considered in Paper II in connection with photoabsorption from excited states.

[50] Within this approximation, the exchange term factorizes too, but it contains the factor $\int \Psi^C_{\mathbf{p}}(\mathbf{r}_1)\Psi^C_i(\mathbf{r}_1)d^3r_1$, which vanishes.

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result for single ionization from $l\neq 0$ states [5,6], but here we see that it also affects ionization from the $l=0$ state with excitations to $l\neq 0$ states.

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[60] Y. Wang, J.M. McGuire, J. Burgdörfer, Y.Z. Tang, and Y. Qiu, Bull. Am. Phys. Soc. **43**, 1356 (1998).

[61] E.G. Drukarev, N.B. Avdonina, and R.H. Pratt, J. Phys. B **34**, 1 (2001).

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